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Article

44-Year Retrospective Analysis of Ultraviolet Absorbents and Industrial Antioxidants in Seabird Eggs from the Canadian Arctic (1975 to 2019)

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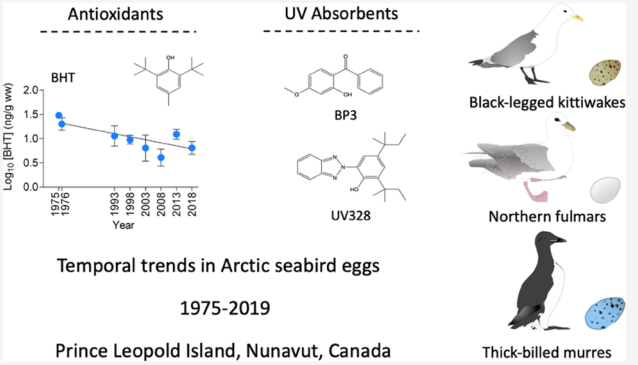
ABSTRACT: Ultraviolet (UV) absorbents and industrial antioxidants are contaminants of emerging concern (CECs), but little is known about their distribution in Arctic wildlife, as well as how these contaminants vary over time, across regions, and between species. We used archived egg samples to examine the temporal patterns of 26 UV absorbents and industrial antioxidants in three seabird species (black-legged kittiwakes *Rissa tridactyla*, thick-billed murres *Uria lomvia*, northern fulmars *Fulmarus glacialis*) sampled in Arctic Canada between 1975 and 2019. Various synthetic phenolic antioxidants, aromatic secondary amines, benzotriazole UV stabilizers, and organic UV filters were detected in the seabird eggs. Overall, kittiwakes had higher levels of several UV absorbents and industrial antioxidants. Most target contaminants reached their peak concentrations at different points during the 44-year study period or did not vary significantly over time. None of these contaminant concentrations have increased in recent years. The antioxidant 2-6-di-*tert*-butyl-4-methylphenol (BHT) was the most frequently detected contaminant in seabird eggs, and its level significantly declined over the course of the study period in kittiwake eggs but did not change in the eggs of murres and fulmars. Future research should examine the effects of these CECs on the health of avian species, the sources, and exposure pathways of these contaminants.



KEYWORDS: *industrial antioxidants, plastic-associated chemicals, seabirds, Arctic, temporal patterns, UV328*

INTRODUCTION

Plastic pollution has been reported in the Arctic Canada for over a decade,[1] with pollution sourced from local and long-range transport.[2−4] Importantly, plastic pollution can have harmful effects on biota and the ecosystem in several ways, including entanglement of animals in the large plastic litter, as well as physical and physiological effects due to the ingestion of litter and microplastics.[5,6] Beyond the physical impact of plastics, there is also increasing awareness of the chemicals associated with marine plastic debris.[7−9] A suite of chemical components such as plasticizers, flame retardants, and stabilizers are added in plastics during production.[10,11]

Ultraviolet (UV) absorbents, including benzotriazole UV stabilizers (BZT-UVs) and organic UV filters (UVFs), are used in various commercial and industrial products (e.g., plastics, paints, coatings, and personal care products) to protect the materials from UV-light-induced degradation (e.g., color change). UV light is absorbed by BZT-UVs over a broad spectrum, whereas UVFs absorb UV over a restricted range of wavelengths.[12] The environmental fate and risks of these chemicals are of emerging global interest. For example, 2-(2*H*-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (UV328) has been classified as a Substance of Very High Concern in Europe (https://echa.europa.eu/) and added to Annex D of the Stockholm Convention on Persistent Organic Pollutants (POPs).[13] UV328 is currently undergoing a risk assessment to see whether its usage should be banned or restricted.[13] One of the major challenges for assessing the environmental risks from UV absorbents is the lack of data on their distribution in the Arctic. BZT-UVs have been in use since the 1950s, and yet their behaviors, distribution, and fate in the environment are largely unknown.[14] BZT-UVs have low solubility in water (e.g., 0.015 mg/L for UV328) and exhibit other chemical behaviors that are characteristic of legacy POPs (e.g., relatively high octanol-water partition coefficient for most BZT-UVs (log K_{ow}

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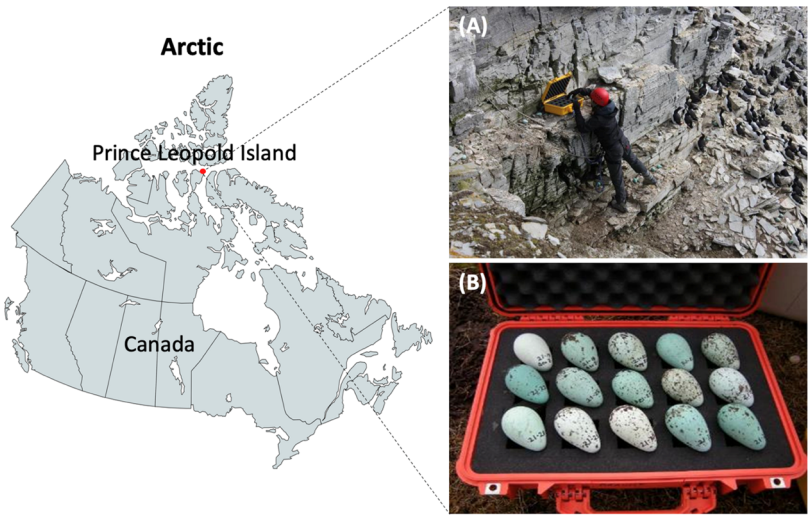

Figure 1. Sampling site at PLI Migratory Bird Sanctuary in Nunavut, Canada. (A) Seabird eggs collection by an experienced climber (photo courtesy of Mark Mallory). (B) Individually labeled murre eggs in a transport case after collection (photo courtesy of Birgit Braune). The map was created with MapChart.

> 5) (Table S1), long half-life in water (≈60 days), and sediment (>1 year)) (predicted by Estimation Program Interface (EPI) Suite (V4.11) modeling), making them of concern from a persistence and bioaccumulation perspective.[15−17] In a study in the eastern United States using dated sediment cores, BZT-UVs peaked in sediment near a chemical production facility in the 1970s,[14] yet to date, there has been no temporal analysis of BZT-UVs, including UV328, in historical biological samples.

UVFs are commonly used in sunscreen products, but they are also added to plastics (e.g., food-related plastics) to protect the materials from photodegradation.[18−20] Several UVFs such as 4-methylbenzylidenecamphor (4MBC), benzophenone (BP), and benzophenone 3 (BP3) are known to adsorb on polyethylene under environmental conditions,[21] and ethylhexyl methoxycinnamate (EHMC) has been detected in plastic debris from the marine environment (e.g., Haeungnam Beach in Geoje, South Korea).[20] UVFs have been found in Arctic surface water,[22] and EHMC is known to accumulate in the muscle of Arctic char (*Salvelinus alpinus*)[23] and several bird species from Svalbard, Norway,[24] raising concerns about the risks of Arctic species exposure to UVFs.

Another group of compounds of interest comprise industrial antioxidants. Synthetic phenolic antioxidants (SPAs) and aromatic secondary amines (Ar-SAs) are two subgroups of antioxidants used in various products such as plastics, rubbers, fuels, and lubricants.[25,26] These chemicals have sparked growing environmental concern because of their large production volumes and suspected toxicities.[27,28] According to current data, SPAs and Ar-SAs may have different trophodynamic properties in the aquatic environment. Trophic magnification of SPAs was determined in six mollusk species from the Chinese Bohai Sea.[29] Bis(4-(2,4,4-trimethylpenta-2-yl)phenyl)amine (C8C8, an Ar-SA), on the other hand, demonstrated biodilution in a Lake Superior food web.[26] Different environmental fates may result in different accumulations of SPAs and Ar-SAs in wildlife, posing varied ecological risks. Some Ar-SAs (e.g., C8C8) have been found in the liver and/or eggs of ringed seals (*Pusa hispida*) and seabirds in the Arctic.[30] The occurrence of SPAs in the Arctic is currently unknown. Examining BZT-UVs, UVFs, SPAs, and Ar-SAs in Arctic species is therefore critical to understanding the potential exposure risks of biota in regions remote from the sources of these contaminants.

Recent work has identified Ar-SAs and BZT-UVs in the eggs and livers of seabirds from Arctic Canada.[30] However, that study was only a snapshot in time. Retrospective analyses are required to elucidate the variations of these deleterious contaminants in wildlife over time and how they may differ in concentrations among species, to better evaluate how UV absorbents and industrial antioxidants may have affected Arctic species in the past, and estimate future trends.

The seabird colony at the Prince Leopold Island (PLI) Migratory Bird Sanctuary in Nunavut (Arctic Canada) has been used to monitor contaminants under the Canadian government's Northern Contaminants Program via a long-term monitoring program administered by Environment and Climate Change Canada (ECCC).[31] Tissues from these studies are archived at the National Wildlife Specimen Bank at the National Wildlife Research Centre in Ottawa, Canada.[32] These archived samples provide an opportunity to undertake retrospective studies on contaminants of emerging concern.[33] Given the emerging concerns over UV absorbents and industrial antioxidants in wildlife, we used archived egg samples from three seabird species, thick-billed murres (*Uria lomvia*; hereafter murres), northern fulmars (*Fulmarus glacialis*; hereafter fulmars), and black-legged kittiwakes (*Rissa tridactyla*; hereafter kittiwakes) collected from PLI in collaboration with the community of Resolute Bay (Nunavut, Canada) between 1975 and 2019 to examine temporal patterns of these contaminants in Arctic seabird eggs.

Murres, fulmars, and kittiwakes all breed on the same cliffs and at the same time at PLI,[34] and generally spend winter in the same areas (northwest Atlantic),[35−37] effectively providing natural controls on spatial and temporal variation. Thus, examining contaminant profiles for these species provides a powerful comparison of the role that different foraging ecologies may play in contaminant exposure (as it does for plastic debris and POPs),[1,2,30] as well as species-specific differences in biotransformation capacity. Given that UV absorbents and industrial antioxidants are widely used in plastics and fulmars have higher occurrence and amounts of

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plastic pollution than either murres or kittiwakes,[1,2] we expected fulmar eggs to have higher concentrations of the target contaminants than murre or kittiwake eggs. Although the temporal trend of industrial antioxidants and UV absorbents production is largely unknown, the increase in the manufacturing of products (e.g., plastics and sunscreens) that may contain these chemicals as additives over the last 40 years led us to expect a general increasing trend of UV absorbents and industrial antioxidants in Arctic seabird eggs.

MATERIAL AND METHODS

Study Site and Sample Collection. PLI is located in Nunavut in the Canadian high Arctic, at 74°N, 90°W (Figure 1). Detailed methods for seabird egg collections at PLI since 1975 can be found in Braune et al.[31] Briefly, during each year of collections, 5 to 15 eggs from seabird nests of each species (one egg per nest) were taken. Eggs were stored in padded boxes for transportation and kept cool (Figure 1). All collections were made under the appropriate Government of Nunavut and Canadian Wildlife Service permits required in the region.[32]

The eggshell protected the contents of bird eggs from contamination during field collection and processing. The outside of the eggshell was rinsed by solvent before retrieving the egg content. All eggs were homogenized using metal tools at the National Wildlife Research Centre in the year of collection and aliquoted for various contaminant studies. The remaining tissues were then stored at −40 °C in acetone-hexane cleaned glass containers (with clean aluminum foil covered on top to avoid contact with plastic caps) in the National Wildlife Specimen Bank for future analyses. This approach was employed for the long-term preservation of biological specimens for organochlorine residue tests because no significant evaporative losses were identified at temperatures as low as −28 °C.[38] This storage method is considered to be suitable for the temporal trend analysis of UV absorbents and industrial antioxidants due to the lower Henry's law constant (K_H: 1.6×10^{-11}−6.9 Pa·m^3/mole at 25 °C), as well as the comparable or higher octanol-air partition coefficient ($\log K_{oa}$: 7.3−20.9) of target contaminants (Table S1) than organochlorines or other POPs (e.g., dichlorodiphenyltrichloroethane (DDT) (K_H: 1.6, $\log K_{oa}$: 10.4); 2,2′,4,4′,5,5′-hexachlorobiphenyl (CB-153) (K_H: 6.9, $\log K_{oa}$: 10.8)). The long-term biodegradation processes of target contaminants in such storage condition are currently unknown. However, a biodegradation half-life estimation using the method provided in the European Chemical Agency's chemical safety assessment revealed that the half-life of target contaminants in water was in the range of 65−778 years under −40 °C.[39] Detailed estimation method and references are shown in the Supporting Information (SI). Availability of samples varied across years and according to prior use,[32] so for this study, we analyzed eggs from the bank for years where ≥4 individual samples were available in glassware (Table 1).

Chemicals and Reagents. Target contaminants included 3 SPAs, 6 Ar-SAs, 7 UVFs, and 10 BZT-UVs. The full names, CAS numbers, acronyms, molecular weights, $\log K_{ow}$, $\log K_{oa}$, K_H, and predicted half-life in live fish at 15 °C and in water at −40 °C of the target contaminants are shown in Table S1. Figure S1 illustrates the structures of the target contaminants. Analytical standards of BP, EHMC, 2-ethylhexyl salicylate (EHS), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (OC), 2-(2*H*-benzotriazol-2-yl)-p-cresol (UVP), 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (UV090), 2-(2*H*-benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol (UV9), 2-*tert*-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl)-4-methylphenol (UV326), diphenylamine (DPA), 2,6-di-*tert*-butyl-4-methylphenol (BHT), and 2,6-di-*tert*-butyl-1,4-benzoquinone (BHTQ) were purchased from Sigma-Aldrich (Oakville, Canada). The standard of C8C8 was purchased from Oakwood Products Inc (Estill), while the standards of *N*-phenyl-1-naphthylamine (AOA), *N*-phenyl-2-naphthylamine (AOD), bis(4-*tert*-butylphenyl)amine (C4C4) and bis[4-(2-phenyl-2-propyl)phenyl]amine (diAMS) were obtained from TCI America (Portland). Analytical standards of BP3, 4MBC, 3,3,5-trimethylcyclohexyl salicylate (HMS), 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (UV234), 2-benzotriazole-2-yl-4,6-di-*tert*-butylphenol (UV320), 2,4-di-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV327), UV328, 2-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl butyl)phenol (UV329), 2-(2*H*-benzotriazol-2-yl)-4-(*tert*-butyl)-6-(*sec*-butyl)phenol (UV350), DPA-d_{10}, and BP-d_{10} were purchased from Toronto Research Chemicals (Toronto, Canada). The standards of BHT-d_{21} and UV328-d_4 were obtained from ACP Chemical, Inc. (Quebec, Canada) and ASCA GmbH (Berlin, Germany), respectively. HPLC-grade methyl *tert*-butyl ether, hexane, acetone, and dichloromethane, as well as anhydrous Na_2SO_4 (450 °C overnight), and the glass silica solid phase extraction (SPE) cartridge Supelclean LC-Si (1g) were purchased from Sigma-Aldrich (Oakville, Canada). The S-X3 biobeads were obtained from Bio-Rad Laboratories Ltd. (Mississauga, Canada).

Table 1. Sample Sizes of Eggs Analyzed for UV Absorbents and Industrial Antioxidants at the PLI Migratory Bird Sanctuary in Nunavut in Three Seabird Species (Black-Legged kittiwakes (*R. tridactyla*), Northern Fulmars (*F. glacialis*), and Thick-Billed Murres (*U. Lomvia*))

year	black-legged kittiwakes (*n*)	Northern fulmars (*n*)	thick-billed murres (*n*)
1975	5	5	5
1976	5	0	0
1977	0	0	5
1987	0	5	5
1993	5	5	5
1998	5	4	4
2003	5	5	5
2006	0	5	4
2008	5	0	0
2010	0	5	4
2013	9	0	5
2017	0	5	5
2018	4	0	0
2019	0	5	5
total	43	44	52

Sample Preparation. The sample preparation procedures were modified from previously reported methods.[30] Details are described in the SI.

Instrumental Analysis. A Thermo Trace gas chromatography (GC) coupled with an Ultra-PolarisQ mass spectrometer (MS) was used for the analysis. Details are described in the SI. Table S2 lists the GC-MS parameters.

QA/QC. Glass materials such as tubes, syringes, cartridges, and vessels were precleaned using solvents and used for the experiment to limit contact with plastics and background

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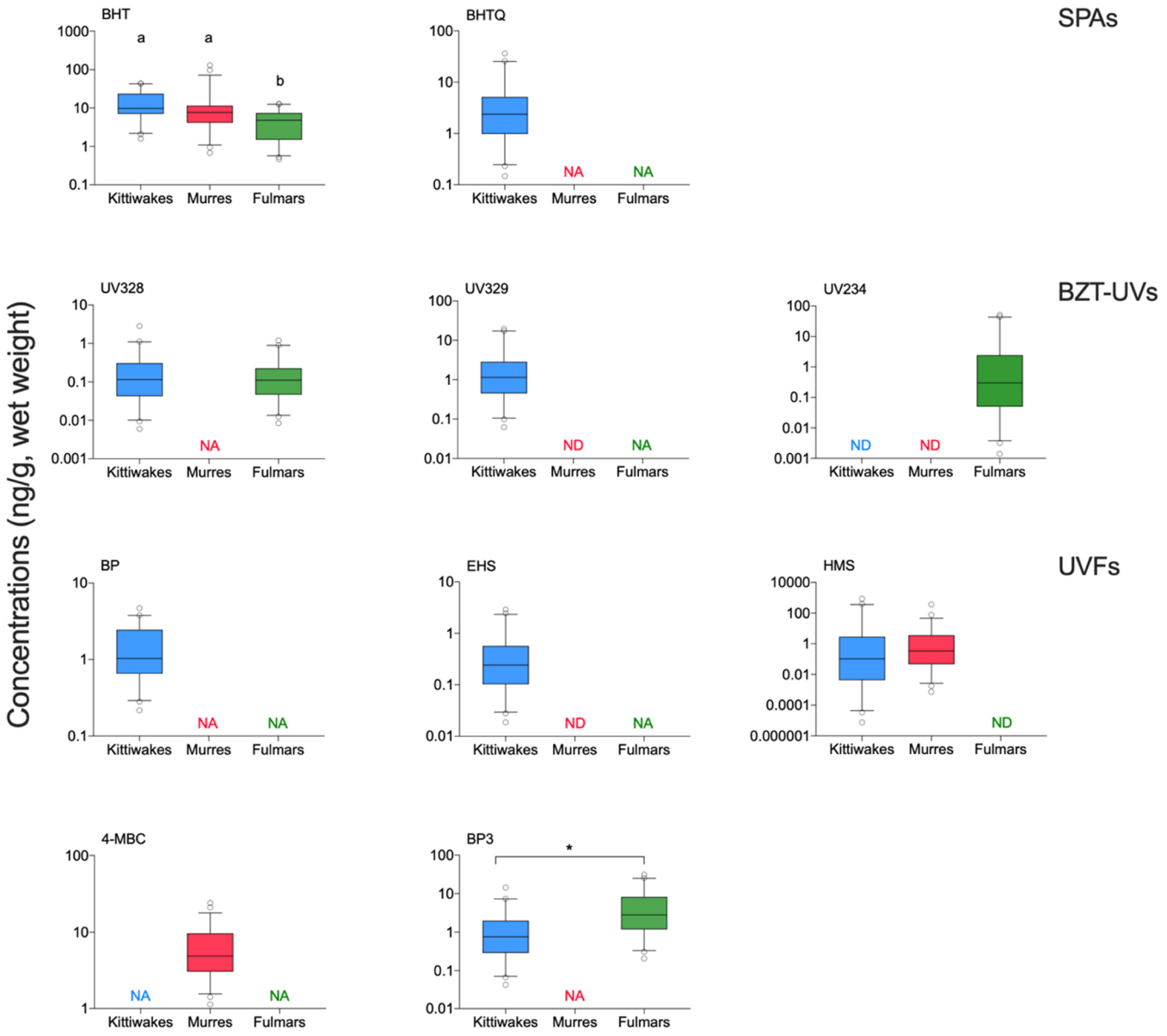

Figure 2. Concentrations of industrial antioxidants and UV absorbents in the eggs of kittiwakes, murres, and fulmars collected between 1975 and 2019 from the PLI Migratory Bird Sanctuary in Nunavut, Canada. Box plots are defined as follows: center line, median; box plot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of the distribution. The circles represent outliers. ND: not detected; NA: statistics was not performed due to low detection frequency (<20%); Different letters indicate significant differences; * $p < 0.01$.

contamination. The operators wore cotton lab coats during the experiment. Five blanks (homogenized deionized water) representing the background contamination of homogenization were analyzed and target contaminants were not detected in the homogenization blanks. Clean aluminum foil was used to cover the top of test tubes and solvent beakers to avoid samples, extracts, and solvents from contact with plastic caps or air particles, if any. An experiment measuring air particle deposition in the laboratory revealed that the possibility of air particles contaminating the samples was negligible (details are shown in the SI). The only procedure where the sample may have come in contact with plastics is during the solvent pumping process for the gel permeation chromatography (GPC) cleaning (some solvent tubes are made of plastics; the column is made of glass). But the eluents were free of the target contaminants.

For each experiment batch (10 to 15 samples), one procedure blank and one spike-recovery sample (spike 50 ng of target contaminants in each matrix) were prepared and analyzed. An additional spike-recovery test was conducted at 5 ng (n = 8 for the pooled eggs of three species because the available individual samples were not enough for more recovery test). To further determine the background contamination, an extra blank contamination test was performed by preparing nine procedure blanks on three different days (n = 3 for each day). The method detection limit (MDL) was established in accordance with the USEPA's guidelines based on eight samples of pooled eggs spiked at 1 or 5 ng/g for different target contaminants.[40] For analytes that were detectable in some but not all blanks (BHTQ, BP, BP3, and EHS), MDLs were based on the highest level in the procedural blanks. BHT was detected in all procedure blanks and the MDL was based on mean plus 3 times the standard

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deviation of the concentrations in blanks.[40] The MDLs ranged from 0.1 ng/g (C8C8) to 3.4 ng/g (BHTQ) ww. The method quantitation limit (MQL) was defined as 3.3 × MDL. The mean recoveries ranged from 67 to 108% and 68 to 110% for the 50 and 5 ng spike tests, respectively. For every five samples, one standard (20 ppb) and two hexane blanks were analyzed as controls. The method's repeatability was assessed by analyzing 10% of samples twice and the relative standard deviations between duplicate measurements were less than 25%. Recoveries, MDLs, and MQLs of target contaminants are presented in Table S3. The concentrations of contaminants in egg samples were corrected using the background contamination in procedure blanks. Calibration curves included standards with nine different concentrations (0, 0.1, 0.5, 1, 5, 10, 20, 50, and 100 ng/mL). Target contaminants having concentrations beyond the calibration curve's concentration range were diluted and reanalyzed.

Data Analysis. Data were analyzed using GraphPad Prism 9.0 (La Jolla, CA) and R 3.4.4 (with RStudio 1.4.1717) (Boston, MA). The Shapiro-Wilk test was used to determine the normality of the data. Because most concentration data do not follow a normal distribution, the present study reports median concentrations and uses nonparametric statistics to compare concentrations. Additionally, mean concentrations are provided to facilitate comparisons to published results. The robust regression on order (ROS) method in R (Nondetects and Data Analysis (NADA) package, V1.6-1) was used to calculate statistics for target contaminants with censored values <80% when considering all sampling years together.[41] For the data analysis of each year, ROS was used to estimate the statistics for target contaminants with censored values <60% due to the smaller sample size (Table 1). Concentration data were reported based on wet weight (ww) unless otherwise indicated. The comparisons of lipid content in eggs and contaminant concentrations were analyzed using the Kruskal−Wallis test followed by Dunn's multiple comparisons among three species or the Mann−Whitney test between two species. For those contaminants simultaneously detected in the same sample, the relationship between log-transformed concentrations was examined using the Pearson correlation test. The temporal trend of BHT was performed on log-transformed concentrations using the Pearson correlation test. We accepted test results as statistically significant where $p \leq 0.05$, and means are presented ± standard error (SE).

RESULTS AND DISCUSSION

A range of industrial antioxidants and UV absorbents was detected in the three species of seabird eggs (Figure 2, Tables S4−S6). The lipid content in the examined eggs of the three seabird species differed significantly ($p < 0.0001$) and followed the order of murre (18.1 ± 0.6%) > fulmar (15.4 ± 1.3%) > kittiwakes (8.5 ± 0.7%). Although the target contaminants are hydrophobic ($\log K_{ow}$: 3.0 to 10.8), no correlation was found between contaminant concentrations and egg lipid content. Therefore, ww-based data were used for data analysis.[42]

Occurrence of Industrial Antioxidants in Arctic Seabird Eggs. *Synthetic Phenolic Antioxidants (SPAs).* BHT was the most frequently detected contaminant of all target analytes across all three species studied, found in 90, 74, and 77% of kittiwake, fulmar, and murre eggs, respectively. For all samples collected between 1975 and 2019, BHT levels in kittiwake eggs (15.6 ± 2.0 ng/g; median 9.8 ng/g) were comparable to concentrations in murre eggs (14.0 ± 3.2 ng/g; median 7.7 ng/g), and both kittiwake and murre egg values were significantly higher than those detected in fulmar eggs (5.0 ± 0.5 ng/g; median 4.8 ng/g) (Figure 2). However, there was no significant difference in BHT levels among three species for the samples collected in recent 20 years (i.e., after 2003). These findings show that kittiwakes and murres may have been exposed to more BHT in the past (e.g., before 2000) than fulmars. There are limited data on BHT in seabirds that allow comparisons with other regions. BHT was previously detected in commercially available Swedish chicken eggs at a mean concentration of 0.62 ng/g (ww),[43] approximately 10-fold lower than the eggs from wild birds measured in this study. After 4 weeks of *in vivo* diet exposure, it was determined that the final levels of BHT and its metabolites in chicken eggs were approximately 4% of the total residues of BHT and its metabolites in the 11 chicken tissues examined.[44] Assuming that BHT has a similar toxicokinetic profile in avian species, the three species examined in this study may have higher BHT levels in other tissues.

The effects of BHT on organisms are variable and have been reviewed in the literature.[25,45] Most *in vivo* data focused on mammals,[25,45] and some studies reported both beneficial and adverse health effects of BHT in avian species. For example, dietary exposure to BHT (1% in diet) for 15 days may increase the activity of *O*-demethylase, a xenobiotic detoxification enzyme found in chickens.[46] BHT has been shown to protect turkeys (1000−4000 ppm in diet for 20 days) and chickens (0.1−1% in diet for 6 weeks) from the negative effects of aflatoxins.[47,48] Other studies have shown that the eggs, liver, and blood of the BHT-treated domestic chickens (0.1% in diet for about 34 weeks) had higher levels of carotenoids and vitamin A than the controls and found no differences in fertility, egg hatchability, or chick health compared to a control group.[49] BHT also significantly reduced the infectivity of the Newcastle disease virus in chickens (100−200 ppm in diet for 2−5 weeks).[50] In contrast, Rao et al.[51] reported marked congestion of the liver, kidney enlargement, and rupture with hemorrhage of the liver in chickens fed BHT (130−2080 mg/kg in diet for 6 weeks). However, to our knowledge, the effects of BHT on wild bird health have not been studied.

BHTQ, a transformation product of other SPAs, was detected in 30% of kittiwake eggs at an estimated median concentration of 2.4 ng/g (mean 5.8 ± 1.3 ng/g) (Figure 2). However, this compound was detected in only one murre sample and two fulmar samples. It is well established that the aromatic ring of SPAs, such as BHT and 26DTBP, can be oxidized in mammals to form BHTQ.[52−54] Nevertheless, it is unknown whether avian species can generate BHTQ via biotransformation of other SPAs, necessitating additional research. According to Wang et al.,[55] BHTQ is more toxic than BHT. BHTQ (≈220 ng/mL) can cleave supercoiled DNA *in vitro* by producing oxygen radicals.[56] It can also cause indirect DNA damage by generating H_2O_2.[57] Thus, based on our results, BHTQ may pose a greater toxicological risk to kittiwakes than fulmars or murres at PLI.

Aromatic Secondary Amines (Ar-SAs). In contrast to SPAs, Ar-SAs were detected sporadically in Arctic seabird eggs. C8C8 had the highest detection rate in kittiwake eggs (18%; <MDL-0.9 ng/g). C8C8 was previously reported in kittiwake and fulmar eggs sampled from PLI in 2013 (median: 0.01 ng/g),[30] and the herring gull (*Larus smithsonianus*) eggs measured from the Great Lakes of North America in 2014 (median: 0.04 to 0.4 ng/g).[26] These findings imply that seabirds breeding in the

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Arctic may be less exposed to, or accumulated fewer, Ar-SAs than birds breeding in temperate locations. Additionally, the differing feeding ecology of Arctic seabirds and herring gulls may contribute to the observed disparities in their exposure to Ar-SAs. Herring gulls are opportunistic foragers that also eat food from a variety of terrestrial sources in the Great Lakes region, including small mammals, and human-disposed food items.[26] Kittiwakes, fulmars, and murres, on the other hand, feed exclusively in the marine environment throughout the year.[58−60] Avian diets with a higher proportion of terrestrial food can accumulate more Ar-SAs;[26] our data support this pattern.

In addition, log-transformed C8C8 and BHT had a significant positive correlation to each other in kittiwake eggs (r = 0.97; p = 0.0008; n = 6), perhaps suggesting that kittiwakes may accumulate these two antioxidants from the same sources. Given that little is known about the diet of kittiwakes in the Canadian Arctic, to understand the route of these additives to kittiwakes, future research should focus on a better understanding of kittiwake diet, contaminants in prey items, and how kittiwakes may be exposed to these additives throughout their annual cycle.

Occurrence of UV Absorbents in Arctic Seabird Eggs. *Benzotriazole UV Stabilizers (BZT-UVs).* UV328, UV329, and UV234 had greater detection frequencies (>20%) in kittiwake and/or fulmar eggs than the other BZT-UVs. UV328 levels were comparable in kittiwake (mean 0.29 ± 0.07 ng/g) and fulmar (0.22 ± 0.04 ng/g) eggs, with the same estimated median concentration of 0.11 ng/g (Figure 2). These levels were equivalent to those previously recorded for eggs of numerous bird species in the Norwegian sub-Arctic and Arctic regions, including kittiwakes (0.19 ng/g ww), common eiders (*Somateria mollissima*; mean 0.16 ng/g ww), European shags (*Phalacrocorax aristotelis*; mean 0.17 ng/g ww), glaucous gulls (*Larus hyperboreus*; mean 0.12 ng/g ww), and common gulls (*Larus canus*; mean 0.17 ng/g ww).[24] In comparison to kittiwakes and fulmars, UV234 and UV329 were not detected in any murre samples, while UV328 was detected in only one murre egg in this study.

Because these chemicals are used as additives in plastics, one of the ways that seabirds are exposed to BZT-UVs is through the ingestion of plastic debris. Kittiwakes, murres, and fulmars have been examined for ingested plastics at two locations in northern Canada, PLI and colonies a little farther south on Baffin Island near Qikiqtarjuaq, Nunavut.[2,61] In both locations, fulmars had the highest frequency of ingested plastics (∼80%), followed by kittiwakes (∼10%), with murres showing no detected accumulated plastics in their stomachs greater than 1 mm in size.[2,61] These results show that fulmars and kittiwakes are likely regularly exposed to ingested plastic pollution, while murres are not in this region.[2,61] With kittiwakes and fulmars showing higher levels of BZT-UVs than murres at PLI, this pattern is consistent with the plastic ingestion in these three species observed at this site.

Plastic debris may act as a carrier of BZT-UVs, increasing the risk of seabird exposure to these additives. Laboratory studies have also shown that ingested plastics in biota can leach additives into the surrounding tissues.[9] UV328, for example, was identified at a concentration of 1.1 μg/g plastic in the polypropylene fragment swallowed by fulmars from the Faroe Islands (62°25′ N 7°20′ W, sub-Arctic).[62] It has been reported that plastic exposure greatly increases UV328 accumulation in the liver, abdominal adipose tissue, and preen gland oil of seabirds (e.g., streaked shearwater *Calonectris leucomelas*).[63] The maternal transfer rate of BZT-UVs to seabird eggs, on the other hand, is still unknown. In the context of both the ingested plastic pollution data[2,61] and the UV328 data obtained in the present study, it suggests that while plastic accumulation levels at the individual level may not influence the uptake of UV328, species that show a higher frequency of occurrence of any ingested plastics may be more exposed to UV328 (i.e., kittiwakes and fulmars) compared to species that have very low or negligible levels of ingested plastics (i.e., murres).

UV Filters (UVFs). BP, BP3, EHS, 4MBC, and HMS were the most frequently detected UVFs in the eggs of kittiwakes, fulmars, and murres (Figure 2). BP3 was found in all three species at PLI, with the highest levels in fulmars (median 2.8 ng/g; mean 5.8 ± 1.1 ng/g), followed by kittiwakes (median 0.8 ng/g; mean 1.8 ± 0.4 ng/g) and murres (statistics not performed due to detection rates <20%) (Figure 2). The BP3 levels in fulmars and kittiwakes from PLI were comparable to those found in the eggs of kittiwakes (40% detection frequency, mean 3.5 ng/g), common eiders (80%; mean 4.2 ng/g), European shags (40%; mean 2.7 ng/g), glaucous gulls (80%; mean 2.9 ng/g), and common gulls (40%; mean 2.7 ng/g) from the Norwegian sub-Arctic and Arctic region, indicating that BP3 is widely distributed in Arctic avian species.[24] In addition, BP3 was previously found in eggs of various bird species from Doñana National Park in Spain, with mean concentrations ranging from 22.1 to 46.7 ng/g (dry weight).[64] Due to the different units of concentration, it is difficult to compare the results from this previous study with the results of the present study, but assuming that avian eggs have a water content between 70 and 85%,[65] the concentrations of BP3 in Doñana National Park bird eggs were around 3.0 to 7.0 ng/g (ww), which were greater than those of fulmar and murre eggs from PLI, suggesting a potential geographic pattern for this contaminant in birds. The adverse effects of BP3 on birds are largely unknown, as with most chemicals of emerging concern, the potential effects associated with the observed wild levels cannot be determined at this time. However, BP3 may reduce egg production, hatching, and testosterone levels in fish.[66] In addition, it is recognized as an endocrine disruptor that can produce a number of reproductive adverse effects in humans, including sex-dependent alterations in birth weight and gestational age, as well as decreased epididymal sperm density in male rats and a longer estrous cycle in female rats.[66] Furthermore, BP3 has been linked to mammary gland cancer.[67]

BP and EHS were more frequently detected in kittiwake eggs (BP: 35%; median 1.0 ng/g; mean 1.6 ± 0.2 ng/g; EHS: 20%, median 0.24 ng/g; mean 0.5 ± 0.1 ng/g), compared to fulmar (BP: 9%; EHS: 12%) and murre eggs (BP: 15%; EHS: not detected) (Figure 2). HMS was detected in 31% of the murre eggs (median 0.3 ng/g; mean 11 ± 7 ng/g) and 35% of the kittiwake samples (median 0.1 ng/g; mean 44 ± 23 ng/g), while not detected in any fulmar eggs (Figure 2). Concentrations of HMS were similar between the murre and kittiwake eggs examined, suggesting similar toxicokinetics. 4MBC was more frequently found in the murre eggs (48%; median 4.9 ng/g; mean 6.8 ± 0.7 ng/g) compared with kittiwakes (15%) and fulmars (2%). BP, EHS, HMS, and 4MBC have not been found in any seabird eggs before, as far as we know.

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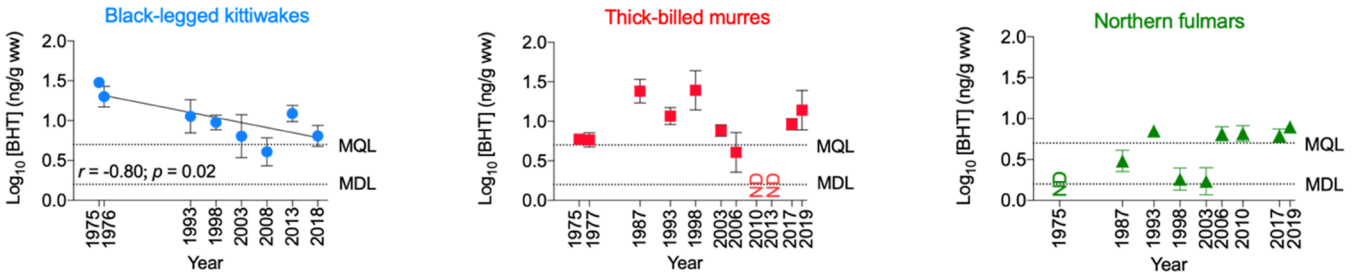

Figure 3. Temporal trend (1975−2019) of BHT in the eggs of kittiwakes, murres, and fulmars collected from the PLI Migratory Bird Sanctuary in Nunavut, Canada. Data are reported as mean ± standard error. Black dashed lines represent the MDL or MQL of BHT. In the plot for kittiwakes, p represents the probability for the correlation to be caused by random sampling and r represents the Pearson correlation coefficient. Some error bars are not shown because they are shorter than the size of the symbol. NA: detection frequency <40%; ND: not detected.

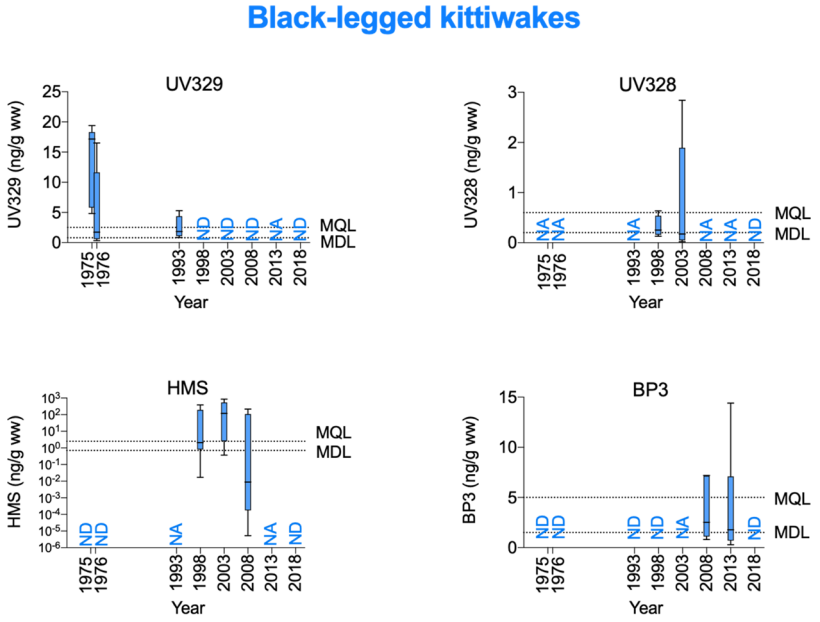

Figure 4. Temporal variations (1975−2018) of UV absorbents in the eggs of kittiwakes collected from PLI Migratory Bird Sanctuary in Nunavut, Canada. Box plots are defined as follows: center line, median; box plot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of distribution. Black dashed lines represent the MDL or MQL of target contaminants. NA: detection frequency <40%; ND: not detected.

Temporal Patterns. BHT levels in kittiwakes declined between 1975 and 2019. The declining trend of BHT in kittiwake eggs was primarily driven by samples collected prior to the year 2008. In contrast, there was no significant temporal variation in BHT levels in fulmar and murre eggs for the entire sampling period (Figure 3). Between 1987 and 2006, there was a decreasing trend in BHT levels in murre eggs, but it was not statistically significant ($r = -0.79$, $p = 0.11$). Such steady levels of BHT in the eggs of three Arctic seabird species after the 2000s are compatible with human BHT exposure observed over time. Specifically, the levels of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, a BHT metabolite, in the urine samples of German adults did not vary significantly between 2000 and 2018, showing that the tested population's exposure to BHT has been stable since 2000.[68]

One possible factor influencing such temporal trends of BHT in seabird eggs is the decrease/variation in BHT production or usage. Although there are no detailed publicly available statistics on annual BHT production/usage, it has been reported that BHT production in the United States was approximately 9000 tonnes in 1976,[69] whereas the production declined to approximately 7000 tonnes in 2011[70] (no data found between 2000 and 2011). Since 2011, the specific annual production of BHT in the United States is unknown, but within the same range of 4536−22,680 tonnes per year until 2015 (no data available after 2015).[70] Some BHT applications are being replaced by new generations of phenolic antioxidants (e.g., 4-*sec*-butyl-2,6-di-*tert*-butylphenol).[71]

Another possible factor affecting such temporal variations of BHT in seabird eggs is the changes in BHT emission/deposition and its levels in the environmental media over time. Although such information in the Arctic aquatic environment (e.g., air, water, or sediment of PLI) is unknown, a study using a dated sediment core (1986−2000) from the Rhine River (Germany) found that the BHT levels peaked around 1989 in that river and showed intermittent emission profiles in other years.[72] In the coastal area of Northern China, BHT was analyzed in three undated sediment cores. The results revealed a similar level of BHT in different layers of the core, indicating that BHT deposition in the coastal area of Northern China has achieved a steady state.[73]

It is necessary to note that BHT can be generated naturally, for example, by freshwater phytoplankton.[74] As a result, the levels and temporal variations of BHT in aquatic species may be influenced not only by human-derived BHT production and use but also by natural sources of this chemical. The

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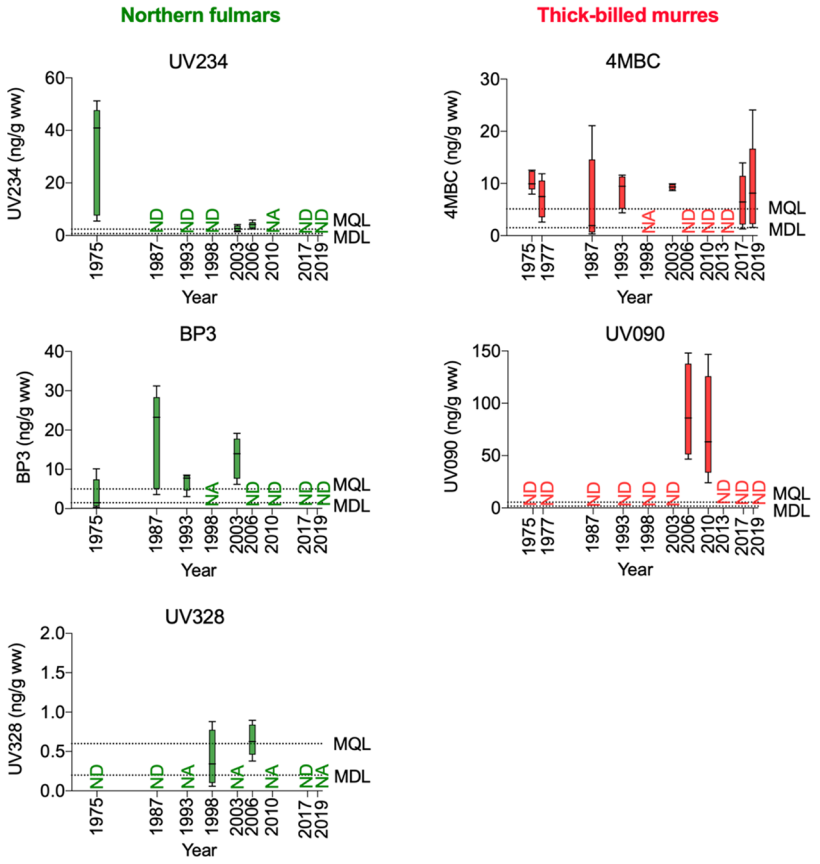

Figure 5. Temporal variations (1975−2019) of UV absorbents in the eggs of fulmars and murres collected from PLI Migratory Bird Sanctuary in Nunavut, Canada. Box plots are defined as follows: center line, median; box plot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of distribution. Black dashed lines represent the MDL or MQL of target contaminants. NA: detection frequency <40%; ND: not detected.

mechanisms underlying these temporal variations are worth investigating further.

While many other compounds examined were not detected in all sampling years, some temporal patterns were observed. UV329 concentrations in kittiwake eggs were higher in samples collected in 1975 and 1976, then appeared to decline over time until levels were below the detection limits (Figure 4 and Table S4). In addition, kittiwake eggs had the highest HMS and UV328 in the 1998−2003 samples, while BP3 levels were higher in the 2008 and 2013 samples (Figure 4 and Table S4). Thus, these contaminants appear to have reached their peak concentrations in breeding bird populations at PLI at various times over the last 44 years.

UV234, C8C8, and EHS levels in fulmar eggs were highest in 1975, while BP3 levels were increased between 1975 and 1987 (median from 1.5 to 23 ng/g), but did not significantly change until 2003 when they began to decrease to below the detection limit (Figure 5 and Table S5). Fulmar eggs, like kittiwakes, had higher levels of UV328 in the 1998 and 2006 samples (Figure 5 and Table S5). While UV328 production and importation are not regularly tracked, summary reports indicate that use in Canada peaked around 2000, with declining amounts since then.[75] Around the year 2000, Canada imported 100,000 to 1,000,000 kg of UV328, which decreased 10-fold to 10,000 to100,000 kg between 2010 and 2013.[75] Nordic countries showed a similar downward trend.[75] This usage pattern corresponds to our finding of higher levels of UV328 in samples from the early 2000s.[75]

Murres accumulated 4MBC consistently in their eggs except for 2006−2013 (Figure 5 and Table S6). The mechanisms underlying such variations are not clear. The distinct regulatory/usage history of 4MBC may be a factor affecting the occurrence and fate of this compound in the environment. 4MBC has been on the European market since the 1970s, with a maximum concentration of up to 4% in sunscreen or other cosmetics. It was on the market in the United States before 1978 but was subjected to a long-term evaluation by the FDA after 1978. It has not yet been approved for use in sunscreen products in the United States since then.[76] It is approved to be used in the Canadian market. However, it is likely that the majority of 4MBC-containing personal care products were gradually phased out of the Canadian market before 2010 according to Health Canada's Drug Product Database.[77] The levels and detection frequency of 4MBC in fulmar and kittiwake eggs were much lower compared to the murres, suggesting lower exposure to 4MBC or different toxicokinetics of this contaminant in these two species compared with murres. Compared to fulmars and kittiwakes, murres feed well below the water surface on mid-water forage species; consequently, the difference in detection and levels of 4MBC may reflect that these additives accumulate in different parts of the food web.

Furthermore, peak levels of UV090 were found in murre eggs in 2006 and 2010 (Figure 5 and Table S6), indicating that murres were more exposed to this contaminant in the late 2000s. In contrast, UV090 was only found in one egg each of kittiwakes and fulmars. UV090 has not been reported in any

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avian species so far, but an *in vitro* study has demonstrated that UV090 can interact with nuclear receptors such as the pregnane X receptor (PXR), the constitutive androstane receptor (CAR), and the peroxisome proliferator-activated receptor (PPAR) in rats.[78] It can also bind with the aryl hydrocarbon receptor in humans.[79] Thus, UV090 may interfere with the physiological processes involving these receptors in mammals and other vertebrates, including birds.

Differences among Species. Contrary to our predictions, fulmars did not have the higher levels of most industrial antioxidants and UV absorbents examined in this study. In fact, kittiwake eggs had significantly higher levels of several additives (e.g., BHTQ, UV329, BP, EHS). UV234 and BP3 were the only additives we examined where fulmar eggs had significantly higher concentrations compared to kittiwake and murre eggs. Similarly, contrary to our expectations based on plastic ingestion levels in these species, in general, most plastic-related antioxidants and UV absorbents did not increase with time, with different compounds having differing apparent peaks in concentration through the last four decades. Based on our data, none of the monitored chemicals demonstrated a consistently increasing trajectory through time across all three species.

Given that we examined three sympatric breeding seabird species with similar ecologies, there are a few factors that could be driving these differences. First, one possible explanation is that these chemicals are used in more than just plastics, and seabirds may accumulate these contaminants through a variety of exposure routes. This includes through secondary ingestion of prey such as fish and invertebrates as the three seabird species have overlapping but distinct foraging patterns.[80] While the proportions and species of fish and invertebrates consumed by the three species (murres, fulmars, and kittiwakes) in the Canadian high Arctic differ slightly, all three species are reported to consume mostly Arctic cod (*Boreogadus saida*), and invertebrates such as amphipods and squid,[81,82] although diet studies for kittiwakes in the Canadian Arctic are interpolated from isotope data.[83] A better understanding of Arctic forage species in relation to industrial additives would help to determine if these contaminants are transferred and biomagnified in Arctic food webs.

Another reason for differences in these contaminants among these species is that they may vary in annual migration patterns. All three species breed in the Canadian Arctic but travel beyond the Canadian Arctic during the winter nonbreeding months, and they spend considerable amounts of time in the North Atlantic.[58−60] Given the wide range of movement of these seabirds across the Atlantic throughout the year, their movements across this broad landscape may influence their uptake of contaminants, either via direct or indirect (e.g., via air particles, prey, or plastic debris) ingestion. However, the precise relationships between individual movements of these seabirds and levels of contaminants are unknown. Such information would aid in determining how variances in winter movements may play a role in exposure to these contaminants.

An additional factor that could influence contaminant accumulation in the three species examined in this study is the metabolism of the compounds by the birds themselves. Although the metabolism of plastic additives in seabirds is not well studied, modeling results (EPI) (Table S1) and recent laboratory studies on fish show that these target contaminants may have a shorter half-life than POPs. For example, UV328's half-life in fish is estimated to be 14 days by EPI and determined to be three days in the liver of rainbow trout (*Oncorhynchus mykiss*),[84] and 6 to 56 days in various tissues of zebrafish (*Danio rerio*) (6 to 7 days in the liver) by *in vivo* studies.[85] In comparison, the half-life of POPs such as DDT (161 days) and CB-153 (525 days) is estimated (EPI) to be longer than that of most target UV absorbents and industrial antioxidants in the present study (Table S1). In addition, the three seabird species have different xenobiotic metabolism capacities. It has been reported that murres and kittiwakes appear to have a greater capacity to metabolize and eliminate chlordane and α-hexachlorocyclohexane, respectively, than other species.[86−88] Therefore, it is possible that metabolic capacities could partially explain some of the differences we observed in additives between the species examined in this study.

An important consideration to interpreting these findings is the total burden of contaminants in these eggs. A recent review by Bianchini et al.[32] illustrated that seabirds at this colony have experienced varying levels of several groups of contaminants through time. Those target contaminants that were detected in recent years' samples (e.g., BHT, 4MBC, BP3, UV328), which are chemicals of emerging concern, should be considered for addition to long-term monitoring programs. Therefore, to understand more accurate indicators of the potential effects of contaminants on seabirds, a cumulative or integrative approach should be considered. Recently, metabolomic and toxicogenomic approaches have been applied to murres in the Canadian Arctic to explore the potential effects of groups of contaminants.[89,90] Given the higher levels of several industrial antioxidants and UV absorbents in kittiwake and fulmar eggs, future work using genomic and metabolomic measures may be useful to explore how industrial chemicals as a group may affect these Arctic seabirds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c05940.

Additional information about target contaminants, experimental details, and results: properties and structures of target contaminants; details about half-life estimation and air particle deposition tests; sample preparation and instrumental analysis; GC-MS parameters; analytical method performance; and detection frequency and concentrations of target contaminants in the eggs of kittiwakes, fulmars, and murres from Arctic Canada (PDF)

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Notes

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