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Dechlorane Plus and Related Compounds in Peregrine Falcon (*Falco peregrinus*) Eggs from Canada and Spain

Paula Guerra,[†] Kim Fernie,[*,‡] Begoña Jiménez,[§] Grazina Pacepavicius,[∥] Li Shen,[⊥] Eric Reiner,[⊥] Ethel Eljarrat,[†] Damià Barceló,[†,#] and Mehran Alaee[∥]

[†]Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona, 18-26, 08034 Barcelona, Spain

[‡]Ecotoxicology and Wildlife Disease, Science and Technology Branch, Environment Canada, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

[§]Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

[∥]Water Science and Technology, Environment Canada, 867 Lakeshore Road, Burlington Ontario, Canada L7R 4A6

[⊥]Ontario Ministry of Environment, 125 Resources Road, Toronto, Ontario, Canada M9P 3 V6

[#]Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, Pic de Peguera 15, 17003 Girona, Spain

Supporting Information

ABSTRACT: Concentrations of Mirex, Dechlorane (Dec) Plus (DP), Dec 602, Dec 603, and Dec 604 were significantly higher in peregrine falcon (*Falco peregrinus*) eggs from Canada than Spain, with the former having the only measurable concentrations of the dechlorinated DP products, decachloropentacyclooctadecadiene (aCl10DP) and undecachloropentacyclooctadecadiene (aCl11DP). Large variations also occurred in the *in ovo* concentrations of the DP monoadduct, DPMA. This is the first study to report the accumulation and metabolism of DP by peregrines, both DP and dechloranes in European biota, as well as dechloranes in a terrestrial organism and one at the top of the food web. The geographical differences in the measured *in ovo* concentrations reflect local exposure of the adult peregrines on their breeding grounds, likely differences in diet of the adults, the production of DP on the Niagara River, and the greater use of Mirex and dechloranes as flame retardants in North America than Europe.

INTRODUCTION

Halogenated flame retardants (HFRs) are a structurally diverse group of chemicals that are generally brominated or chlorinated. These compounds are added to or reacted with polymers, textiles, and electronic circuitry to reduce the risk of fire. Dechlorane Plus (DP) is a chlorinated flame retardant ($C_{18}H_{12}Cl_{12}$) manufactured in China[1] and for more than 40 years by Oxychem in North America (Niagara Falls, NY). In commercial DP products, two stereoisomers, syn- and anti-DP, occur at a ratio of approximately 1:2 respectively, and plastic formulations may contain as much as 35% (weight basis) of DP.[2] These stereoisomers are the products of the Diels−Alder reaction of 2 mol of hexachlorocyclopentadiene with 1 mol of 1,5-cyclooctadiene.[3] This DP formulation is used primarily in products such as cable coatings, plastic roofing materials, and hard connectors in computers and televisions, and there are recent reports of DP isomers in biotic and abiotic samples from the Great Lakes of North America.[3−5]

DP is a high volume production chemical (500−5000 tons/year) that has been in use since 1986 and is sold worldwide, including Europe and Asia.[5] It replaced Dechlorane ($C_{10}Cl_{12}$), or Mirex, previously used as a pesticide and as a flame retardant until it was banned in the 1970s in North America. DP is also listed on Canada's Domestic Substances List (DSL), but in terms of bioaccumulation it is not considered to be of high risk because of its high molecular mass (648 Da) and high log K_{ow} (9.3).[6] DP has been measured in air,[4,6] indoor dust,[7] sediments,[4,8−11] and biota.[3−5,10−13] In the eggs of herring gulls (*Larus smithsonianus*), the sum (Σ) DP concentrations were generally <15 ng/g wet weight (ww) and the anti-DP values suggested a nonstereoselective enrichment of the DP stereoisomers.[5] However, there was an enrichment of the syn-DP isomer relative to the commercial mixture in smelt and alewife from Lake Ontario.[3]

Similar to DP, Dechlorane (Dec) 602, Dec 603, and Dec 604 were developed and manufactured by the same manufacturer as DP, Oxychem, in order to improve the flame retardant property of polymers in the late 1960s and 1970s. Shen et al.[10] provided the initial study of these compounds in sediments and fish from the Great Lakes, and this is the only assessment in biota to date. The concentrations of Dec 602, Dec 603, and Dec 604 in sediments were 0.97−11000, 0.61−600, and nd-8000 pg/g dry weight (dw), respectively, and in fish the concentrations ranged from 470 to 34000, 14−550, and nd-1300 pg/g lipid weight (lw), respectively.

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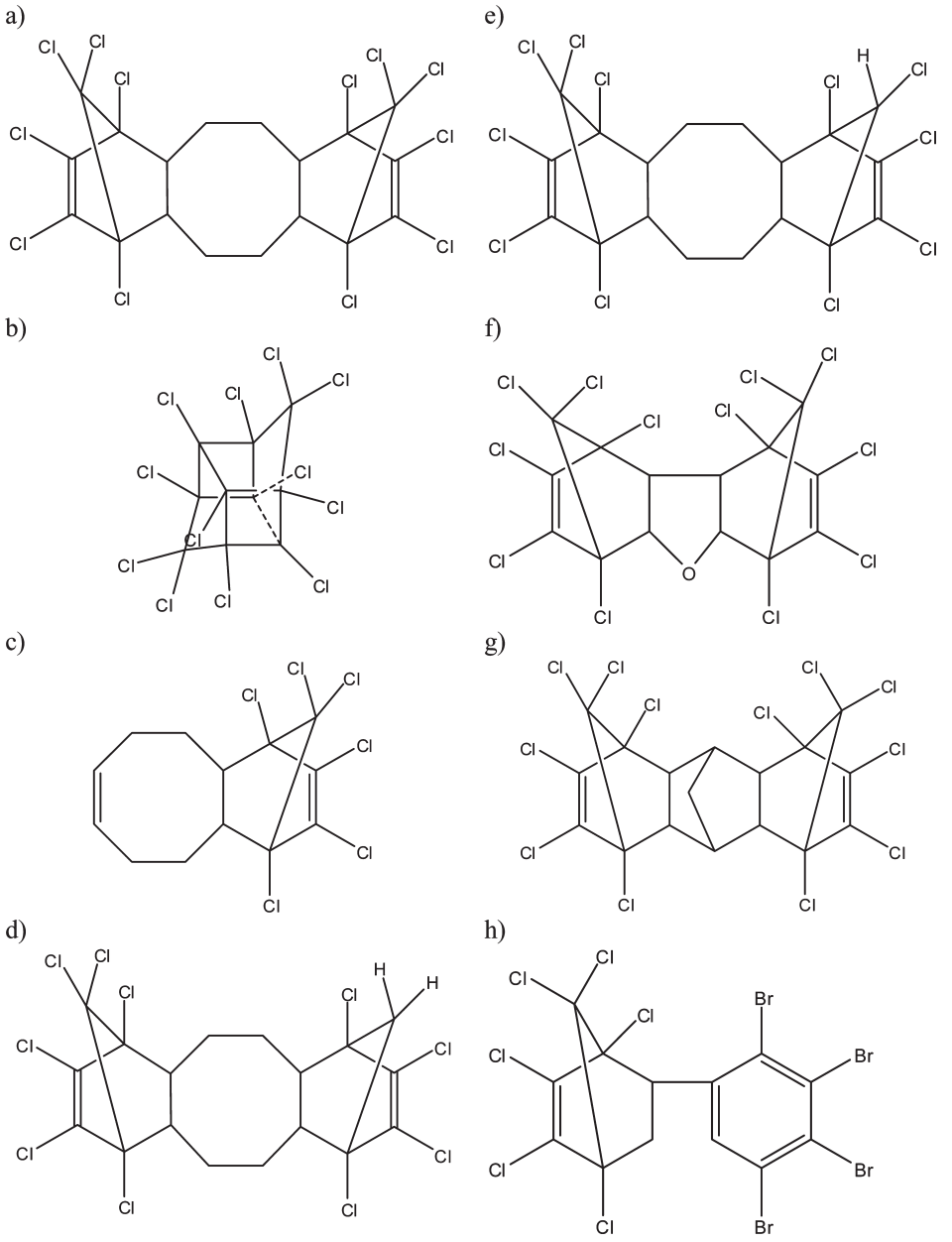

Figure 1. Molecular structures of a) DP, b) Mirex, c) DPMA, d) Cl10DP, e) Cl11DP, f) Dec 602, g) Dec 603, and h) Dec 604.

Peregrine falcons were previously endangered in the northern hemisphere partly because of the bioaccumulation of organochlorine pesticides, but their populations are now recovering. Peregrines are an excellent sentinel species for monitoring environmental organic contaminants[14−19] because they are at the top of the food chain and consume avian prey from the aquatic and terrestrial environments. A female bird of prey gains weight immediately before egg laying, and her ability to lay eggs is related to the availability of food on her breeding territory during egg formation (ref 20 and references therein). Most peregrines that breed in the northern hemisphere, especially in Canada, overwinter in the southern hemisphere. Their exposure to organochlorine pesticides on these overwintering grounds declined between 1978 and 2004 as measured in female peregrines during migration from Central and South America.[19] Peregrine eggs and nestlings have been used to assess concentrations of new and emerging chemicals of concern, including polybrominated diphenyl ethers (PBDEs), with some of the highest PBDE concentrations ever found in biota reported in this species.[15,17,18]

In this study, the eggs of peregrine falcons nesting in the Canadian Great Lakes and the Maritimes, as well as central and coastal Spain, were used to investigate the occurrence of halogenated norbornenes, specifically Mirex, DP, Dec 602, Dec 603, and Dec 604. Since DP is a diadduct compound, it may be affected by a retro-Diels−Alder process, leading to the possibility of a monoadduct formation. Consequently, the peregrine falcon eggs were also analyzed for the DP monoadduct, DPMA, as well as two of the dechlorinated products of DP, decachloropentacyclooctadecadiene (aCl10DP) and undecachloropentacyclooctadecadiene (aCl11DP). The molecular structures of these chemicals are illustrated in Figure 1.

EXPERIMENTAL SECTION

Chemicals. Dec 602 (95%), Dec 603 (98%), and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). DP, DPMA, aCl10DP, and aCl11DP were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada), and Mirex was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). Silica gel (100−200 mesh) was purchased from Merck (Germany). All solvents were of analytical grade (J.T. Baker, USA). Individual stock standard solutions were prepared on a weight basis in toluene and stored at −20 °C. A mixture of all selected standards was prepared by appropriate dilution of individual stock solutions.

Sampling. In Canada, all collections were completed with necessary permits that prohibit the collection of eggs with live embryos. Between 2007 and 2009, eggs that had failed to hatch ($n = 12$) were collected from active nests ($n = 12$ nests) located in the Canadian Great Lakes Basin (Figure SI-1), usually from the same nests in which plasma concentrations of polychlorinated biphenyls (PCB), PBDE, and HBCD were assessed in nestlings in 2004 and 2005.[15] The nests were designated as upstream (Lake Superior) of the DP manufacturing plant on the Niagara River or downstream of the plant and involved the nests on Lake Ontario and the St. Lawrence River but excluded the one nest (egg C1) in Eastern Canada (near St. John, New Brunswick) that was more than 1000 km east of the Niagara River (Table 1; Figure SI-1). From 2003 to 2006, 13 eggs were collected from 13 active nests in Central and coastal Spain, specifically Guadalajara in Central Spain and Bilbao on the North-Cantabric Coast of Spain (Figure SI-2).

Over the past 15 years, eggs that have failed to hatch, feathers, and other prey remains have been collected at Canadian nest sites when the nestlings were banded. The prey remains were identified to species and categorized according to aquatic (e.g., gull colonies) or terrestrial (e.g., passerine species) habitats. Following Fernie and Letcher,[15] this information provided a preliminary classification of the diet of the adult peregrines laying eggs in this study. The classification of the Spanish eggs was based on nest location: coastal-aquatic nests and inland-terrestrial nests. Because this is a preliminary classification, the subsequent results should be interpreted with caution and subsequent stable isotope analysis is recommended.

Sample Preparation. Before extraction, sampled eggs were lyophilized, homogenized, and stored at −22 °C; 3−5 g dry weight (dw) of sample was spiked with $^{13}C_{12}$−BDE-77 and $^{13}C_{12}$−BDE-153 (Wellington Laboratories, Canada). Extraction was carried out by Soxhlet method using 250 mL of dichloromethane (DCM) (Caledon Laboratories, Canada). The Soxhlet extract was passed through an Allihn funnel filled with prerinsed sodium sulfate (EMD, Tracepur, GR ACS 10−60 mesh). After extraction, the crude extracts were concentrated to approximately 2 mL, and then lipids were removed by Gel Permeation Chromatography (GPC) using a column packed with BioBeads (SX-3) (Bio-Rad Laboratories, Inc.) and eluted with DCM:hexane (1:1) solution.[21] 150 mL of DCM:hexane (1:1) was obtained with the compounds of interest. The lipid-free extracts were concentrated to 3 mL and transferred to a silica gel column (ACP Chemicals Inc., Grad 62, 60−200 mesh) and eluted with a mixture of DCM:hexane (1:1). Samples were finally concentrated to incipient dryness and redissolved, obtaining 500 μL of stable isotope labeled compound mixture containing $^{13}C_{12}$−BDE-79 and $^{13}C_{12}$−BDE-139 (Wellington Laboratories, Canada) in isooctane prior to analysis by gas chromatography high resolution mass spectrometry (GC-HRMS). The percent lipid in the egg homogenates ranged from 5.2 to 8.6% as determined gravimetrically.

Chemical Analysis. The sample extracts were analyzed on a HRMS Micromass AutoSpec Ultima MS (Micromass, Manchester, UK) connected to a Hewlett-Packard 6890 GC (Hewlett-Packard, Palo Alto, CA, USA) equipped with a 15 m DB-5HT column (0.25 mm i.d., 0.10 μm film thickness J&W Scientific, Folsom, CA). The temperature program was 100 °C for 2 min, ramped to 250 at 25 °C/min, ramped to 260 at 1.5 °C/min, ramped to 325 at 25 °C/min, and then held for 10 min. The HRMS system was operated in EI positive mode and was tuned up to 10,000 resolving power (RP) according to 10% valley definition. Concentrations of Mirex, DP, Dec 602, Dec 603, Dec 604, aCl10DP, Cl11DP, and DPMA in peregrine eggs were determined by monitoring the two most abundant ions of the fragment cluster at m/z 271.81/273.80 for Mirex, syn- and anti-DP and Dec 602, 262.85/264.85 for Dec 603, 417.70/419.70 for Dec 604,[10] 263.86/265.86 for DPMA, 201.89/203.88 for aCl10DP, and 237.84/239.84 for Cl11DP.

QA/QC. Method blank samples were run every five samples to check for interference or contamination from solvents and glassware. No presence of analytes of interest was observed. Identification and quantification were based on the following criteria: (a) sample peaks had an approximately Gaussian shape, and their GC retention times matched those of the standard compounds within ±0.1 min; (b) all peaks had a signal-to-noise ratio of greater than 5:1; and (c) peak areas were within 15% of the corresponding theoretical isotopic ratios. The limits of detection were between 0.004 and 0.3 ng/g lipid weight (lw), and the limits of quantification ranged from 0.01 to 1.0 ng/g lw. The recovery efficiencies, based on $^{13}C_{12}$−BDE-77 and $^{13}C_{12}$−BDE-153 internal standards, were 85 ± 8% and 92 ± 11%, respectively. All sample concentrations were recovery-corrected.

Statistical Analysis. Concentrations of DP, Dec 603, Dec 604, and DPMA were log-transformed prior to statistical analysis using one-way ANOVAs. All other data were analyzed using nonparametric Wilcoxon statistical tests. Potential differences relating to diet were not assessed in the peregrine eggs from Canada because of the very small sample size of aquatic-based eggs ($N = 2$) but were evaluated using the peregrine eggs from Spain since there was sufficient sample sizes (aquatic diet $N = 8$; terrestrial diet $N = 5$). Comparisons were made between eggs from Canada ($N = 10$) and Spain ($N = 5$) based solely on peregrines having a terrestrial diet.

RESULTS AND DISCUSSION

The concentrations of mirex, DP, Dec 602, Dec 603, Dec 604, DPMA, aCl10DP, Cl11DP, and lipids measured in the peregrine eggs (Table 1) mostly reflect contaminant exposure of the peregrines on the breeding grounds. Prior to and throughout the egg laying period, adult peregrines capture prey within their breeding territory. The occurrence of egg laying is related to the body condition of the female and the availability of food on the breeding territory (ref 20 and references therein). During egg formation, the prey of the peregrines may include migrating birds, including birds from the southern Great Lakes and those that have overwintered in Central and South America. Since 1978, concentrations of organochlorine pesticides have declined in female peregrines captured during their Spring migration from

Table 1. Concentrations of Mirex, Dechlorane (Dec) Plus (DP), *f* anti, Dec 602, Dec 603, Dec 604, the DP Monoadduct, DPMA, DPMA:DP Ratios, and the Dechlorinated DP Products, Decachloropentacyclooctadecadiene (aCl10DP), and Undecachloropentacyclooctadecadiene (aCl11DP) (ng/g Lipid Weight (lw)) in Peregrine Falcon (*Falco peregrinus*) Eggs from Canada and Spain[a]

country, presumed diet		N	lipid (%)	Mirex	ΣDP	*f* anti*	Dec 602	Dec 603	Dec 604	DPMA	DPMA:DP	aCl10DP	Cl11DP
limit of detection				0.021	0.012		0.027	0.011	0.028	0.045		0.39	0.048
limit of quantification				0.053	0.036		0.091	0.023	0.072	0.15		0.91	0.124
Spain - Overall	overall GM	13	5.7	18.9	1.78	0.77	8.36	3.98	0.23	21.1	12.3	.	0.18
Spain − terrestrial	geometric mean	5	5.5	13.5	0.6	0.8	9.78	2.33	0.33	2.19	3.75	.	.
	range	5		2.4 − 17	0.3 − 3.6	0.62 − 0.75	n.d. − 15	1.5 − 6.2	n.q. − 0.35	1.7 − 37	2.2 − 10	-	-
	median	5		14	0.6	0.74	4.8	2.4	0.32	2.5	4.8	-	-
	# eggs detected in	of 5		5	5		4	5	4	5		0	0
Spain − aquatic	geometric mean	8	5.7	29	2.81	0.77	13.3	4.91	0.18	71.2	25	.	0.18
	range	8		9.2 − 78	0.4 − 17	0.65 − 0.78	n.d. − 25	3.0 −7.5	n.d. − 0.32	n.d. − 469	2.2 − 336	-	n.d. − 0.28
	median	8		29	2.3	0.69	15	5.2	0.31	51	22	-	0.13
	# eggs detected in	of 8		8	8		8	8	5	7		0	3
Canada − overall	overall GM	12	5.8	641	36.4	0.58	73.3	35.6	3.38	30.2	1.17	1.62	1.84
Canada − terrestrial	geometric mean	10	5.6	733	38.4	0.58	89.2	43.9	3.7	30.5	1.2	1.58	1.81
	range	10		425−1353	7.5 − 209	0.41 − 0.69	44 − 211	12 − 220	1.4 − 9.8	1.2 − 1660	0.02 − 41	n.d. − 1.9	1.3 − 2.3
	median	10		744	43	0.63	71	52	3.9	62	2.1	1.7	1.9
	# eggs detected in	of 10		10	10		10	10	10	10		9	10
Canada − aquatic	geometric mean	2	7.1	330	27.7	0.55	27.4	12.4	2.13	28. 8	1.04	1.79	1.96
	range	2		94 − 1160	6.3 − 122	0.52 − 0.60	7.2 − 104	5.3 − 29.0	1.3 − 3.5	3.8 − 218	0.6 − 1.8	1.6 − 2.0	1.6 − 2.4
	median	2		626	64	0.56	55	17	2.4	111	1.2	1.8	2
	# eggs detected in	of 2		2	2		2	2	2	2		2	2

egg	year	location	presumed diet	lipid (%)	Mirex	ΣDP	*f* anti*	Dec 602	Dec 603	Dec 604	DPMA	DPMA:DP	aCl10DP	Cl11DP
S1	2004	Guadalajara, SP	terrestrial	6.9	2.4	3.6	0.62	0.24	6.2	0.25	37	10	n.d.	n.q.
S2	2003	Guadalajara, SP	terrestrial	6.0	14	0.81	0.75	n.d.	2.2	0.35	1.7	2.2	n.d.	n.q.
S3	2004	Guadalajara, SP	terrestrial	5.2	10	0.03	1.00	13	3.7	n.q.	2.1	6.9	n.d.	n.q.
S4	2003	Guadalajara, SP	terrestrial	5.4	14	0.9	0.75	15	2.4	0.32	2.5	2.7	n.d.	n.q.
S5	2003	Guadalajara, SP	terrestrial	5.5	17	0.62	0.73	4.8	1.5	0.31	2.6	4.8	n.d.	n.q.
S6	2006	Bilbao, SP	aquatic	5.2	9.2	1.2	0.65	15	6.5	n.d.	45	37	n.d.	n.q.
S7	2006	Bilbao, SP	aquatic	5.1	21	2.5	0.73	n.d.	5.5	n.d.	n.d.	-	n.d.	0.13
S8	2006	Bilbao, SP	aquatic	6.1	25	1.2	0.70	7.6	3.6	0.09	26	22	n.d.	n.d.
S9	2006	Bilbao, SP	aquatic	5.9	23	8.3	0.67	8.3	4.1	0.29	18	2.2	n.d.	n.d.
S10	2006	Bilbao, SP	aquatic	5.6	42	9.00	0.78	15	2.9	0.11	57	6.3	n.d.	0.16
S11	2006	Bilbao, SP	aquatic	6.4	43	17	0.68	22	4.9	0.32	123	7.2	n.d.	0.28
S12	2006	Bilbao, SP	aquatic	6.1	78	2.1	1.00	25	7.5	0.24	469	223	n.d.	n.q.
S13	2006	Bilbao, SP	aquatic	5.6	32	0.41	1.00	10	6.0	n.q.	134	336	n.d.	n.q.
C1	2008	New Brunswick, CD	terrestrial	5.6	1353	40	0.67	211	220	3.7	1656	41	1.8	1.8
C2	2008	Toronto, CD	terrestrial	5.4	471	16	0.68	143	19	2.6	72	4.6	1.7	1.7

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Table 1. Continued

egg	year	location	presumed diet	lipid (%)	Mirex	ΣDP	*f* anti*	Dec 602	Dec 603	Dec 604	DPMA	DPMA:DP	aCl10DP	Cl11DP
C3	2008	Toronto, CD	terrestrial	7.0	759	49	0.41	196	12	9.8	1.2	0.02	1.3	1.3
C5	2009	Toronto, CD	terrestrial	5.3	767	33	0.64	66	20	4.2	30	0.91	1.8	1.9
C6	2009	Toronto, CD	terrestrial	5.2	425	68	0.55	44	62	2.9	1.8	0.03	n.d.	2.3
C7	2009	Toronto, CD	terrestrial	5.9	1200	209	0.58	158	106	4.1	624	3.0	1.6	1.9
C11	2007	Montreal, CD	terrestrial	5.2	671	45	0.69	48	20	5.1	52	1.2	1.5	2.1
C12	2007	Montreal, CD	terrestrial	5.9	728	82	0.68	58	75	6.8	517	6.3	1.1	1.6
C4	2008	Thunder Bay, CD	terrestrial	5.3	1020	7.5	0.61	55	45	2.1	196	26	1.9	1.9
C10	2009	Thunder Bay, CD	terrestrial	5.6	474	17	0.43	77	60	1.4	1.5	0.088	1.7	1.8
C8	2009	North L. Superior, CD	aquatic	8.6	1160	122	0.52	104	29	3.5	218	1.8	1.8	2.4
C9	2009	North L. Superior, CD	aquatic	5.9	94	6.3	0.61	7.2	5.3	1.3	3.8	0.6	1.6	1.6

[a] The anti-DP fraction (*f* anti) is calculated as the concentration of anti-DP divided by the concentration of total DP. Geometric mean DPMA concentrations exclude the outlier Egg C1 collected from a nest in New Brunswick, Canada. GM: geometric means; n.q.: not quantifiable; n.d.: not detectable. For individual eggs: S: Spain, C: Canada.

overwintering in Central and South America.[19] Thus, the contaminant burden in the peregrine falcon eggs largely reflects local exposure on the breeding territory. In addition, differences in the *in ovo* contaminant concentrations in this study are not related to differences in the *in ovo* lipid concentrations, since they were comparable in the peregrine eggs from Canada and Spain, and regardless of diet for the peregrines nesting within Spain (all Ps $\geq$ 0.83).

Prior to being banned in the 1980s in North America, Mirex was used as a flame retardant and a widely used pesticide. Although Mirex was produced and used in China as late as 2009,[22] the peregrine falcons in this study are unlikely to have ever been in China since they migrate to the southern hemisphere from Spain or Canada. Despite the North American ban of Mirex more than 20 years ago, it was detectable in measurable quantities in all of the peregrine eggs from the Canadian Great Lakes and Spain (Table 1). *In ovo* concentrations of Mirex were the highest of the measured compounds in the peregrine eggs, although concentrations of DPMA were higher in some of the individual eggs from Spain and the one egg from New Brunswick, Canada (Table 1). Overall, the Mirex concentrations were greatest in the eggs laid by Canadian peregrines with a terrestrial diet than the Spanish birds with a terrestrial diet (χ = 5.5, df =1, P = 0.02) (Table 1), reflective of the production of Mirex in North America and not Spain. Interestingly, Mirex concentrations were significantly higher in the eggs laid by peregrines on the Spanish coast compared to the inland birds in Spain (χ = 5.5, df = 1, P = 0.02) (Table 1).

DP was also detected in all of the peregrine eggs, with ΣDP values ranging from 0.30 to 209 ng/g lw (Table 1). This is the first study reporting ΣDP concentrations in European biota, and there was no dietary influence on the ΣDP concentrations in these eggs from Spain (P = 0.10). In the peregrines with a terrestrial diet, ΣDP concentrations in the Canadian peregrine eggs were significantly and 40× higher than in the Spanish eggs ($F_{1,14}$ = 55.5, P < 0.0001; Table 1), suggesting localized exposure consistent with the DP manufacturing site on the Niagara River (Figure S1); this is further supported by the geographical pattern observed in the Canadian Great Lakes Basin in which ΣDP concentrations were significantly higher ($F_{1,8}$ = 15.26, P = 0.006) in the eggs collected from nests on Lake Ontario and the St. Lawrence River that are downstream of the DP manufacturing site, than from nests which were upstream on Lake Superior (Table 1). A similar pattern was also reported in herring gull eggs nesting on the same Laurentian Great Lakes.[5] However, the ΣDP concentrations in the peregrine eggs from Canada, both overall and laid by those birds having a terrestrial diet, are twice that of those measured in herring gull eggs (<15 ng/g ww) from the same Laurentian Great Lakes.[5] Herring gulls can fall prey to peregrine falcons, and so may be considered at a lower trophic position than peregrine falcons. These results suggest that DP is bioaccumulating.

Commercial grade DP is synthesized by the Diels−Alder addition of 2 mol fully chlorinated cyclopentadiene to 1 mol of cyclooctadiene, and the main products of the reaction are two stereoisomers, *syn* and *anti*, along with small amounts of by-product arising from impurities within the cyclooctadiene starting material. The anti-DP fraction (*f* anti) has been reported in fish[3] and herring gulls[4] as well as sediments[9] in the Laurentian Great Lakes, and these studies indicate that DP has been subject to stereoselective processes in the environment. In order to determine if such enrichment had occurred in the peregrines, either prior to uptake by the birds or via internal biochemical

processes by the adult prior to egg laying, *f* anti was calculated as the concentration of anti-DP divided by the concentration of total DP (Table 1). The *f* anti values for the peregrine eggs of Spanish birds with a terrestrial diet were significantly higher than their Canadian counterparts ($F_{1,14}$ = 6.7, P = 0.02) (Table 1), possibly reflecting the closer proximity of the Canadian birds to the manufacturing source of DP on the Great Lakes. There was no apparent dietary influence on the *f* anti values of the Spanish birds (P = 0.86), and 3 of these eggs had *f* anti values of 1.0 with no contribution of syn-DP (S3, S12, and S13) (Table 1) perhaps suggesting differences in bioavailability. The mean *f* anti values in the peregrine eggs (Table 1) are similar to the *f* anti values for herring gull eggs from the same Great Lakes[4] and in technical DP manufactured by OxyChem (0.65-0.80).[3−6,8−10] Both peregrine falcons and herring gulls are at or near the top of their food webs, respectively, whereas fish, including rainbow smelt *(Osmerus mordax)* and alewife *(Alosa pseudoharengus*), are at a relatively lower trophic level and had lower mean *f* anti values (0.53) in Lake Ontario.[3] Furthermore, stereoselective enrichment of anti-DP (0.86) occurred in the sediments of Lake Ontario.[9] Together, the results of these studies suggest that peregrine falcons are exposed to an already transformed DP prior to uptake and support the hypothesis that there are interspecies differences in bioaccumulation and biotransformation of DP.[3]

This is the first study to report the detection of Dec 602, Dec 603, and Dec 604 in a terrestrial organism, an organism at the top of the food web, and in European biota. Previously, only one other study reported these compounds in sediment and fish from the Laurentian Great Lakes.[10] Concentrations of Dec 602, Dec 603, and Dec 604 were detected in 92%, 100%, and 84% of the peregrine egg samples, respectively (Table 1). The results of this study are consistent with the high chlorination of these compounds and indicate their persistence and bioaccumulation in biota at the top of the food web. Overall, the contaminant profile of the peregrine eggs from Canada had higher concentrations of Dec 602 than DPMA, followed by Dec 603, whereas in the Spanish peregrine eggs, concentrations of DPMA dominated the Dec compounds. For the peregrines with a terrestrial diet, eggs from Canada had significantly higher concentrations of Dec 602, 603, and 604 than the Spanish eggs (all Ps ≤ 0.005), likely reflecting the production and possible greater use of these dechloranes as flame retardants in North America than Europe.[10] In Spain, only the concentrations of Dec 603 were significantly higher in the eggs laid by peregrines with an aquatic diet than those with a terrestrial diet ($F_{1,12}$ = 5.5, P = 0.04), suggesting that exposure to these compounds on the north coast of Spain may be greater than inland but further research is required.

DP is a diadduct compound that is synthesized by the Diels−Alder process, during which DPMA may be formed through partial reactions through abiotic processes.[11] DPMA was analyzed and detected in 24 out of 25 peregrine eggs with concentrations from 1.7 to 469 ng/g lw and 1.2 to 1660 ng/g lw in Spanish and Canadian peregrine eggs, respectively (Table 1). Furthermore, within Spain, the peregrines with an aquatic diet had significantly higher *in ovo* DPMA concentrations than the birds with a terrestrial diet ($F_{1,11}$ = 17.8, P = 0.002). The variation in the *in ovo* DPMA concentrations likely explains the statistical similarity between the eggs laid by peregrines with a terrestrial diet from Spain and Canada, including with the removal of the outlier egg from New Brunswick, Canada (P = 0.11). With the removal of this outlier, the contaminant profile of the eggs from Canada and Spain is dominated by similar concentrations of DPMA and Mirex that are much higher than ΣDP (Table 1), although the ratio of DPMA to ΣDP is similar in the eggs from both countries (P = 0.10). DPMA concentrations were greater than ΣDP likely because of the smaller size and lower molecular weight of DPMA resulting in DPMA having greater bioavailability.[11] In comparison, mean DPMA concentrations (34 ± 43 ng/g lw) in lake trout (*Salvelinus namaycush)* from Lake Ontario were comparable to those measured in the peregrine eggs, especially from Canada, but the trout had lower mean concentrations of ΣDP (0.21±0.12 ng/g lw)[11] especially compared to levels in the peregrine eggs from Canada.

DP may be dechlorinated into two species or moieties, aCl11DP and aCl10DP, which were previously reported in sediment samples from Lake Ontario.[9] In the current study, analysis of the elemental composition confirmed these peaks as $C_{18}H_{13}Cl_{11}$ and $C_{18}H_{14}Cl_{10}$ that correspond with aCl11DP and aCl10DP, respectively. Based on this methodology, concentrations between 1.1 to 2.4 ng/g lw were measured for aCl10DP (N = 11 of 12) and aCl11DP (N = 12 of 12) in the peregrine eggs from Canada (Table 1). This is the first study reporting quantifiable data about two dechlorinated species of DP in a terrestrial species. However, aCl11DP was detected in only three Spanish peregrine eggs at levels 10 times lower than those measured in the Canadian peregrine eggs, and aCl10DP was not detected in any of the Spanish peregrine eggs (Table 1). This pattern likely reflects the higher ΣDP concentrations measured in the Canadian peregrine eggs.

The findings of this study confirm the presence of DP and related compounds in peregrine eggs from Canada and Spain. This is the first study to document that DP is accumulated and metabolized by peregrine falcons prior to egg laying; it is also the first study to report DP and dechloranes in European biota, as well as to report dechloranes in a terrestrial organism and an organism at the top of the food web. Compared to the eggs laid by Spanish peregrines with a terrestrial diet, the peregrine eggs from Canada had significantly higher *in ovo* concentrations of Mirex, ΣDP, Dec 602, 603, and 604, the only detectable concentrations of aCI10DP and aCI11DP, and lower *f* anti values. The geographical differences in the measured *in ovo* concentrations between Canada and Spain reflect local exposure of the adult peregrines on the breeding grounds during egg laying, likely differences in the diet of the adult birds, the production of DP on the Niagara River in Canada (Figure SI-1), and the greater use of Mirex and dechloranes as flame retardants in North America than Europe.

■ ASSOCIATED CONTENT

Supporting Information. Figure SI-1, map of the Canadian sampling area; Figure SI-2, map of the Spanish sampling area. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (905)336-4843. Fax: (905)336-6430. E-mail: kim.fernie@ec.gc.ca.

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REFERENCES

(1) Wang, D. G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W. L.; Li, Y. F.; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-specific source of Dechlorane Plus: Concentration, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010**, *44*, 6608–6613.

(2) Tomy, G. T.; Thomas, C. R.; Zidane, T. M.; Murison, K. E.; Pleskach, K.; Hare, J.; Arsenault, G.; Marvin, C. H.; Sverko, E. D. Examination of isomer specific bioaccumulation parameters and potential in vivo hepatic metabolites of syn- and anti-Dechlorane Plus isomers in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Sci. Technol.* **2008**, *42*, 5562–5567.

(3) Tomy, G. T.; Pleskach, K.; Ismail, N.; Whittle, D. M.; Helm, P. A.; Sverko, E. D.; Zaruk, D.; Marvin, C. H. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007**, *41*, 2249–2254.

(4) Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1184–1189.

(5) Gauthier, L. T.; Letcher, R. J. Isomers of Dechlorane Plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. *Chemosphere* **2009**, *75*, 115–120.

(6) Ren, N.; Sverko, E.; Li, Y. F.; Zhang, Z.; Harner, T.; Wang, D.; Wan, X.; McCarry, B. E. Levels and isomer profiles of Dechlorane Plus in Chinese air. *Environ. Sci. Technol.* **2008**, *42*, 6476–6480.

(7) Zhu, J.; Feng, Y. L.; Shoeib, M. Detection of Dechlorane Plus in residential indoor dust in the City of Ottawa, Canada. *Environ. Sci. Technol.* **2007**, *41*, 7694–7698.

(8) Qiu, X.; Marvin, C. H.; Hites, R. A. Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **2007**, *41*, 6014–6019.

(9) Sverko, E.; Tomy, G. T.; Marvin, C. H.; Zaruk, D.; Reiner, E.; Helm, P. A.; Hill, B.; McCarry, B. E. Dechlorane Plus levels in sediment of the Lower Great Lakes. *Environ. Sci. Technol.* **2008**, *42*, 361–366.

(10) Shen, L.; Reiner, E. J.; Macpherson, K. A.; Kolic, T. M.; Sverko, E.; Helm, P. A.; Bhavsar, S. P.; Brindle, I. D.; Marvin, C. H. Identification and screening analysis of halogenated norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. *Environ. Sci. Technol.* **2010**, *44*, 760–766.

(11) Sverko, E.; Reiner, E. J.; Tomy, G. T.; McCrindle, R.; Shen, L.; Arsenault, G.; Zaruk, D.; Macpherson, K. A.; Marvin, C. H.; Helm, P. A.; McCarry, B. E. Compounds structurally related to dechlorane plus in sediment and biota from Lake Ontario (Canada). *Environ. Sci. Technol.* **2010**, *44*, 574–579.

(12) Gauthier, L. T.; Hebert, C. E.; Weseloh, D. V. C.; Letcher, R. J. Current-use flame retardants in the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes. *Environ. Sci. Technol.* **2007**, *41*, 4561–4567.

(13) Ismail, N.; Gewurtz, S. B.; Pleskach, K.; Whittle, M.; Helm, P. A.; Marvin, C. H.; Tomy, G. T. Brominated and chlorinated flame retardants in Lake Ontario, Canada, Lake Trout (*Salvelinus namaycush*) Between 1979 and 2004 and possible influences of food-web changes. *Environ. Toxicol. Chem.* **2009**, *28*, 910–920.

(14) Merino, R.; Bordajandi, L. R.; Abad, E.; Rivera, J.; Jimenez, B. Evaluation of organochlorine compounds in peregrine falcon (*Falco peregrinus*) and their main prey (Columba livia) inhabiting central Spain. *Environ. Toxicol. Chem.* **2005**, *24*, 2088–2093.

(15) Fernie, K. J.; Letcher, R. J. Historical Contaminants, Flame Retardants, and Halogenated Phenolic Compounds in Peregrine Falcon (*Falco peregrinus*) Nestlings in the Canadian Great Lakes Basin. *Environ. Sci. Technol.* **2010**, *44*, 3520–3526.

(16) Vorkamp, K.; Thomsen, M.; Falk, K.; Leslie, H.; Moller, S.; Sorensen, P. B. Temporal development of brominated flame retardants in peregrine falcon (*Falco peregrinus*) eggs from South Greenland (1986−2003). *Environ. Sci. Technol.* **2005**, *39*, 8199–8206.

(17) Chen, D.; La Guardia, M. J.; Harvey, E.; Amaral, M.; Wohlfort, K.; Hale, R. C. Polybrominated diphenyl ethers in peregrine falcon (*Falco peregrinus*) eggs from the northeastern U.S. *Environ. Sci. Technol.* **2008**, *42*, 7594–7600.

(18) Chen, D.; Hale, R. C.; Watts, B. D.; La Guardia, M. J.; Harvey, E.; Mojica, E. K. Species-specific accumulation of polybrominated diphenyl ether flame retardants in birds of prey from the Chesapeake Bay region, USA. *Environ. Pollut.* **2010**, *158*, 1883–1889.

(19) Henny, C. J.; Yates, M. A.; Seegar, W. S. Dramatic declines of DDE and other organochlorines in spring migrant peregrine falcons from Padre Island, Texas, 1978−2004. *J. Raptor Res.* **2009**, *43*, 37–42.

(20) Durant, J. M.; Gendner, J. P.; Handrich, Y. Behavioural and body mass changes before egg laying in the Barn Owl: cues for clutch size determination? *J. Ornithol.* **2010**, *151*, 11–17.

(21) Tomy, G. T.; Halldorson, T.; Danell, R.; Law, K.; Arsenault, G.; Alaee, M.; MacInnis, G.; Marvin, C. H. Refinements to the diastereoisomer-specific method for the analysis of hexabromocyclododecane. *Rapids Commun. Mass Spectrom.* **2005**, *19*, 2819–2826.

(22) The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, April 2007. http://www.pops.int/documents/implementation/nips/submissions/China_NIP_En.pdf (accessed December 15, 2010).