Levels and profiles of perfluorinated alkyl acids in liver tissues of birds with different habitat types and trophic levels from an urbanized coastal region of South Korea

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Abstract

Contamination status and characteristics of perfluorinated alkyl acids (PFAAs) including perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) was examined using liver tissue of birds - black-tailed gulls (*Larus crassirostris*), domestic pigeons (*Columba livia var. domestica*), pacific loons (*Gavia pacifica*), herons (*Ardea cinerea*), and egrets (*Egretta garzetta and Ardea alba*) - with different trophic levels, habitat types and migratory behaviors from an industrialized coastal region of South Korea. A wide range of PFAAs (1.09 ng/g to 1060 ng/g; median=52.6 ng/g) were detected in bird livers from the Korean coasts with high detection frequency. Accumulation features of PFAAs in birds indicated that primarily trophic position and secondly habitat type influence the levels and composition of PFAAs, e.g., relatively high PFAA levels and high composition of odd-numbered long carbon chain PFCAs (perfluoroundecanoic acid (PFUnDA) and perfluorotridecanoic acid (PFTriDA)) and PFOS in higher trophic and marine birds. The prevalence of long carbon chain (≥ 14) PFCAs likely implies a wide use of fluorotelomer-based substances in Korea. Interspecies comparison in the accumulation profile of persistent organic pollutants (including polychlorinated biphenyls (PCBs), organochlorine pesticides, polybrominated diphenylethers (PBDEs), and PFAAs) reveals relatively high load of PFAAs in inland (pigeons) and estuarine (egrets/herons) species compared to marine bird species, indicating wide use of PFAAs in the terrestrial environment.

Keywords: Bird; Biomonitoring; Perfluorinated alkyl acids; Habitat type; Trophic level; Interspecies comparison

Introduction

Perfluorinated alkyl acids (PFAAs) are a group of synthetic organic chemicals consisting hydrophobic alkyl chain that are fully saturated with fluorine atoms, and a hydrophilic functional group. Their useful physicochemical properties such as surface tension-reducing properties, thermal stability, and surfactant properties make them useful in a wide range of industrial applications such as paints, lubricants, mist suppression, and firefighting foams, and oil and water repellents for paper, leather, and textiles (Lindstrom et al., 2011). PFAAs can be released to the environment during industrial manufacture, use or disposal of PFAA-containing products. As a result of their stability, PFAAs become ubiquitously present in the environment. PFAAs have been detected in wildlife globally since 2001 (Kannan et al., 2001; Giesy and Kannan, 2001) with studies showing the bioaccumulation and biomagnification through terrestrial and aquatic food webs (Houde et al., 2006, 2011; Tomy et al., 2009; Butt et al., 2010; Reiner et al., 2011; Renzi et al., 2013). Like other persistent organic pollutants (POPs), PFAAs share the characteristics of persistency, bioaccumulation, toxicity and long-range transport potential leading to perfluorinated alkyl substances being listed in the Stockholm Convention on POPs (UNEP, 2019). Specifically, perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride were included in Annex B (restriction) in 2009, and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds included in Annex A (elimination) in 2019.

About 120 individual PFAAs were registered in National Chemicals Information System in Korea (NIER, 2013), and PFAAs were widely included in various industrial and consumer goods such as outdoor wear, tent, carpet, kitchen utensils and paper cup, *etc*., resulting in ultimate release to the environment. In 2010, PFOS levels exceeding quality criteria for the protection of wildlife (avian wildlife value: 47 ng/L, Giesy et al., 2010) were detected in streams from an industrial zone located in the western coast of Korea (Rostkowski et al., 2006). Afterward, efforts have been made to reduce environmental level of PFAAs in Korea. The use

of PFOS in aqueous fire-fighting foam (AFFF) has been prohibited since 2012, its residual stocks in fire-fighting stations were voluntarily replaced from 2011 until 2016 (UNEP 2019), and a legal amendment to regulate PFOA in AFFF was announced in March 2020. However, stockpiles still exist in private facilities, and PFOS and its salts have been allowed for specific exemptions (e.g. photo imaging, photo-resistant and anti-reflective coatings for semiconductors, *etc.*). PFOS, PFOA, and related compounds have widely appeared in various environmental matrices, wildlife, and human in Korea (Barghi et al., 2018; Lee et al., 2020; Seo et al., 2018, 2019). In 2018, an increase in perfluorohexane sulfonate (PFHxS) levels up to 454 ng/L was detected in tap water at water treatment plant that used the Nakdong River water as raw water, which drew public attention and concern about human exposure to PFAAs (MOE, 2018b). Because of this case, PFOS, PFOA and PFHxS were designated as targets for regular monitoring in the National Water Quality Assessment and the National Environmental Health Survey in 2018 (MOE, 2018a).

Birds have been useful bioindicators for assessing the environmental exposure of anthropogenic chemicals, and related human and ecological impacts because of the following reasons (Burger and Gochfeld, 2004; Smits and Fernie, 2013, Vander Pol and Becker, 2007): (1) are often at the top of the food chain (e.g., seabirds or raptors), thereby concentrating contaminants transferred through food webs at high levels, (2) are sensitive to environmental changes, (3) have relatively low metabolic capacity to degrade contaminants, (4) are useful to long term monitoring because of long lifespan, and (5) can represent human impacts because their habitat and prey overlap with those of human. Many studies have documented PFAAs in birds in North America and Europe (Butt et al., 2010; Houde et al., 2011; Valsecchi et al., 2013); however, there are limited studies existing from Asia (Zhao et al., 2012), most of which are from China. Only three papers are available for PFAA biomonitoring of birds in Korea (Kannan et al., 2002; Yoo et al., 2008; Barghi et al., 2018). The present study investigated the

contamination of PFAAs using marine, estuarine, and inland birds as biomonitors, collected from the estuary of Nakdong River, flowing through diverse industrial facilities and large cities, and nearby coasts. For this study, we used liver tissues for PFAA analysis of the same individuals of five bird species investigated in our previous paper (Hong et al., 2014) to be able to compare the contamination characteristics with other POPs in muscle (such as PCBs, dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordane compounds (CHLs), hexachlorobenzene, PBDEs, and hexabromocyclododecans (HBCDs)). The target bird species (seagull, pigeon, loon and heron/egret) covers different feeding habitats (inland, estuary, and marine), diet types (granivorous and piscivorous), and migratory behavior (resident and migrant).

Material and Methods

Biomonitoring species and sample collection

Taking into account feeding habitats, diet types, and migratory behavior, five species were targeted for biomonitoring: black-tailed gulls (*Larus crassirostris*, hereafter referred to seagulls), domestic pigeons (*Columba livia var. domestica*), pacific loons (*Gavia pacifica*), herons (*Ardea cinerea*), and egrets (*Egretta garzetta and Ardea alba*) (Fig. 1). The ecological characteristics of each bird is as follows (Table 1): seagulls – piscivorous and resident bird living in coastal regions, domestic pigeons - granivorous and resident bird living on land, loons – piscivorous and winter migrant living mostly at sea, herons and egrets – piscivorous and summer migrant (recently, herons became resident birds in the southern part of Korea) living in estuaries. Liver samples from the birds (seagull, n=10; loon, n=5; pigeon, n=7; hero/egret, n=6) were collected from 2009 to 2010. Collection of the samples was performed by the Korea Institute of Ocean Science Technology (KIOST) Team in collaboration with the Nakdong Estuary Eco Centre in Busan. The Nakdong Estuary Eco Centre provided the frozen bird

carcasses to KIOST. An ornithologist in the center classified and recorded the bird species. The dead birds were transferred to the KIOST campus in Geoje. After thawing and de-feathering the birds, liver tissues were dissected with pre-cleaned stainless dissection knives and stored in pre-cleaned glass bottles in temperatures at -20 °C in freezers located at KIOST.

Study area

The estuarine wetland in the Nakdong River provides important habitats for wildlife. Nakdong River is the longest river in Korea, passing two big metropolitan areas, the cities of Daegu and Busan, and large-scale industrial complexes. A variety of domestic (such as residential and commercial activities) and industrial sources (including semiconductor, electronics, textile, dying, car industrial complexes, etc.) for PFAAs are distributed at the middle and lower reaches of the river. Previous studies reported that PFAA emission from wastewater treatment plants (WWTPs) and PFAA levels in river water were the highest in Nakdong River among major rivers of Korea (Kwon et al., 2017; Lam et al., 2014).

Chemical analysis

Chemicals: Calibration solutions were created by combining two solutions produced by NIST: Reference Materials (RMs) 8446 Perfluorinated Carboxylic Acids (PFCAs) and Perfluorooctane Sulfonamide in Methanol and, RM 8447 Perfluorinated Sulfonic Acids (PFSAs) in methanol, and three solutions produced by Wellington Laboratories (Guelph, Ontario) perfluoro-n-hexadecanoic acid (PFHxDA), perfluoro-n-octadecanoic acid (PFODA), and perfluoro-1-decanesulfonate (PFDS). Together, the solution contained 18 PFAAs: PFHxDA, PFODA, PFDS, PFBA, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic

acid (PFDoDA), perfluorotridecanoic acid (PFTriDA), perfluorotetradecanoic acid (PFTDA), PFBS, perfluorohexanesulfonic acid (PFHxS), PFOS, and perfluorooctanesulfonamide (PFOSA). Internal standards (IS) were purchased from Wellington Laboratories to create IS mixture comprised of isotopically labeled PFAAs: $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_8$-PFOSA.

Extraction and cleanup: Extraction and cleanup methods for PFAAs have been previously described in Reiner et al. (2012). Briefly, liver samples (approximately 1 g), blanks, and SRM 1947 Lake Michigan Fish Tissue (used as a quality control material; NIST, Gaithersburg, MD) aliquots were extracted using 0.01 mol/L of KOH in methanol, filtered, and further cleaned using graphitized non-porous carbon solid phase extraction (ENVI-Carb, Supelco). PFAAs were determined using liquid chromatography-tandem mass spectrometry (LC-MS/MS) in the multiple-reaction monitoring (MRM) mode on an Agilent 1100 HPLC system coupled to an Applied Biosystems API 4000 triple quadrupole mass spectrometer (Applied Biosystems) with electrospray ionization in negative mode. Two MRM transitions for each PFAA were monitored to ensure the validity of results, one MRM for quantitation and one MRM for confirmation.

Quality Control: Blanks and SRM 1947 aliquots were processed alongside liver samples for quality control. SRM 1947 has reference values for PFOS. Reporting limits (RLs) were calculated in each sample as the greater of either the lowest detectable calibration point or mean ± 3 standard deviations in the procedural blanks, all divided by the extracted sample wet mass. Acceptable r^2 values (≥ 0.99) were observed for the calibration curves of all compounds. Mass fractions of PFOS determined in SRM 1947 were within the certified values given on the Certificate of Analysis. RLs were generally less than 0.5 ng/g as received, except for PFHxA (<0.6 ng/g), PFBA, PFHpA, PFOA, PFDS (all <1.3 ng/g), and PFODA (<2.1 ng/g).

Nitrogen and carbon stable isotope analysis

Muscle tissues of birds were used for nitrogen and carbon stable isotope analysis. The data for seagull and domestic pigeon were presented in our previous report (Hong et al., 2014). The analysis for loon, heron, and egret were additionally performed in the present study. The analytical procedures of nitrogen and carbon stable isotopes were described elsewhere (Hong et al., 2014).

Statistical analysis

Sstatistical analyses were performed using SPSS ver. 19 (IBM Corp., Armonk, NY, USA). PFAA levels and carbon isotopes among bird groups were compared with the Kruskal-Wallis test followed by the Mann-Whitney U test. Pearson correlation analysis was used to examine the relationship between nitrogen isotope ratios and PFAA levels. Principal component analysis (PCA) was applied to identify differences among bird species for the following characteristics: (1) trophic levels and food sources using stable isotope ratios (‰) of nitrogen and carbon, (2) accumulation profile of PFAA compounds, and (3) accumulation pattern of PFAAs and other POPs.

3. Results and Discussion

Stable nitrogen and carbon isotope profiles

To compare their trophic position and carbon source, carbon and nitrogen isotope analyses were performed. Higher trophic animals are generally enriched in the heavier isotopes of nitrogen (^{15}N) and carbon (^{13}C) relative to lower trophic species. Particularly, nitrogen isotope ratio ($\delta^{15}N=((^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard} -1) \times 1000$) is used to estimate the trophic positions of organisms, while carbon isotope ratio ($\delta^{13}C=((^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{standard} -1) \times$

1000) provides information about carbon/energy sources at the base of food webs (Peterson et al., 1985). The mean ± standard deviation (range) $\delta^{15}N$ values in seagulls were 13 ‰ ± 1 ‰ (12 ‰ to 15 ‰), pigeons: 7 ‰ ± 1 ‰ (6 ‰ to 8 ‰), loons: 13 ‰ ± 1 ‰ (13‰ to 14‰), and herons/egrets: 14 ‰ ± 2 ‰ (12 ‰ to 17 ‰), (Fig. 2). The lower $\delta^{15}N$ values in pigeons suggest their lower trophic position than those of other species, whereas seagulls, loons, and egrets/herons presented similar $\delta^{15}N$ values, implying similar trophic levels. Seagulls, loons and herons/egrets are piscivorous birds that feed on primarily fish and invertebrates, while pigeons are granivorous and opportunistic birds that feed on corn, fruit, and worms. The mean ± standard deviation (range) $\delta^{13}C$ values in seagulls were –17 ‰ ± 1 ‰ (–19 ‰ to –15 ‰), pigeons: –21 ‰ ± 3 ‰ (–24 ‰ to –15 ‰), loons: –18 ‰ ± 1 ‰ (–19 ‰ to –18 ‰), and herons/egrets: –21 ‰ ± 2 ‰ (–2 3‰ to –17 ‰) (Fig. 2). Pigeons and egrets/herons, inhabiting on land or river (or brackish) waters, had lighter carbon isotopes than coastal and marine species (seagulls and loons) ($p < 0.05$, Mann-Whitney *U* test). This difference is in accordance with a previous observation on freshwater and marine fish inhabiting this region ($\delta^{13}C$: −23.2 ‰ ± 1.6 ‰ for freshwater fish and −17.3 ‰ ± 0.8 ‰ for marine fish) (Kang et al., 2009). This result emphasizes that carbon isotopic values in birds reflect isomeric patterns of their diet and habitat. Overall, the profiles of nitrogen and carbon stable isotopes can be summarized as follows: (1) pigeons have lower trophic position, (2) seagulls, loons, and herons/egrets have similar trophic position. (3) pigeons and herons/egrets use terrestrial (riverine)-derived carbon source, and seagulls and loons use marine-derived carbon source.

Levels of PFAAs in bird livers

A wide range of PFAAs were detected in bird livers from the Korean coast (Tables 1 and S1). PFHxDA and PFOS were detected in all samples, and PFNA, PFDA, PFUnDA, PFDoDA,

PFTriDA, PFTDA, and PFHxS were also frequently detected (75 % to 96 % of the samples). PFOA, PFODA, and PFOSA were detected much less frequently (4 % to 25 %). Most of short-chain PFCAs (PFBA, PFPeA, PFHxA, and PFHpA) except for PFOA were below the limit of quantitation in samples. The levels of hepatic PFAAs (unit: ng/g wet mass) in all bird liver samples ranged from 1.09 ng/g to 1060 ng/g with the median value of 52.6 ng/g. The PFAA levels were the highest in herons/egrets, followed by seagulls, loons, and pigeons (Table 1). Pigeons accumulated significantly lower levels of PFAAs than other species (Kruskal–Wallis test, $p < 0.05$), which could be explained by their lower trophic position as shown in nitrogen stable isotope values (Fig. 2). Overall, the hepatic PFAA levels showed a relationship with nitrogen isotope ratios in the birds ($r = 0.54$, $p < 0.01$). The previous study using the same species also detected the lowest levels of PCBs, organochlorine pesticides, and brominated flame retardants in muscle tissues of pigeons (Hong et al., 2014). Meyer et al. (2009) also reported significantly higher level of PFOS in higher trophic birds (grey heron *Ardea cinerea*, herring gull *Larus argentatus*, and sparrow hawk *Accipiter nisus*) than those of collared doves (*Streptopelia decaocta*) highlighting that diet may play a role in PFAA exposure to birds.

The total PFAAs in piscivorous birds (seagulls, loons and herons/egrets) in this study (154 ng/g ± 262 ng/g, range: 16.2 ng/g to 1060 ng/g) are higher than those of marine invertebrates (2.63 ng/g to 39.1 ng/g; Naile et al., 2013; Choi et al., 2020; Lee et al., 2020) (Mann-Whitney *U* test, $p < 0.05$) and predatory fish (liver, 2.24 ng/g to 113 ng/g; Yoo et al., 2009; Hung et al., 2020) (Mann-Whitney *U* test, $p < 0.05$) from the Korean coasts, indicating biomagnification potential of PFAAs in coastal food web. Among PFAAs measured in this study, PFDA, PFUnDA, PFDoDA and PFOS present high gradients between bird and invertebrates (one or two orders of magnitude greater PFAA levels in birds), which is consistent with the previous observations from other regions (Kelly et al., 2009; Fang et al, 2014).

The total PFCAs in all bird liver samples ranged from 0.45 ng/g to 452 ng/g with the median value of 26.0 ng/g. Among the bird groups, PFCAs were highest in herons/egrets, followed by seagulls, loons, and pigeons (Table 1). Total PFSAs ranged from 0.64 ng/g to 740 ng/g (median: 24.1 ng/g) with highest levels in herons/egrets, followed by loons, seagulls, and pigeons (Table 1). Overall, the levels of PFCAs and PFSAs in the bird liver tissues were comparable to each other in all species with the high proportion of long-chain PFCAs (> C_9) and PFOS. Among all PFCA and PFSA analytes, PFOS was predominant across all species (range: 0.6 ng/g to 714 ng/g, mean: 60.7 ng/g, median: 21.5 ng/g) compromising 25 % to 67 % of total PFAAs (Fig. 3 and Table 1). Most of the hepatic PFOS levels are lower than the toxicity reference values (TRV, 600 ng/g) and the predicted no-effect concentration (PNEC, 350 ng/g) derived from northern bobwhites quail and mallards (Newsted et al., 2005). The exception is from one egret liver tissue (714 ng/g) measured in this study. Therefore, the current seabird hepatic PFOS levels are unlikely to pose adverse health effects, but some birds inhabiting inland and estuarine zones are being exposed to high PFOS that may cause adverse health effects and sensitivity may vary among species. Among PFCA compounds, PFUnDA was the highest measured (range: <0.31 ng/g –714 ng/g, mean: 21.5 ng/g), followed by PFTriDA > PFHxDA > PFDA > PFDoDA > PFTDA > PFNA > PFOA. PFUnDA and PFTriDA accounted for over 50 % of total PFCAs. No detection of short-chain PFCAs (< C_7) indicates their low bioaccumulative potential (Conder et al., 2008). PFOA (C_8) was detectable only in four birds (one pigeon and three loons), as opposed to being detected as the most predominant compound in abiotic environmental matrices across water, sediment and air from the Korean environment (Naile et al., 2013; Seo et al., 2019). The high detection frequency and high tissue residuals of long-chain PFCAs and PFOS in all bird species demonstrate their strong biomagnification potential in food webs. The levels and compositions of PFAAs varied among environmental matrices, species, and locations in Korea. In general, long-carbon chain PFCAs and PFOS were also

abundant in most biotic matrices such as fish, bird, marine mammal, and human blood (Yoo et al., 2009; Moon et al., 2010; Lam et al., 2014; Barghi et al., 2018; Seo et al., 2018, 2019), while congeners with short-carbon chain such as PFOA and PFBS were relatively abundant in abiotic matrices such as air, water and sediment (Naile et al., 2013; Seo et al., 2019). Xu et al. (2014) and Zhang et al. (2015) verified that long chain PFCAs (> C_8) and PFOS could be significantly biomagnified in marine (invertebrates to seagull) and freshwater food webs (phytoplankton to egret). The related mechanism is not clear, but a previous study (Jones et al., 2003) presented the binding affinity for hormone-binding protein in avian blood is strong for PFASs including PFOS and increases with increasing carbon chain length of PFCAs.

Among PFSA compounds, PFHxS and PFOS were detected in most samples, implying their wide use in Korea. PFOSA, a PFOS precursor, was not detected in resident birds (seagulls and pigeons) but was detected in migratory birds (loons and herons/egrets), although PFOS levels in seagulls was comparable to loons and herons/egrets. This result may suggest that loons and herons/egrets may be exposed to PFOSA in other regions before migration, or that the presence of PFOSA could also be an indicator of the differences in metabolism of PFOSA across species. Although PFBS, a PFOS alternative, was widely detected in wastewater treatment plant (influent, effluent, and sludge), air, and river water from Korea (Kim et al., 2012; Seo et al., 2019), it was not detected in any bird livers in this study, indicating low bioaccumulative potential of PFBS.

The hepatic PFOS level in black-tailed gulls collected from the Nakdong River estuary in 2009-2010 (mean: 32.5 ng/g, range: 7.06 ng/g to 82.1 ng/g; this study) is lower than those collected in 1993 (mean: 112 ng/g, range: 36 ng/g to 215 ng/g, n = 7), and within a similar range as in 1997 (range: 71 ng/g to 74 ng/g, n = 2) (Kannan et al., 2002), while hepatic PFOS in egrets/herons (mean: 195 ng/g, range: 7.34 ng/g to 714 ng/g; this study) is higher than those collected in 1993 (24.8 ng/g, n = 1; Kannan et al., 2002). Barghi et al. (2018) reported high

level of PFOS in black-tailed gulls (mean: 475 ng/g, range: 34.2 ng/g to 2510 ng/g, n = 8; sampling: 2010-2011) from other regions (west and east side) of Korea. The global production and use of PFOS-based chemicals for industrial applications have declined since 2000 (Paul et al., 2009), but this trend in PFOS levels seems to be not clear in coastal birds. Vertical profiles of PFAAs in sediment cores from semi-enclosed coastal bays (dated age range: 1955-2011; Shen et al., 2018) showed that PFOS levels stopped increasing after 2000 and the proportion of longer-chain PFCAs increased toward surface layer in industrialized bays, implying a shift in industrial use pattern of PFAAs from PFOS to longer-chain PFAAs. However, a steady increase of PFOS was also observed in some cores near domestic wastewater discharge and aquaculture farms. A 10-year (2006 to 2015) trend in PFAAs in serum of the Korean general population (Seo et al., 2018) showed gradual increases of PFAAs including PFOS from 2006 to 2013 and decreasing thereafter. Overall, available data on wildlife, including birds, is very limited and temporal trends are not able to be discerned. A long-term biomonitoring programme using black-tailed gulls is recommended because it is the most common resident bird with a large population across the Korean coasts. Non-destructive sampling, such as egg, blood, or serum, would also be a good choice for PFAA biomonitoring along with carcass tissues.

Compound or species-specific bioaccumulation

The homologue and isomer profiles of PFCAs may provide information on their sources and transport pathways. After release from diverse direct or indirect sources, the chain length composition of PFCAs is altered as a consequence of various phase-partitioning behaviours and biotic uptake and clearance in the ecosystem (Prevedouros et al., 2006). It is therefore difficult to estimate their sources from the data. The prevalence of long carbon chain (≥ 14)

PFCAs in bird livers is likely to imply that fluorotelomer-based substances is an important source of PFCAs in Korea.

Overall, odd-numbered carboxylates were more abundant than the even-numbered carboxylates in bird liver tissues; more specifically, odd-numbered carboxylates compared to the one carbon shorter even-numbered carboxylates (Fig. 3; i.e. PFNA > PFOA, PFUnDA > PFDA and PFTriDA > PFDoDA). It is known that fluorotelomer-based precursors (e.g., 8:2 fluorotelomer alcohol (FTOH) and 10:2 FTOH) generate both even and odd-numbered PFCA products (one or two carbons shorter than original fluorotelomer chain) in similar proportions through environmental degradation processes (e.g., atmospheric oxidation, aqueous photolysis, and biodegradation), and then higher bioaccumulation potential of longer-chain-length PFCAs results in the dominance of odd-chain length PFCAs over adjacent even-chain length PFCAs in high trophic level organisms (Prevedouros et al., 2006; Rotander et al., 2012). This odd-even chain pattern is consistent with previous wildlife studies worldwide (Hound et al., 2006; Verreault et al., 2007; Muir et al., 2019; Vorkamp et al., 2019; Schulters et al., 2020). The Korean bird and marine mammal studies also reported the dominance of long-chained and odd-numbered PFCAs (Yeo et al., 2008; Moon et al., 2010; Barghi et al., 2018), while this pattern was not observed in abiotic matrices (water, sediment, and soil) and low trophic level invertebrates (Yoo et al., 2009; Naile et al., 2013). Among the four bird groups, this homologue pattern was relatively weak in pigeons (for PFUnDA/PFDA and PFTriDA/PFDoDA) and herons/egrets (for PFTriDA/PFDoDA) compared to marine species.

To identify species-specific bioaccumulation of PFAAs, principal component analysis (PCA) was applied to the normalized data (relative mass fraction of individual compound to total PFAAs). For the PCA analysis, nine PFAA compounds (PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTDA, PFHxDA, PFHxS and PFOS) with high detection frequency in bird livers were used (Table S1). The relationship among bird samples is displayed on the score

plot, and the relationship among the variables (PFAA compounds) is displayed on the loading plot (Fig. 4). Three principal components explained 73 % of the total variation. The distribution pattern of the samples is based on the species difference. PFUnDA, PFTriDA, and PFOS are relatively abundant in higher trophic piscivorus birds (seagulls, loons, and egrets/herons), which is more pronounced in marine birds (seagull and loons) than estuarine birds (egret/heron). On the other hand, PFNA and even numbered PFCAs (PFDA, PFDoDA, PFTDA, PFHxDA), and PFHxS are relatively abundant in lower trophic granivorous birds (pigeons) and land/estuarine birds. This result reveals that the bioaccumulation profile of PFAAs is strongly influenced by trophic positions and habitats, which may be related with diet, metabolic potential of species, and degradable properties of PFAA itself.

In our previous study, we found different accumulation profiles of POPs in between marine and inland resident birds (seagulls and pigeons; Hong et al., 2014). The relative composition of emerging (or currently in use) contaminants such as PBDEs to total POPs (sum of PCBs, DDTs, CHLs, HCHs, and PBDEs) was greater in inland birds (pigeons) than in coastal bird (seagulls). Compound-specific congener or isomeric signatures also reveals direct exposure of inland species (pigeons and herons/egrets) to commercial chemical mixtures in use: high abundance of BDE 209, γ-HCH, and γ-HBCD that are main component of PBDE, HCH and HBCD commercial mixtures, respectively, but readily biodegradable and less bioaccumulative. To compare bioaccumulation feature of PFAAs with other group of POPs, (PCBs, DDTs, CHLs, HCHs, and PBDEs; Hong et al., 2014) data for the same individuals was combined with the PFAAs, and then PCA analysis was performed (Fig. 5). The log transformed mass fraction ratio of each chemical to total POPs was used for the analysis. Over 80 % of the variation in the data was explained the first two components of the PCA. PFOS and PFCAs were negatively loaded along with PBDEs and γ-HCH on the loading plot, which were the variables separating the distribution of pigeons and egrets/herons at the left side of the score plot. The relatively

high proportion of PFOS and PFCAs in pigeon and egret/heron is likely explained by direct and high load of PFAAs to inland (pigeons) and estuarine (egrets/herons) species as a result of wide use of PFAAs in the terrestrial environment. Relatively low bioaccumulation/biomagnification potentials of PFAAs compared to other POPs (PCBs, DDTs, HCB and CHLs) may also lead to less trophic transfer to birds having a longer food chain length (piscivorous birds: seagulls, loons, herons/egrets) compared to a shorter food chain length (granivorous birds; pigeons) (Haukås et al., 2007).

Conclusion

Perfluorinated compounds have been widely used in a variety of items and industrial processes, ultimately being released to the environment and becoming chemicals of global regulation. Notably, these chemicals are one of priority chemicals of concern in Korea due to recent detection of them in water, in water treatment plant, and effluent of wastewater treatment plant located in an industrialized riverine system. The present study identified that PFAAs broadly reached the upper trophic level organisms in the riverine ecosystems. Bioaccumulation of PFAAs differed according to trophic positions and habitat areas of birds; that is, granivorous and/or inland birds accumulated more less-bioaccumulating PFAA compounds (e.g. long-chained and odd-numbered PFCAs, and PFOS) compared to piscivorous and marine birds, and had higher ratio of PFAAs to legacy POPs, indicating the use of PFAAs in the terrestrial environment. Stockholm Convention has strengthened the regulation on the use of PFOS, PFOA, and their related compounds, but also allowed its specific exemptions such as semiconductor, textile, and photographic industries. Improper chemical management in the industrial processes (as seen in the Korean case) and chemical leaching from existing items can still be sources of PFAAs. Birds are good sentinels, not only for environment exposure, but also for human health hazard of regulated PFAAs and their alternatives because their habitat

and prey overlap with those of humans. A long-term biomonitoring programme using resident birds with a large population across a country is recommended (e.g., black-tailed gulls, heron/egret and pigeon for coastal, estuarine, and terrestrial environment, respectively).

Disclaimer

Any mention of a commercial product is for information purposes only. It does not imply any recommendation nor endorsement by the National Institute of Standards and Technology (NIST).

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Figure captions

Figure 1. Photo of study site (Nakdong River estuary and Busan coast) and biomonitoring species. Black-tailed gull (*Larus crassirostris*, hereafter referred to seagull), domestic pigeon (*Columba livia var. domestica*), pacific loon (*Gavia pacifica*), heron (*Ardea cinerea*), and egret (*Egretta garzetta and Ardea alba*)

Figure 2. Stable isotope ratios (‰) of nitrogen and carbon in muscle tissues of seagull, pigeon, loon and egret/heron. In case of seagull and pigeon, the stable isotope data published in the previous paper (Hong et al., 2014) was used.

Figure 3. Composition of perfluorinated compounds in seagull, pigeon, loon and heron/egret from the Nakdong River estuary, Korea.

Figure 4. Principal component analysis score plot (black symbols) and loading plot (blue arrows) of the accumulation pattern of PFAAs in seagull (G, ●), pigeon (P, ○), loon (L, ▼), and egret/heron (EH, △). Mass fractions of individual compounds are normalized to total PFAAs.

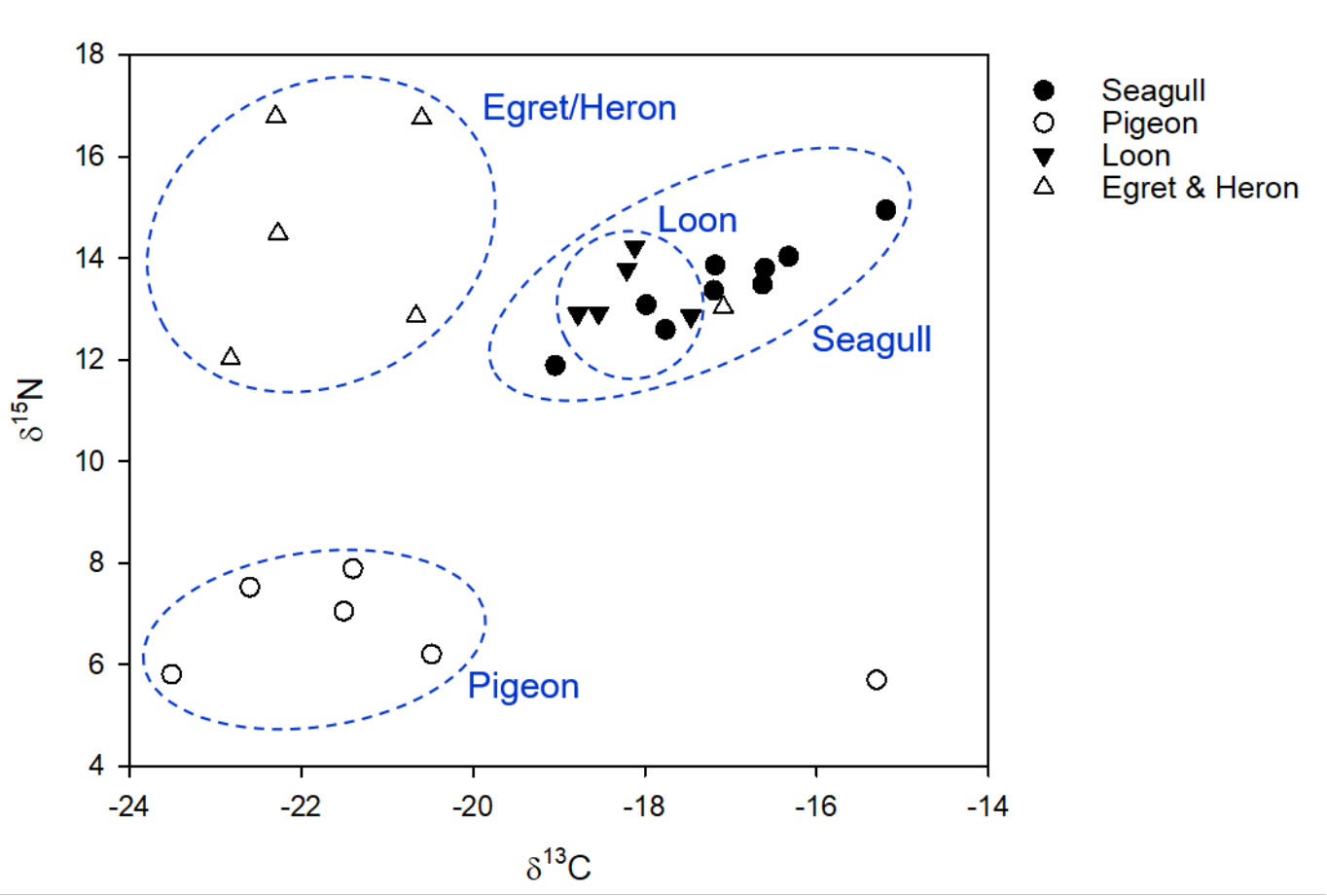
Figure 5. Principal component analysis score plot (black symbols) and loading plot (blue square) of the accumulation pattern of POPs including PCBs, DDTs, CHLs, γ-HCH, PBDEs, PFOS, and PFCAs in seagull (G, ●), pigeon (P, ○), loon (L, ▼), and egret/heron (EH, △) from the Nackdong River estuary and Busan coast. For the comparison of PFAAs with other POPs, the PFCAs and PFOS data were processed with the PCBs, DDTs, CHLs, γ-HCH, and PBDEs data for the same individual that was previously published in Hong et al. (2014). The lipid weight based mass fractions of PCBs, DDTs, CHLs, γ-HCH, and PBDEs were converted to wet weight based mass fractions prior to PCA analysis.

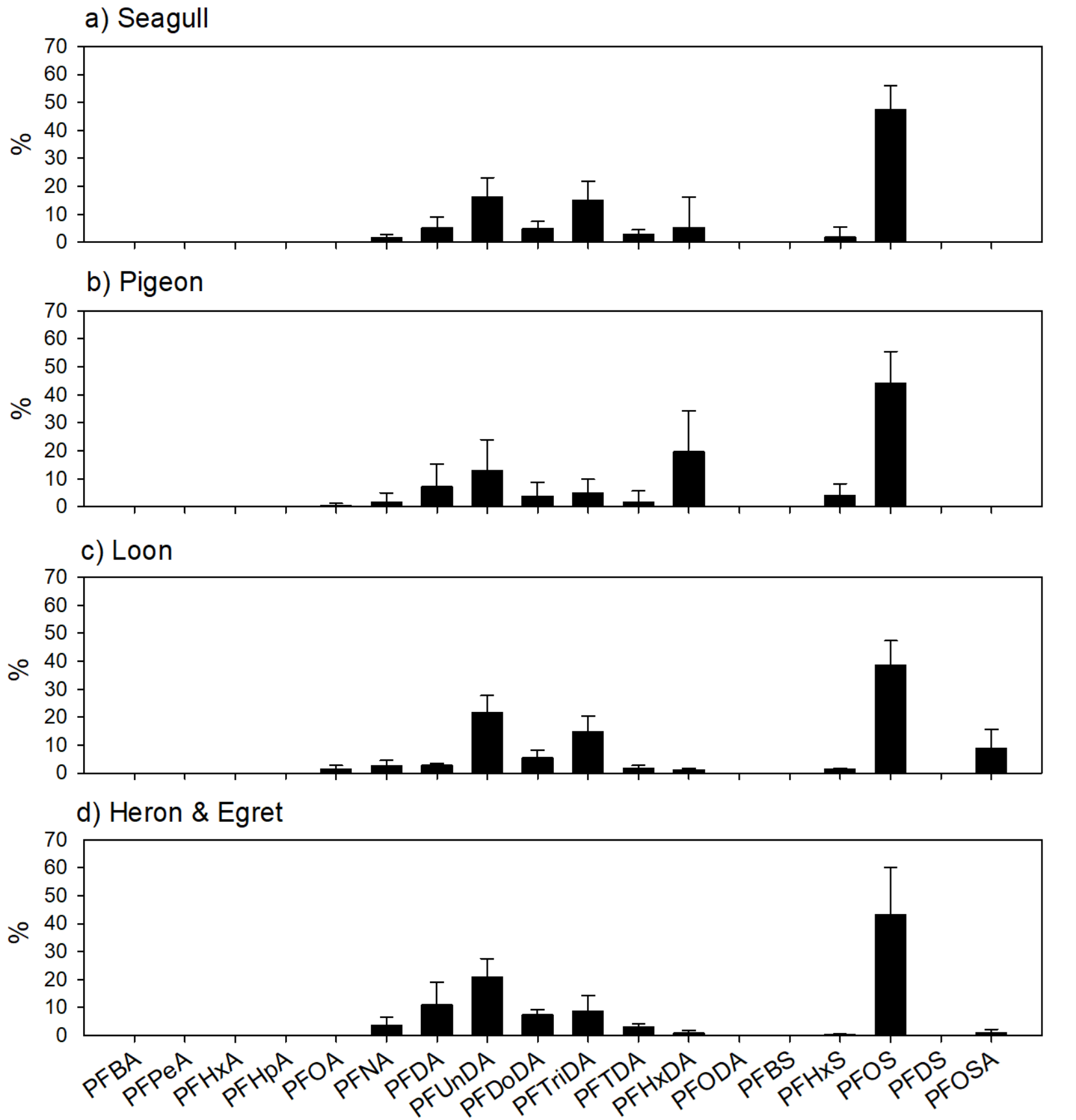
Black-tailed Gull

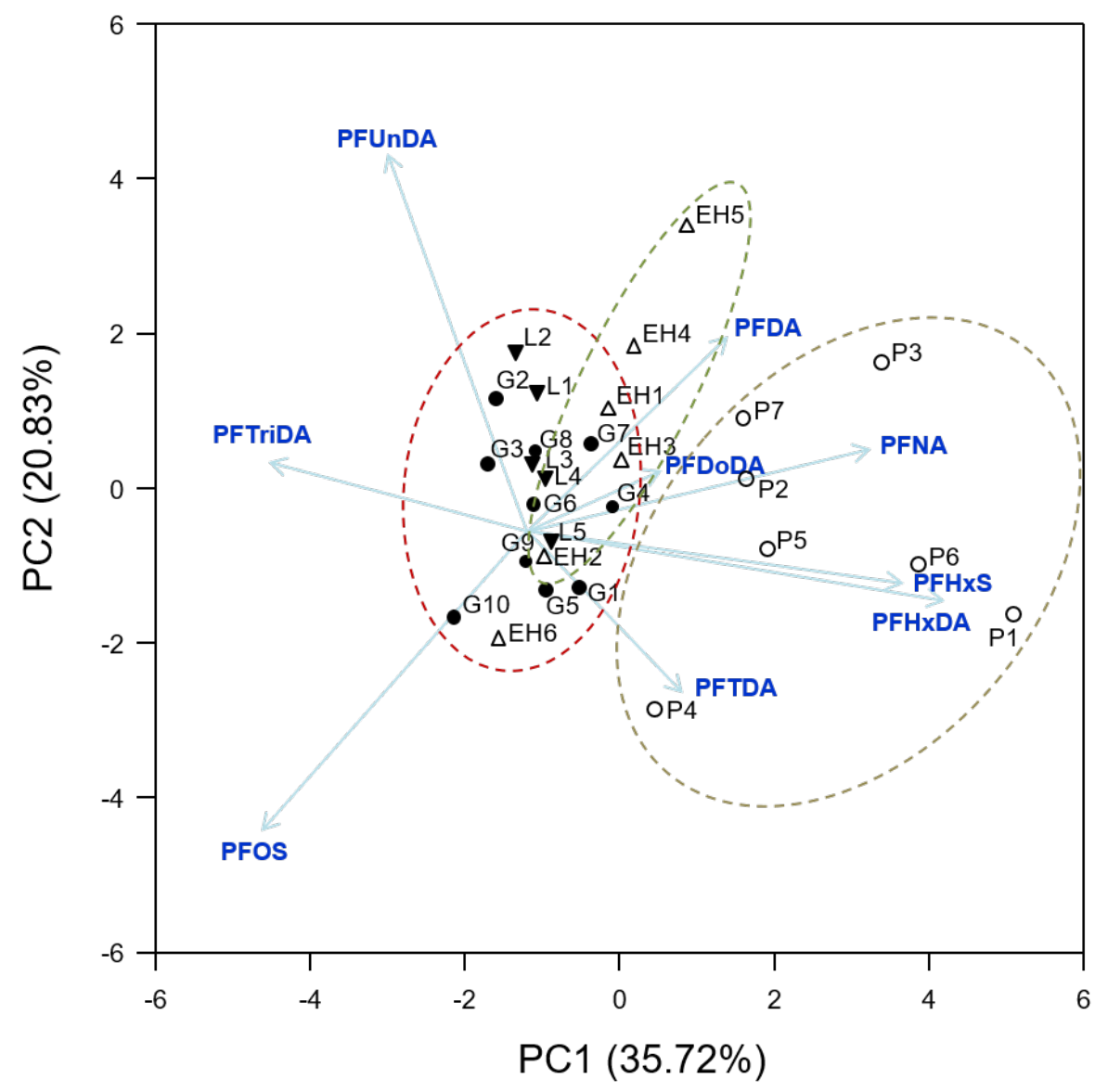
Domestic Pigeon

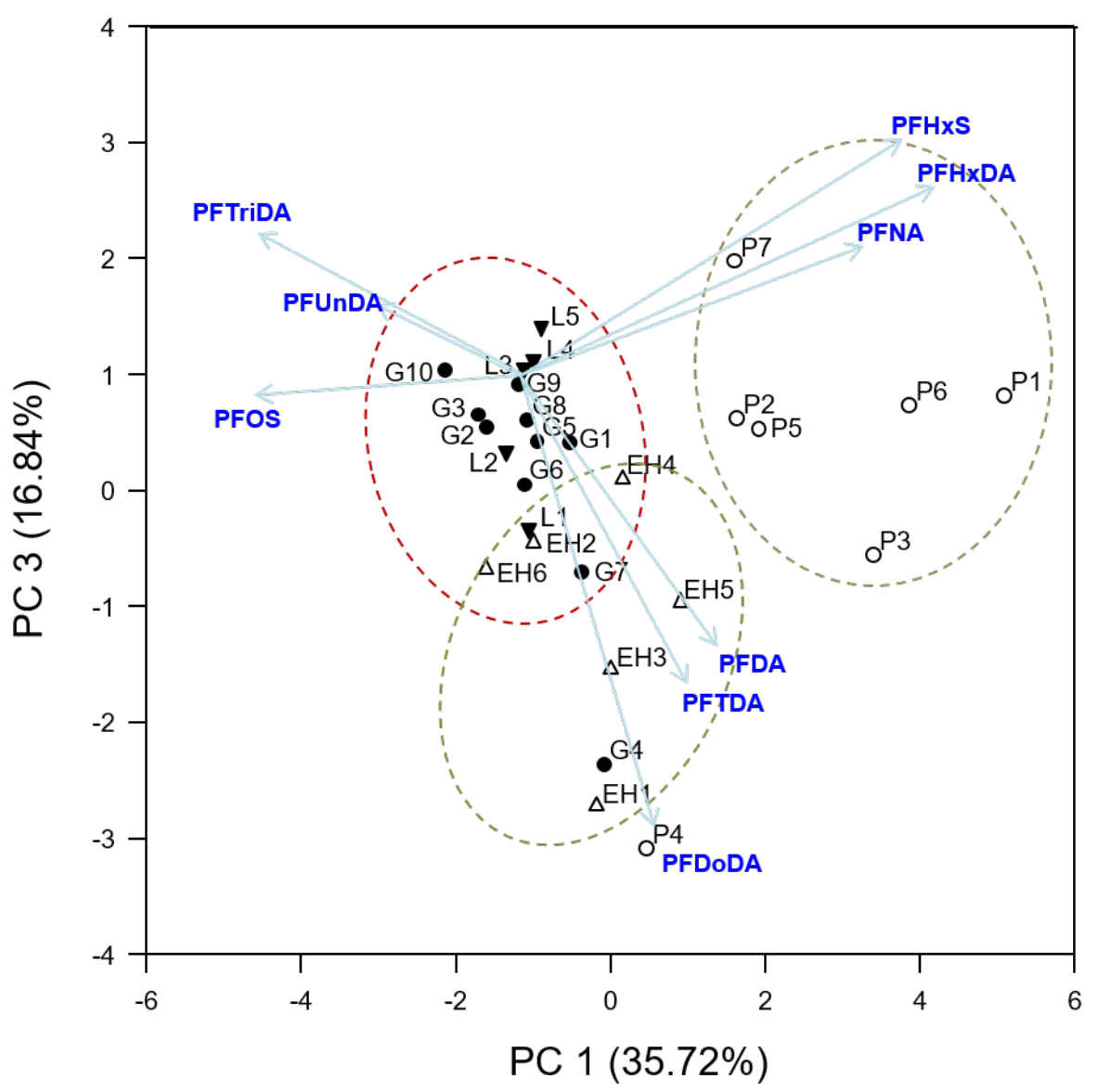
Pacific loon

Heron, Egret


Egret/Heron
Loon
Seagull
Pigeon
Seagull
Pigeon
Loon
Egret & Heron
18
16
14
12
10
8
6
4
-24
-22
-20
-18
-16
-14
δ15N
δ13C


a) Seagull
b) Pigeon
c) Loon
d) Heron & Egret
%
0
10
20
30
40
50
60
70
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
PFDoDA
PFTriDA
PFTDA
PFHxDA
PFODA
PFBS
PFHxS
PFOS
PFDS
PFOSA


PFUnDA
PFTriDA
PFOS
PFDA
PFNA
PFDoDA
PFHxS
PFHxDA
PFTDA
L1
L2
L3
L4
L5
G1
G2
G3
G4
G5
G6
G7
G8
G9
G10
EH1
EH2
EH3
EH4
EH5
EH6
P1
P2
P3
P4
P5
P6
P7
PC1 (35.72%)
PC2 (20.83%)


PFHxS
PFHxDA
PFTriDA
PFNA
PFUnDA
PFOS
PFDA
PFTDA
PFDoDA
L1
L2
L3
L4
L5
G1
G2
G3
G4
G5
G6
G7
G8
G9
G10
EH1
EH2
EH3
EH4
EH5
EH6
P1
P2
P3
P4
P5
P6
P7
PC 1 (35.72%)
PC 3 (16.84%)

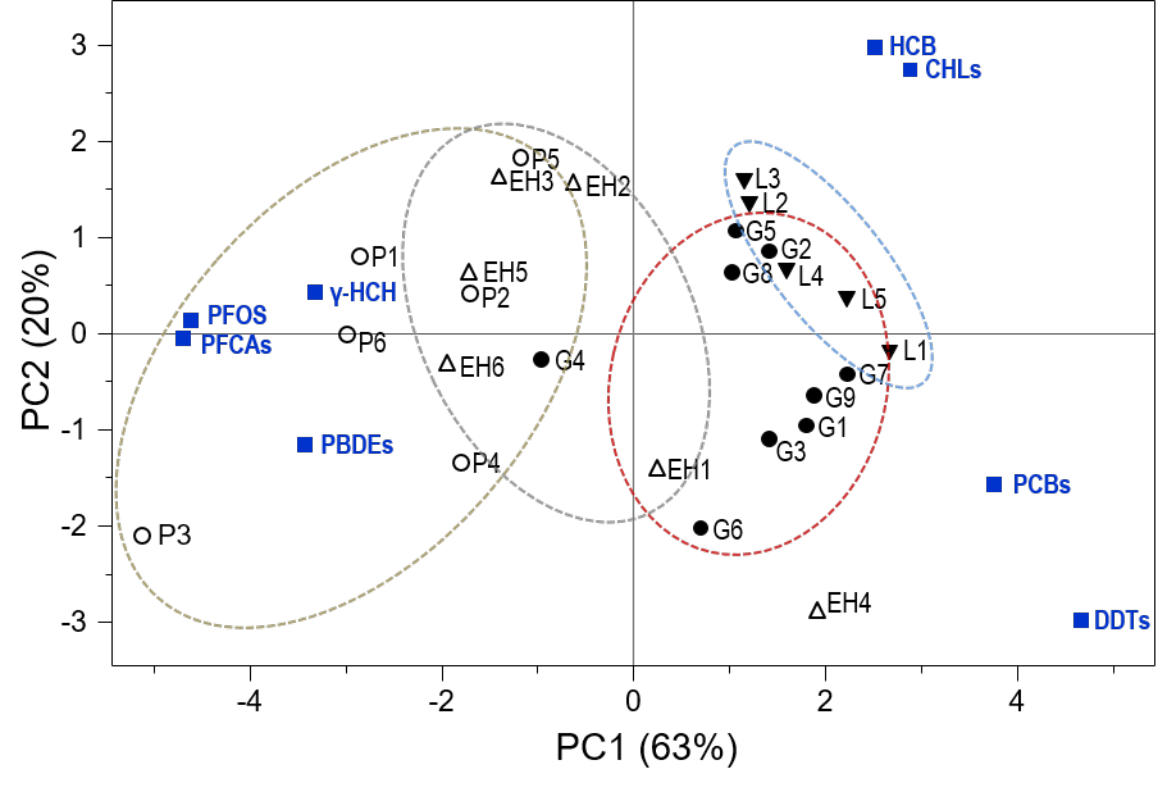
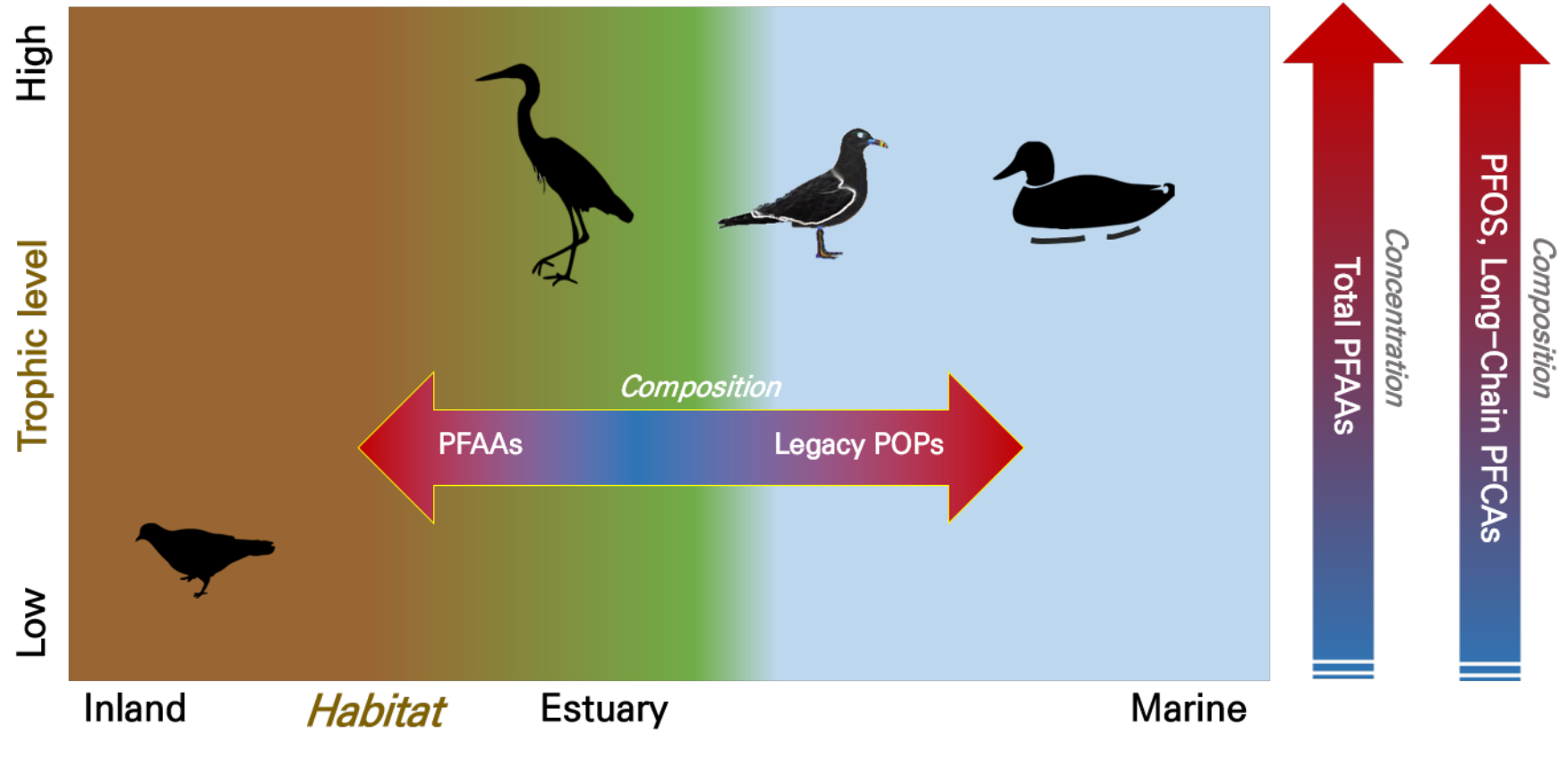

HCB
CHLs
PFOS
PFCAs
γ-HCH
PBDEs
PCBs
DDTs
P1
P2
P3
P4
P5
P6
EH1
EH2
EH3
EH4
EH5
EH6
G1
G2
G3
G4
G5
G6
G7
G8
G9
L1
L2
L3
L4
L5
PC1 (63%)
PC2 (20%)
3
2
1
0
-1
-2
-3
-4
-2
0
2
4

Table 1. Mass fractions (ng/g wet weight) of PFAAs in bird livers from South Korea

Species	Black-tailed gull (n=10) (coast, resident, piscivorous) [a]	Pacific loon (n=5) (marine, winter migrant, piscivorous)	Domestic pigeon (n=7) (inland, resident, granivorous)	Heron & Egret (n=6) (estuary, resident or summer migrant, piscivorous)
PFBA	<1.28	<1.24	<1.22	<1.21
PFPeA	<0.19	<0.18	<0.18	<0.18
PFHxA	<0.56	<0.54	<0.53	<0.53
PFHpA	<0.1.25	<1.21	<1.19	<1.18
PFOA	<1.25	<1.12–2.0 (1.12±1.02, 1.79)	<1.29–2.74 (0.39±1.04, <1.29)	<1.18
PFNA	<0.41–4.21 (1.39±1.36, 0.83) [b]	<0.31–3.94 (1.94±1.43, 2.17)	<0.43–3.38 (0.58±1.26, <0.43)	9.45–8.15 (4.85±2.78, 5.55)
PFDA	0.68–18.7 (4.34±5.48, 2.15)	0.44–2.57 (1.95±0.87, 2.19)	<0.32–8.08 (1.47±2.95, 0.44)	<0.31–137 (31.4±53.7, 9.7)
PFUnDA	2.03–47.9 (13.8±14.6, 6.78)	5.76–21.2 (13.5±5.75, 13.1)	<0.35–5.19 (1.43±1.78, 1.32)	7.7–151 (64.4±68.1, 33.8)
PFDoDA	0.72–18.7 (4.30±5.56, 1.88)	2.03–4.80 (3.11±1.08, 2.96)	<0.35–10.9 (1.72±4.06, <0.35)	1.78–80.1 (30.8±37.7, 10.6)
PFTriDA	3.60–34.0 (11.0±9.88, 6.25)	4.55–14.7 (8.96±3.80, 7.65)	<0.29–12.6 (1.99±4.69, 0.31)	4.82–53.2 (22.3±23.5, 9.24)
PFTDA	0.61–9.30 (2.37±2.77, 1.16)	0.43–1.87 (0.92±0.57, 0.68)	<0.40–13.5 (1.93±5.10, <0.40)	1.37–27.3 (10.2±11.7, 4.21)
PFHxDA	0.61–1.38 (0.83±0.21, 0.80)	0.44–0.70 (0.62±0.11, 0.67)	0.45–2.74 (0.96±0.80, 0.69)	0.68–1.74 (1.08±0.38, 1.05)
PFODA	<2.05	<1.99	<2.12	<1.95–2.23 (0.37±0.91, <1.95)
PFBS	<0.19	<0.18	<0.20	<0.18
PFHxS	0.18–0.95 (0.38±0.23, 0.29)	0.37–1.13 (0.78±0.31, 0.70)	<0.15–0.25 (0.17±0.08, 0.19)	0.14–5.95 (1.27±2.30, 0.33)
PFOS	7.06–82.1 (32.5±25.7, 20.4)	6.92–38.4 (26.0±12.3, 30.7)	0.64–64.8 (10.6±23.9, 1.67)	7.34–714 (195±279, 50.6)
PFDS	<1.25	<1.21	<1.29	<1.18
PFOSA	<0.19	<0.14–14.7 (6.91±5.76, 4.97)	<1.95	<0.18–20.4 (5.47±8.02, 2.13)
∑PFCA	8.82–107 (38.1±36.3, 21.6)	13.8–46.8 (32.1±12.2, 31.3)	0.45–59.1 (10.5±21.5, 3.30)	21.8–452 (165±178, 87.3)
∑PFSA	7.42–83.0 (32.8±25.9, 20.7)	7.29–48.6 (33.7±17.0, 42.3)	0.64–65.0 (10.8±23.9, 1.90)	7.48–740 (202±289, 53.0)
∑PFAA	16.2–182 (70.9±60.6, 40.5)	21.1–86.9 (65.8±25.6, 73.6)	1.09–124 (21.3±45.4, 5.19)	29.3–1060 (367±438, 138)

[a] Habitat and diet type; [b] Mass fraction: min–max (mean ± standard deviation, median)


High
Trophic level
Low
Inland
Habitat
Estuary
Marine
Composition
PFAAs
Legacy POPs
Total PFAAs
Concentration
PFOS, Long-Chain PFCAs
Composition