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RESEARCH PAPER

PERSISTENT ORGANIC POLLUTANTS IN AUSTRALASIAN HARRIERS (*CIRCUS APPROXIMANS*) FROM NEW ZEALAND

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ABSTRACT

Birds of prey are widely used internationally as bioindicators of environmental contamination of persistent organic pollutants (POPs). However, there is a dearth of information on POPs concentrations in New Zealand birds of prey. We assessed tissue concentrations of established and emerging POPs in Australasian harriers (*Circus approximans*) from the Canterbury Region of New Zealand. ∑DDTs comprised up to 98% of the POPs detected, with concentrations up to 200 µg/g lipid weight. Similar concentrations were measured approximately 35 years ago in harriers from the same region, and are among the highest reported internationally for raptors. DDE concentrations were above those anticipated to cause detrimental effects in other bird species. Polychlorinated biphenyls (PCBs) were present at the next highest concentrations with up to 3060 ng/g lipid weight in harriers. Concentrations of PCBs, polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-furans (PCDD/PCDFs) in harriers were at the lower end of the range of concentrations reported in international surveys of raptors, with our results including the first reported detection of PBDEs in New Zealand raptors.

Keywords: Birds of prey; POPs; bioindicator; DDE; PBDE.

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INTRODUCTION

Persistent organic pollutants (POPs) have increasingly been the subject of environmental surveys and research, as they biomagnify through the food chain reaching potentially toxic concentrations in top order predators (e.g. Jaspers et al. 2013). Although uses of legacy contaminants such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have been largely discontinued, and reductions in emission of unintentional by-products such as polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans (PCDDs and PCDFs) have been achieved, the ongoing presence of residual concentrations of these compounds and their degradation products in various environmental compartments presents concern for adverse effects on birds, such as impaired reproduction, and detrimental effects on the immune system (e.g. Hellou et al. 2013; Gómez-Ramírez et al. 2014). Other environmentally persistent compounds in current or recent use such as polybrominated diphenyl ethers (PBDEs) are now emerging as POPs.

Pastoral agriculture and horticulture across New Zealand made widespread use of the OCP dichlorodiphenyltrichloroethane (DDT) in the 1950/60s, and although such uses largely ceased by the mid-1970s (Buckland et al. 1998a), residues still persist in agricultural soils (Boul 1995; Gaw et al. 2006). PCBs were never manufactured in New Zealand, but were imported and used extensively in the electrical goods industry, before importation was prohibited in 1986 and then use and storage prohibited in 1995 (Buckland et al. 1998a). Historical releases of polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans (PCDDs and PCDFs) to the New Zealand environment are primarily attributed to manufacture and use of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), the use of pentachlorophenol in the timber industry and from accidental releases of PCBs (Buckland et al. 1998a). PBDEs are flame retardants used internationally since the early 1970s, with some commercial mixtures being phased out of use during the early-mid 2000s in certain regions because of concerns about their environmental effects (European Union 2006, Dodson et al. 2012). In New Zealand the main source of PBDE is considered to be electronic products manufactured up until the mid-2000s, and management of PBDEs centres on the development of appropriate waste management programmes (Environ Australia 2013).

Given these uses of locally or globally sourced POPs in New Zealand, there have been national studies on residual concentrations of OCPs, PCBs, PCDD/Fs and PBDEs in human breast milk and serum, and of concentrations of OCPs, PCBs and PCDD/Fs in shellfish and fish, which have shown that POPs concentrations in New Zealand people and environments are typically at the lower end of those observed internationally (Buckland et al. 1998a, b, c, 1999, 2001; Scobie et al. 1999, ‘t Mannetje et al. 2010, 2013). In contrast to the extensive current international literature documenting the ongoing presence and effects of POPs in terrestrial wildlife, particularly avian raptors (e.g. Gómez-Ramírez et al. 2014), there has been no comparable monitoring or research of New Zealand wildlife – presenting a marked information gap. The most extensive studies of POPs in New Zealand birds were undertaken in the 1970s, when a wide range of species were targeted (Lock and Solly 1976; Solly and Shanks 1976; Fox and Lock 1978). Subsequent studies were more limited in spatial extent and the contaminants investigated (Reid and Jones 1999; Reid 2000). To build on these previous data we report the results of a small-scale survey of known and emerging POP residues in the New Zealand raptor, the Australasian harrier (*Circus approximans*).

Birds of prey sit atop the food chain, whereby concentrations of persistent compounds can accumulate, and thus, these animals represent bioindicators which can provide evidence to support management actions towards reducing environmental burdens or anticipating unwanted legacy effects of POPs (e.g. García-Fernández et al. 2008; Helander et al. 2008; Gómez-Ramírez et al. 2014). Raptors also have cultural and biodiversity value (Chen and Hale 2010), and thus, have potential for achieving community-wide recognition of the extent and risks of POP contamination in the wider

environment. While numerous raptor biomonitor studies have been undertaken in the Northern Hemisphere, there have been comparatively few parallel studies in the Southern Hemisphere. The Australasian harrier is a candidate biomonitoring species in the Southern Hemisphere, breeding widely throughout Australasia and islands in the south-west Pacific (Heather and Robertson 1996). In New Zealand, this species is widespread and common throughout open country, feeding on small live prey and carrion (Baker-Gabb 1981a, b; Heather and Robertson 1996), often scavenging road-killed carcasses. This foraging habit in New Zealand populations often results in harriers themselves being killed by vehicle collision, facilitating opportunistic acquisition of fresh tissue samples. On this basis we chose Australasian harriers for a New Zealand survey and acknowledge the preliminary nature of the data; our sample was very small (four birds) and localised. However, we tested for a wider suite of established and emerging POPs than any previous New Zealand study to include OCPs, PCBs, PCDD/Fs and PBDEs and their congeners.

MATERIALS AND METHODS

Study area and sample collection

Birds were sampled from the Canterbury Region, South Island, New Zealand, from an area south-west of Christchurch City (Figure 1). Agriculture, primarily sheep and cattle grazing and cropping, is the dominant land-use with a number of small towns distributed throughout the area. Searches of roads for freshly killed harriers yielded four birds in suitable condition (not decayed, relatively intact) between March and May 2012 (Figure 1, Table S1). No permits were required to collect these birds, from which samples of abdominal and subcutaneous fat were removed and stored at –20 °C until analysis.

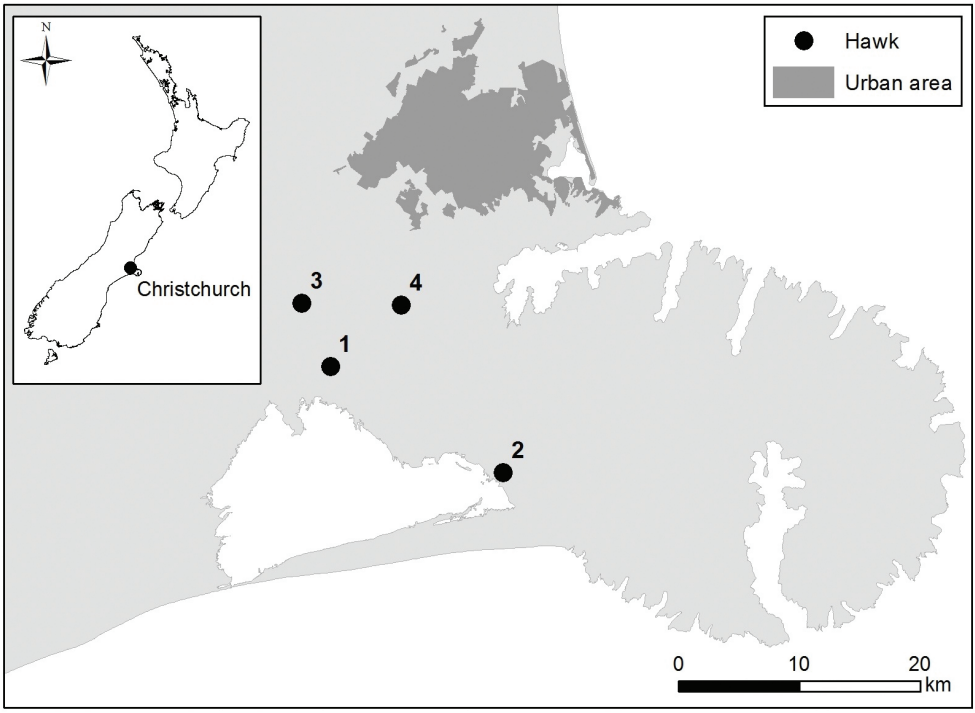

Figure 1. Collection locations of Australasian harriers *(Circus approximans)*.

Analysis

Samples were analysed by AsureQuality laboratories, Wellington. Combined abdominal and subcutaneous fat from each bird was treated as one sample, and blended with a known quantity of sodium sulfate at a ratio of approximately 3:1 (sodium sulfate:sample) to provide a dry, free-flowing sample. Portions of this mix were used for analysis of the different compounds as described below. Reagent blanks and matrix spikes were prepared for each analysis run. All concentrations are reported on the basis of lipid weight (lw). A full list of the individual compounds analysed is provided in Table S2.

OCPs, including toxaphene, were analysed following USEPA Method 1699. A sample portion equivalent to ~1 g of tissue was spiked with ^{13}C-labelled recovery standards and the sample extracted using accelerated solvent extraction (Dionex ASE 200) with a 1:1 dichloromethane:hexane solvent mix (100 °C, 1500 PSI). An in-house freezing-out technique was used to remove the majority of lipid, and the extracts were further cleaned and purified using gel permeation and florisil column chromatography. The cleaned extracts were concentrated and spiked with internal standard solution before evaporating to a final volume of 50 µL. The extracts were analysed by gas chromatography-high resolution mass spectrometry (GC-HRMS, Agilent 6890 gas chromatograph coupled with Waters Ultima/Premier high resolution mass spectrometer).

PCBs, PCDD/Fs and PBDEs were analysed following US EPA Methods 1613B, 1668A, 1614 respectively. A sample equivalent to ~10 g of tissue was spiked with ^{13}C-labelled recovery standards prior to overnight Soxhlet extraction with 1:1 dichloromethane:hexane solvent mix and rotary evaporation to reduce solvent volume. Lipid content was determined for the whole sample extract by evaporating solvent until a constant residue weight was obtained, with the lipid defined as the residue. Extracts were then re-dissolved in hexane and lipids removed by acidification (concentrated sulfuric acid), prior to further clean-up using individual acidic/basic silica, acidic alumina and florisil columns. The PCDD/Fs were separated from the PCBs/BFRs on the florisil column. The cleaned extracts were concentrated and spiked with recovery standard solution before evaporating to a final volume of 10 µL (PCDD/Fs) and 100 µL (PCBs/BFRs).

Seventeen tetra-, penta-, hexa-, hepta-, and octa-CDD and CDF congeners substituted at 2,3,7,8-positions, 45 PCB congeners and 40 brominated flame retardants were determined using GC-HRMS as described above. Toxic equivalent concentrations (TEQ) were calculated for PCDD/Fs and dioxin-like PCBs using WHO avian toxic equivalence factors (Van den Berg et al. 1998).

Quality assurance/Quality control: Matrix spike recoveries were generally between 70 and130% of the expected value and within the respective method acceptance limits. POPs were mostly not detected in the analytical blanks, with the exception of some PCBs and PBDEs found at trace levels. Of note is that BDE 209 in the blank was detected at similar concentration (115 pg/g) to the some of the harrier samples (130 to 421 pg/g). All other detected concentrations were significantly greater (i.e. > x10) than the blank concentration. Recovery of radiolabelled recovery standards is reported in the supplementary material (Tables S3 to S6).

RESULTS AND DISCUSSION

Organochlorine pesticide concentrations

A range of OCPs were detected (Table 1, Table S3) with ∑DDTs, comprising predominantly p,p'-DDE, present at the highest concentrations (>88% of total OCPs, median concentration 53 065 ng/g lw). Dieldrin was the next most abundant, while only low concentrations of chlordanes, comprising primarily trans-nonachlor, HCH comprising mainly β-HCH, HCB and mirex were present. Toxaphene appeared elevated in one harrier sample (22 ng/g lw) but was typically present

Table 1. Summary of persistent organic pollutant concentrations (ng/g lw) in Australasian harriers from the Canterbury Region, New Zealand. Detailed results are available in the supplementary material (Tables S3- S6).

Analyte	Harrier 1	Harrier 2	Harrier 3	Harrier 4	Median (ng/g lw)	Median (ng/g ww)
Lipid content (%)	41.1	34.7	28.4	40.8	37.8	-
∑DDTs	10 509	55 993	199 070	50 137	53 065	19 429
Dieldrin	314	355	1503	441	398	129
∑CHL	23.2	40.1	53.9	69.4	47.0	13.9
∑HCH	4.70	18.4	5.53	3.82	5.12	1.57
HCB	8.54	9.65	11.37	9.41	9.53	3.35
Mirex	7.27	15.5	10.4	10.4	10.4	2.99
Toxaphene	1.91	1.97	0.30	22.4	1.94	0.73
Other OCPs	4.08	6.54	8.35	27.0	7.45	2.27
∑PCBs	691	1017	2535	3063	1776	536
∑PCDD/Fs	0.167	0.084	0.352	0.126	0.15	61.30
∑PBDEs	46.76	48.95	73.44	116.36	61.2	20.03
BDE 209	0.35	0.41	0.46	1.03	0.43	0.14
BB-153	280	4.38	2.58	3.33	3.96	1.44
DBDPE	1.98	2.14	1.6	0.89	1.80	0.60
Total load	11 893	57 513	203 276	53 907	55 710	

∑CHL = chlordanes (∑trans-chlordane, trans-nonachlor), ∑HCH = hexachlorocyclohexane (∑α,β,γ,δ isomers), HCB = hexachlorobenzene; Other OCPs = ∑heptachlor epoxide and endrin.

around 1 ng/g lw in the other harriers. To our knowledge, this is the first time toxaphene and mirex residues have been reported in wild birds in New Zealand.

The ∑DDT concentrations we found were similar to those reported in harriers sampled during the late 1970s from the same general region (1990 – 64 910 ng/g wet weight (ww); Fox and Lock 1978). In the earlier survey, DDE also dominated the overall ∑DDT burdens. Acknowledging the limitation of the small sample size in both studies (n = 4 current study, n = 3 Fox and Lock 1978), there appears to have been no substantial decrease in the concentrations of ∑DDT in harriers from Canterbury over ~35 years. Fox and Lock (1978) also found ∑DDT concentrations in harriers were higher than in other New Zealand terrestrial birds of prey.

DDE and dieldrin residues in harriers in the current study were similar to concentrations in white-bellied sea eagles (*Haliaeetus leucogaster*, 9000 – 35 000 ng/g ww and 3000 – 12 000 ng/g ww respectively) collected from the vicinity of a known contaminated site in Sydney, Australia (Manning et al. 2008). However, in general ∑DDT concentrations in the harriers were higher than those reported in tissue and eggs in the few other studies on Southern Hemisphere birds, including Antarctic studies. For example, an Australian study found maximum concentrations of ∑DDTs of 6200 ng/g ww in tissue of peregrine falcons (*Falco peregrinus*), whereas lower concentrations were found in white-bellied sea eagles and ospreys (*Pandion haliaetus*) (Falkenberg et al. 1994). Similarly, ∑DDT concentrations in birds' eggs from South Africa (Bouwman et al. 2008), Chile (Muñoz Cifuentes et al. 2003) and Antarctica (Corsolini et al. 2011) were lower than those in the harriers in this study.

The ∑DDT concentrations found in the harriers were also higher than those reported for most terrestrial raptors from the Northern Hemisphere with the exception of sparrowhawks (*Accipiter*

species). Concentrations exceeding those in the harriers were found in the muscle of Eurasian (max. 1020 µg/g lw, median 151 µg/g lw) and Japanese sparrowhawks (max. 107 µg/g lw, median 52.5 µg/g lw) from China (Chen et al. 2009) and in Eurasian sparrowhawks (860 µg/g lw, median 200 µg/g lw) from Belgium (Jaspers et al. 2013). ∑DDT concentrations in starling (*Sturnus* spp.) eggs collected from New Zealand were also found to be higher than those from 13 other countries (Eens et al. 2013). The concentrations of other commonly reported OCPs, notably chlordanes and HCH, were lower in the New Zealand harrier compared with various birds in other international studies (e.g. Tanabe et al. 2004; Chen et al. 2009; Dhananjayan 2013) as were mirex and toxaphene residues (Muir et al. 2002).

In general, the distribution of OCP residues we measured reflects past usage of these compounds in New Zealand with DDT being the most used. Dieldrin and lindane were also widely used, but in lower volumes. Despite the limited use of toxaphene (Buckland et al. 1998a) in New Zealand, residues were detectable in harriers. We could not source any information indicating the use of mirex in New Zealand, but there may have been minor past uses or the concentrations we measured reflect ambient levels of contamination. The high concentrations of ∑DDTs in the harriers were unexpected as residues in agricultural soils are not expected to be high. The limited information available on DDT residues in soils suggests that concentrations in grazing land, the predominant land-use in Canterbury, are no higher than 2 mg/kg dry wt and more typically <1 mg/kg (Boul et al. 1994; Roberts et al. 1996; Gaw et al. 2006). Concentrations may be markedly higher in orchards (Gaw et al. 2006) although there are few orchards in the study area. High concentrations of POPs in sparrowhawks, and some other bird of prey species, have been attributed to a high proportion of birds in their diet and the reduced metabolism of POPs by birds compared to other organisms, e.g. rabbits (Van Drooge et al. 2008). Harriers may have a high proportion of birds in their diet (Redhead 1969; Baker-Gabb 1981b), suggesting a reason for the apparent marked biomagnification up the food chain. Concentrations of POPs in a composite sample of five individual mallard ducks collected from the same region were much lower (data not shown), which we attribute to dietary differences. Further research is required to ascertain the pathway of bioaccumulation in the harriers from this region, and whether this pathway is similar for harriers in other regions.

Polychlorinated biphenyl, polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofuran and brominated flame retardant concentrations

A range of these contaminants was detected (Table S4–S6). PCBs were the next most abundant contaminant group after OCPs, with concentrations in the harriers lower than those reported from harriers in the North Island of New Zealand (median 2698 ng/g lw, range 852 to 10 530 ng/g lw; Reid 2000), for royal albatross eggs and chicks (254 to 1280 ng/g lw; Reid and Jones 1999), and harriers in an earlier New Zealand study (1320 to 12 070 ng/g ww (fat); 1620 ng/g ww (muscle tissue, 16 200 ng/g lw assuming 10% lipid), while 460 ng/g ww was found in muscle tissue from a single morepork (owl, *Ninox novaeseelandiae*) (Solly and Shanks 1976).

Except for Antarctic birds' eggs (e.g. Corsolini et al. 2011), PCB concentrations in the harriers were at the lower end of those reported in both Southern and Northern Hemisphere studies on various bird species. For example, dioxin-like PCB concentrations in the harriers (57 to 301 ng/g lw) were at the lower end of the range of 1.2 to 3835 ng/g lw reported for Australian birds of prey (Corell et al. 2004). Guruge et al. (2001) found PCB concentrations ranging from 230 to 5800 ng/g ww in subcutaneous fat (~80% lipid) of various migratory petrels and albatrosses from the Southern Ocean. Concentrations in the harriers were comparable with those in birds of prey from Greece (Hela et al. 2006), but markedly lower than those from Belgium (Jaspers et al. 2013), northern

goshawks from Germany (Kenntner et al. 2003), and eggs of various raptor species in Spain (e.g. Gómara et al. 2008; Gómez-Ramírez et al. 2012).

The concentrations of PCDD/Fs found in harriers from Canterbury (Table 1, Table S5) were lower than those in harriers collected previously from the North Island of New Zealand (range 460 to 3570 pg/g lw; Reid 2000), but were higher than those in royal albatross eggs and chicks (8.6 to 38.7 pg/g lw) from New Zealand (Reid and Jones 1999). The concentrations in the harriers were also typically lower than that reported internationally for birds of prey. For example, Correll et al. (2004) reported concentrations of 2.7 to 6700 pg/g lw PCDD/DFs in birds of prey collected across Australia, with 11 of 17 birds having concentrations < 1000 pg/g lw. Gómara et al. (2008) reported concentrations ranging from 7.2 to 42 pg/g ww (or 90 to 525 pg/g lw based on 8% lipid content reported by the authors) in red kite eggs from Spain, whereas higher concentrations were found in Japanese birds of prey (480 000 to 490 000 pg/g lw; Senthilkumar et al. 2002) and livers of Canadian bald eagles (44 to 6550 pg/g ww; Elliot et al. 1996).

When expressed as toxicity equivalents (TEQ) using avian TEFs (Van den Berg et al. 1998), the concentrations of dioxin-like PCBs and PCDD/Fs in the harriers ranged from 99 to 374 pg-TEQ/g lw with dioxin-like PCBs contributing 56% to 81% of the TEQ. These concentrations were similar to those determined in Australian birds of prey in which 12 of 17 birds had TEQ concentrations < 380 pg/g lw, although concentrations ranged up to 3900 pg/g lw (Correll et al. 2004). In that study, dioxin-like PCBs or dioxins (and not furans) were the primary contributors to the TEQ. Higher TEQ concentrations than in the harriers were found in two white-bellied sea eagles collected from a known contaminated area in Australia (87 500 to 648 000 pg/g lw in adipose tissue); TEQ concentrations were primarily associated with TCDD (Manning et al. 2008). Similarly, higher TEQ concentrations were found in birds of prey from Japan (Senthilkumar et al. 2002; Kubota et al. 2006) and Canada (Elliott et al. 1996).

To our knowledge this is the first study to report concentrations of brominated flame retardants in New Zealand raptors. ∑PBDE concentrations found in the harriers (Table 1) were at the lower end of the range reported in international studies. For example, ∑PBDE concentrations of 2400 to 8600 ng/g lw were found in the liver of white bellied sea eagles from a known contaminated area in Australia (Manning et al. 2008), whereas ∑PBDE concentrations in the eggs of various bird species from South Africa ranged from 61 to 396 ng/g lw (Polder et al. 2008). In the Northern Hemisphere, ∑PBDE concentrations in terrestrial-feeding birds ranged from 20 to 7850 ng/g lw (Chen and Hale 2010), with the highest reported ∑PBDE concentration of 68 040 ng/g lw in the liver of Eurasian sparrowhawks from the United Kingdom (Crosse et al. 2012).

Remarkably high concentrations of BB-153 were found in one harrier (Table 1), whereas those in other harriers spanned the range reported in Northern Hemisphere raptors. For example, BB-153 was present at concentrations of 0.25 to 95 ng/g lw in the muscle of buzzards and owls and 0.28 to 310 ng/g lw in sparrowhawks from Belgium (Voorspoels et al. 2006; Jaspers et al. 2013) and 26 to 370 ng/g lw in peregrine falcon eggs from Sweden (Johansson et al. 2009). BB-153 is the major congener in Firemaster FF-1 and BP-6, and was banned in the 1970s in North America and in 1984 in Europe (Leslie et al. 2011). The presence in the harriers is somewhat surprising, although given that the source of brominated flame retardants in New Zealand is imported goods, the presence may reflect the import of goods from countries which did not ban it, and/or atmospheric transport. Low concentrations of DBDPE were also detected in all harriers (Table S6). Low concentrations have been reported in other wildlife (Klosterhaus et al. 2012). DBDPE continues to be used as a flame retardant as a replacement for deca-BDE, thus residues in the environment may increase with increased future usage (Klosterhaus et al. 2012). Perfluorooctanesulfonic acid (PFOS) was found in

one harrier at a low concentration (2.8 ng/g ww or 6.9 ng/g lw; data not shown). The general non-detection of PFCs in our samples is unsurprising, as unlike other POPs, which tend to accumulate in lipid-rich tissues, PFCs bind to serum albumin and are predominantly found in blood and liver.

POPs profile

DDTs dominated the contaminant load comprising between 88% and 98.2% of the load, PCBs 0.9% to 5.8%, while all other contaminant groups typically <1% (Figure 2). The dominance of DDTs was similar to the distribution of POPs reported in other New Zealand wildlife, including freshwater fish collected from South Canterbury (Stewart et al. 2011) and starlings collected from Wellington (Eens et al. 2013), although PCBs were a more significant contributor to the contaminant load in royal albatross (Reid and Jones 1999). Such dominance of the contribution of ∑DDTs has rarely been reported in the literature, although some studies do report greater contributions of ∑DDTs than PCBs to contaminant loads (e.g. Gómez-Ramírez et al. 2012).

The distribution of PCB congeners between individual harriers was relatively consistent with dominant 138, 153 and 180 congeners comprising 60% to 65% of ∑PCB (Figure 3a). Congeners 170, 187 and 118 together comprised 16% to 20% of ∑PCBs. These profiles were similar to those measured in other New Zealand birds, e.g. harriers (Reid 2000) and albatross (Reid and Jones 1999). Several international bird studies also report dominance of 138, 153, and 180 congeners in PCB profiles of birds (e.g. Herzke et al. 2002; Kenntner et al. 2003; Chen et al. 2009). This has been attributed to a chlorine substitution that makes these congeners less susceptible to enzymatic metabolism and more stable in the environment (Gómara and González 2006). PCB 118 is also reported as a significant contributor to ∑PCB in some birds (e.g. Elliott et al. 2001; Kunisue et al. 2003; Chen et al. 2009) but we measured a relatively low (2 to 4%) contribution from PCB 118 in harriers and a higher contribution from PCBs 187 and 180. An increased concentration of 118 has been attributed to presence of Aroclor 1254 while a greater contribution from 187 and 180 is indicative of contamination from Aroclor 1260 (Van den Steen et al. 2006). PCB 118 was, however,

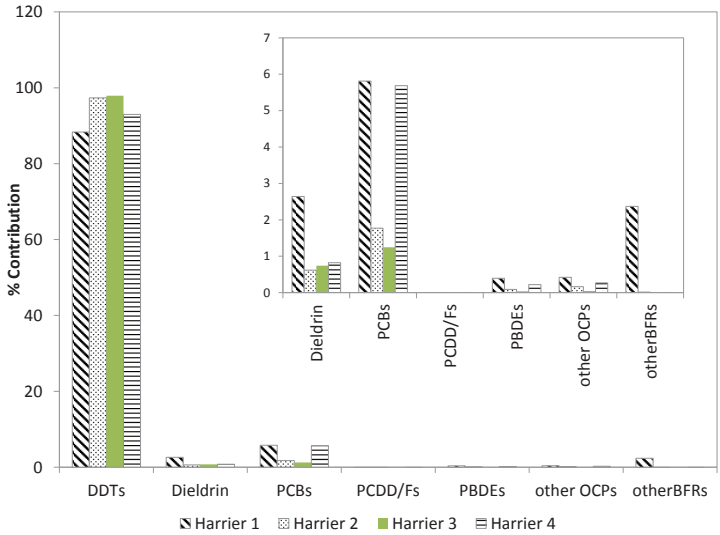

Figure 2. Relative contributions of DDTs, dieldrin, PCBs, PCDD/Fs, PBDEs to the total contaminant load. Inset shows the contribution of dieldrin, PCBs, PCDD/Fs, PBDEs at an enlarged scale.

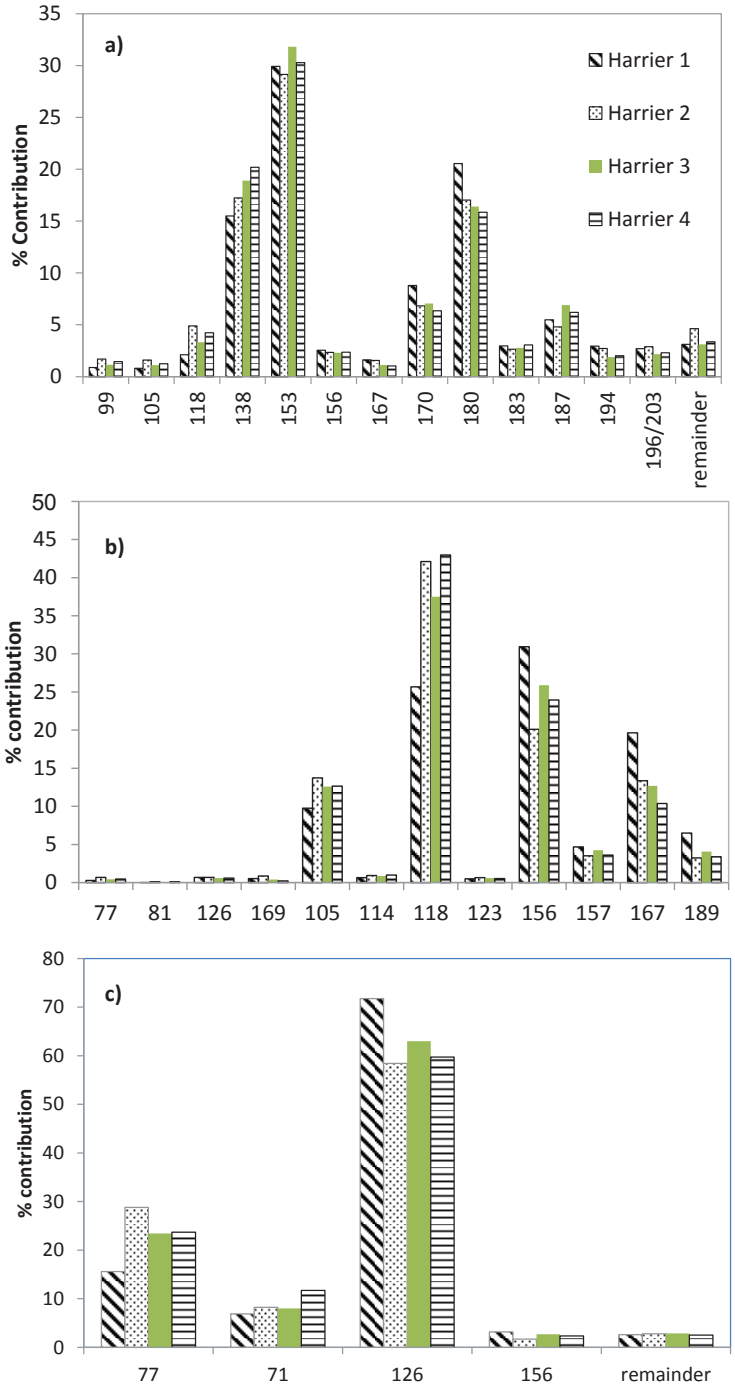

Figure 3. Relative contributions of a) individual PCB congeners to ∑PCBs; b) individual dioxin-like PCB congeners to ∑dioxin-like-PCBs ; c) TEQ of individual dioxin-like PCB congeners ∑TEQ.

the most abundant dioxin-like PCB congener in 3 of the 4 harriers (Figure 3b), as in other studies (e.g. Kunisue et al. 2003; Correll et al. 2004). When PCB concentrations were converted to toxic equivalents (TEQ), PCB 126 dominated the profile (Figure 3c). While some studies have reported 118 as the most significant contributor to PCB-TEQ (e.g. Elliott et al. 1996), this may be due to the toxic equivalence factor used; the avian TEF for PCB 118 (van den Berg et al. 1998) is 10-fold less than the value specified by Ahlborg et al. (1994). Overall, we found that PCBs were the dominant contributor to the total TEQs, consistent with some international studies (e.g. Nordlof et al. 2012).

Distribution of PCDD/Fs varied between individual harriers with 1,2,3,6,7,8-HxCDD the dominant PCDD/F congener in three, whereas 1,2,3,4,6,7,8-HpCDD was the dominant congener in one other (Figure 4). Two harriers had greater contributions from TCDD and PeCDD, PeCDF and low contributions of HpCDD and OCDD, whereas the other two harriers had greater contributions from HpCDD and OCDD and 2,3,4,7,8-PeCDF. Differences between individuals presumably reflect differences in local contamination sources. Another New Zealand study (Reid 2000) measured 1,2,3,6,7,8-HxCDD as the dominant congener in one harrier that also had the highest PCDD/F concentrations (3500 pg/g lw), whereas OCDD was the dominant congener in the remaining specimens, which typically had lower concentrations (<1950 pg/g lw). Reid and Jones (1999) found PeCDF congeners were dominant in royal albatross chicks and eggs collected near Dunedin in the South Island of New Zealand.

The PCDD/F profiles we found differed from those reported elsewhere, which typically show furans present at greater concentrations than dioxins, and OCDD or PeCDF as the dominant congeners (e.g. Elliott et al. 1996, 2001; Nordlof et al. 2012). This distribution is primarily attributed to industrial sources of PCDD/PCDFs. For example, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDF are typically associated with pulp and paper mills (Elliott et al. 1996; Nordloff et al. 2012), industrial combustion such as iron and steel manufacture produce more PCDFs than PCDDs, whereas contamination by wood preservatives such as pentachlorophenol is dominated by HpCDD and OCDD (Buckland 1998a). In 19 species of Australian birds OCDD was, on average, the dominant

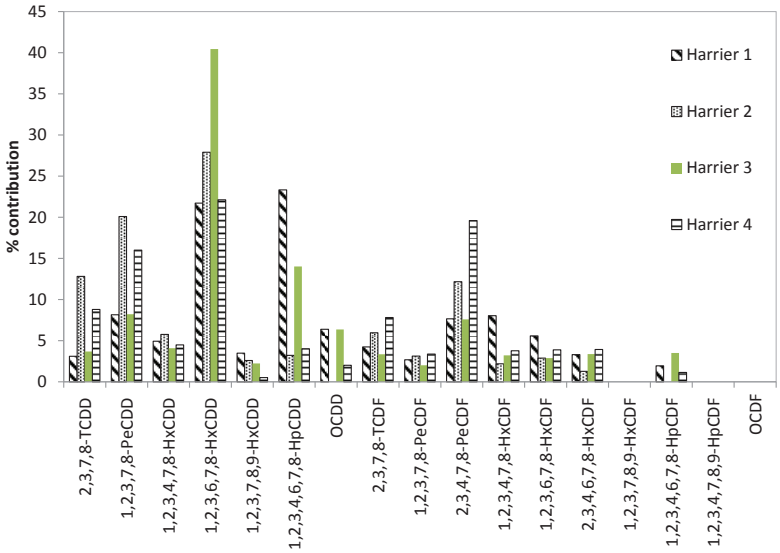

Figure 4. Relative contributions of individual PCDD/F congeners to ∑PCDD/F.

congener found, mainly due to dominance of OCDD in five species (Correll et al. 2004). However, profiles of raptors in the latter study, including peregrine falcons, goshawks and sparrowhawks, were dominated by other congeners including 1,2,3,6,7,8-HxCDD, and had PCDD/F profiles similar to those we measured in New Zealand harriers.

The distribution of PBDE congeners in the harriers was similar to that observed in other studies on terrestrial birds of prey with BDE 47, BDE 99, BDE 153 the dominant congeners (Law et al. 2003; Voorspoels et al. 2006; Johansson et al. 2009; Jaspers et al. 2013), although there was some variation between individual harriers (Figure 5). Variation in the dominant congeners in different birds, and within the same species, is attributed to variations in diet, metabolic capacity and difference in PBDE mixtures used (e.g. Drouillard et al. 2007; Chen et al. 2012). The dominance of 47, 99 and 153 congeners is suggestive of contamination by penta-BDE mixtures (e.g. Crosse et al. 2012), whereas an increased contribution of 183 or 209 is indicative of contribution from octa-BDE and deca-BDE respectively (La Guardia et al. 2006; Chen et al. 2010). Thus, the PBDE profiles in the harriers are most consistent with contamination predominantly by penta-BDE mixtures.

Toxicological significance

Eggshell thinning, resulting in population declines, has been associated with POPs in birds since it was first attributed to p,p'-DDE in the late 1960s (Ratcliffe 1970). As a result, effect concentrations for POPs, particularly in early studies, have primarily been reported on the basis of egg concentrations and there are fewer studies that report effect levels based on tissue concentrations. We converted effect concentrations reported for DDE on the basis of egg concentrations to nominal tissue concentrations to estimate whether the concentrations measured in the harriers have the potential to cause detrimental effects on their theoretical offspring. Specifically, we used a ratio of egg: maternal tissue of 1:0.4 on the basis of results for peregrine falcons in Russell et al. (1999), and assuming 8% lipid in the egg (lipid content varies between species, although for raptors and many species it largely ranges between 5% and 10%; e.g. Herzke et al. 2002; Chen et al. 2012). Although some studies report that lipid normalisation yields ratios of egg to maternal tissue of ~1 (e.g. Russell et al.

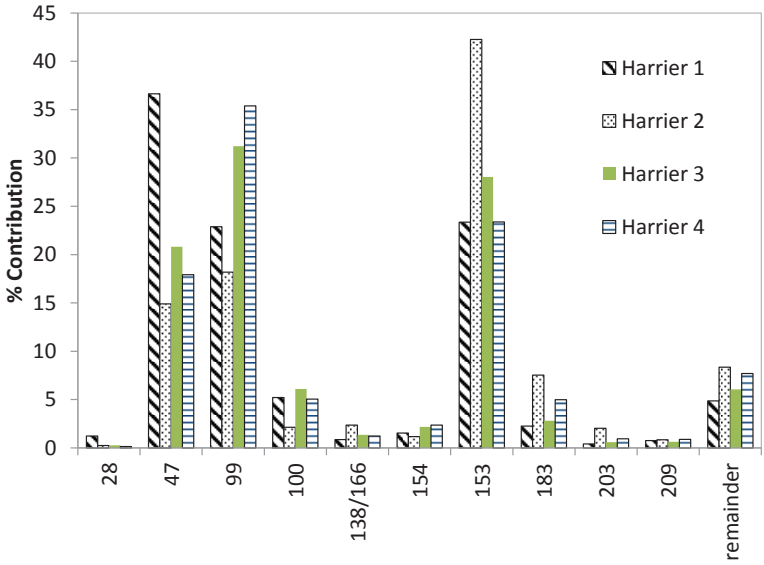

Figure 5. Relative contributions of selected PBDE congeners to ∑PBDE.

1999; Van den Steen et al. 2009), Drouillard and Norstrom (2001) suggest that reproductive strategy (e.g. precocial vs altricial) influences the transfer of POPs to eggs. Altricial birds, which include birds of prey, invest relatively small quantities of lipids to a clutch of eggs and were observed to have lower egg-to-maternal tissue contaminant concentration ratios than precocial birds that invest larger quantities of lipids and energy into egg production. Some of these estimated toxicological effect levels (Table 2) are lower than the DDE concentrations in some or all of the individual harriers from the current study. This suggests that DDE concentrations may have had, and may still be causing, negative impacts on Australasian harriers in New Zealand, although further research is required to characterise potential effects. Specifically, research is required to determine whether the high concentrations of DDE are unique to this region of New Zealand or more widespread, and also, whether contaminant-related impacts could be occurring at a population level. No population

Table 2. Estimated tissue-effect concentrations derived from egg concentrations of DDE determined to have detrimental effects in birds of prey from international studies.

Species	Effect concentration in egg (ng/g ww)	Effect	Comment	Reference	Estimated tissue effect level[1] (µg/g)
Bald eagle (*Haliaeetus leucocephalus*)	15 000	75% reduction in productivity		Bowerman et al. 1995	75
Bald eagle	4500	reduced productivity	based on statistical modelling	Best et al. 2010	22.5
Bald eagle	6500	0.7 young/ occupied nest	based on statistical modelling	Best et al. 2010	32.5
Bald eagle	3600	egg, young production-hatching success	measured value	Weimeyer et al. 1993	18
Barn owl (*Tyto alba*)	12 000	eggshell thinning	measured value	Mendenhall et al. 1983	60
Booted eagle (*Hieraaetus pennatus*)	1520	10% eggshell thinning	measured value	Martinez-Lopez et al. 2007	7.6
Booted eagle	2200	15% thinning and potential population effect	predicted concentration	Martinez-Lopez et al. 2007	11
Eurasian Eagle owl (*Bubo bubo*)	100 000[2]	17% thinning	measured value	Gómez-Ramírez et al. 2012	40
Merlin (*Falco columbarius*)	4000	not specified	measured value	Noble and Elliott 1990	20
Osprey (*Pandion haliaetus*)	2000	12% thinning	measured value	Wiemeyer et al. 1988	10
Osprey	5000	not specified	measured value	Noble and Elliott 1990	25
Prairie falcon (*Falco mexicanus*)	1200	not specified	measured value	Noble and Elliott 1990	6

[1]Conversion assuming 8% lipid in egg and 1:0.4 egg:maternal tissue ratio; [2] ng/g lw

declines have been reported for harriers; rather they are considered to be New Zealand's most abundant native diurnal bird of prey (Eakle 2008). The conversion of native forests to livestock pastures and related increases in non-native rats, mice, rabbits and bird prey are suggested to have contributed to increasing populations of the harrier since the late 1960s (Carroll 1968; Eakle 2008), potentially masking any contaminant-induced population decline.

Recent studies suggest that endocrine disruption, including androgenic, anti-androgenic, estrogenic, anti-estrogenic and thyroid effects, occur at DDE concentrations lower than those affecting reproductive success (Quinn et al. 2006, 2008; Cesh et al. 2010). For example, Quinn et al. (2008) observed that in ovo exposure of Japanese quail at 20 µg DDE per egg (~2000 ng/g ww) negatively impacted on reproductive behaviours, while Quinn et al. (2006) observed that this concentration altered the bursa of Fabricius, a lymphoid organ unique to birds and essential for the development of the immune system.

The concentrations of PCBs we measured in the fat of harriers were well below the lowest reported effect concentration for PCBs, of 6000 ∑PCBs ng/g ww in eggs (Bowerman et al. 1995), suggesting it is unlikely that PCBs are causing detrimental effects in the harriers. However, effects associated with non-dioxin-like PCBs, in particular thyroid effects, have recently gained attention (Hamers et al. 2011), although there is currently limited understanding of these effects in birds. Dioxin-like PCB and PCDD/F concentrations expressed as TEQ in harriers were below reported effect concentrations of a lowest-observed-effect level (LOEL) of 20 to 50 pg/g egg for wood duck (White and Seginak 1994), or tissue concentrations of approximately 100 pg/g lw using the conversions described above. Elliott et al. (2001) reported a LOEL of 130 pg/g ww (~2600 pg/g lw) in ospreys based on cytochrome P450 induction, while the no-observed-effect level for CYP1A induction in the common tern was 25 000 pg TEQs/g liver lipid (Bosveld et al. 2000).

A range of effects of PBDE have been reported in birds, mainly kestrels, including increased growth in kestrel nestlings, and changes in thyroid and retinol concentrations, and pipping and hatching success (Fernie et al. 2005, 2006; Henny et al. 2009; McKernan et al. 2009). Fernie et al. (2006) observed increased growth in PBDE dosed at a body burden of 87.6 ng/g ww (876 ng/g lw) while McKernan et al. (2009) suggested a LOEL for penta-BDEs of 32 µg/g lw in kestrel eggs (equivalent tissue concentration of 12 800 ng/g lw using the conversions above). The PBDE concentrations in harriers in the current study are far below these values.

CONCLUSIONS

Little is known about the exposure of New Zealand terrestrial wildlife to locally or globally sourced POPs, perhaps due to a perception that New Zealand is relatively free of such contaminants because of its limited industrialisation and geographic isolation from most major industrial sources. However, concentrations of DDTs, comprised primarily of p,p'-DDE, were remarkably high in Australasian harriers collected from the Canterbury Region. These concentrations are among the highest reported internationally for terrestrial birds. The high ∑DDT concentrations probably reflect the dominant agricultural land-use in the study area and likely historical usage of DDT for grass grub (*Costelytra zealandica*) control in this region. The concentrations of DDE are above those suggested to cause adverse effects in some other species, although any historical contaminant-related population declines may have been masked by favourable land-use change, which has increased the abundance of the harriers. Further investigation is required to understand the potential impact of DDE concentrations on the harrier, and to determine whether similarly high concentrations are present in other bird species throughout New Zealand.

In contrast, PCB, PCDD/F and PBDE concentrations were at the lower end of the range reported internationally and below any concentrations reported to be causing effects. The lower concentrations of these POPs in the harriers compared with Northern Hemisphere studies is consistent with studies on migratory seabirds that have found that birds from the Southern Hemisphere tend to have lower concentrations of OCP, PCBs, PCDD/Fs, which is attributed to the general lack of industrialisation in the Southern Hemisphere (Guruge et al. 2001; Tanabe et al. 2004; Colabuono et al. 2012). There are no readily identifiable sources of PCBs, PCDD/Fs and PBDEs and the concentrations found suggest a relatively clean environment, although they may reflect general background concentrations in New Zealand of atmospherically transported contaminants.

This study has demonstrated the potential use of the Australasian harrier (*Circus approximans*) as a biomonitoring species, provides some baseline data for New Zealand, and contributes to the limited knowledge on the distribution of POPs in the Southern Hemisphere.

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Table S1. Sample information for the Australasian harriers collected from the Canterbury Region, New Zealand.

Sample	Geographical location (Lat, Long)	Date	General condition of carcass	Body weight (g)
Harrier 1	43.69576S, 172.47892	March 2012	Reasonable	720
Harrier 2	43.77058S, 172.09553	March 2012	Poor	600
Harrier 3	43.64563S, 172.46453	March 2012	Average	674
Harrier 4	43.64880S, 172.55273	May 2012	Average	628

Table S2. Suite of persistent organic pollutants analysed.

Contaminant Group	Individual Analytes
Organochlorine pesticides (OCP)	α-hexachlorohexane (HCH), β-HCH, γ-HCH, δ-HCH, *o,p′*-dichlorodiphenyltrichloroethane (DDT), *p,p′*-DDT, *o,p′*-dichlorodiphenyldichloroethane (DDD), *p,p′*-DDD, *p,p′*-dichlorodiphenyldichloroethylene (DDE), aldrin, heptachlor, dieldrin, endrin, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, endrin aldehyde, heptachlor epoxide, methoxychlor, mirex, endosulfan A, endosulfan B, endosulfan sulfate, pentachlorobiphenyl, hexachlorobiphenyl (HCB) Toxaphene (Parlars 26, 40/41, 44, 50 and 62)
Polychlorinated biphenyls (PCB)	1, 3, 4/10, 15, 28, 37, 44, 49, 52, 54, 70, 74, 77, 81, 99, 101, 104, 110, 105, 114, 118, 123, 126, 138/163/164, 153, 155, 156, 157, 167, 169, 170, 180, 183, 187, 188, 189, 194, 196/203, 200, 202, 205, 206, 208, and 209
Polychlorinated dibenzodioxins and furans	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF
Brominated flame retardants	PBDE (BDE 7, 15, 17, 28/33, 30, 47, 49, 66, 71, 77, 85, 99, 100, 119/120, 126, 138/166, 139, 140, 153, 154, 156/169, 171, 180, 183/175, 184, 191, 196, 197, 201, 203, 204, 205, 206, 207, 208, and 209) PBEB, HBB, polybrominated biphenyl 153 (BB-153), and decabromodiphenylethane (DBDPE)
Perfluorinated compounds	perfluoroalkylsulfonic acids, perfluoroalkylcarboxylic acids, perfluorooctanesulfonamide, N-ethyl-perfluorooctanesulfonamidoacetic acid, N-methyl- perfluorooctanesulfonamidoacetic acid, 1H,1H,2H,2H-perfluorohexanesulfonic acid, 1H,1H,2H,2H-perfluorooctanesulfonic acid and 1H,1H,2H,2H-perfluorodecanesulfonic acid

Table S3. Individual organochlorine pesticide concentrations (ng/g lw) in Australasian harriers collected from the Canterbury Region, New Zealand.[1]

Analyte	Harrier 1	Harrier 2	Harrier 3	Harrier 4
Pentachlorobenzene	0.294	0.360	0.504	0.414
HCB	8.54	9.65	11.37	9.41
Beta-BHC	4.45	18.41	5.53	3.82
Gamma-BHC	0.251	<0.13	<0.1	<0.05
Heptachlor epoxide	3.60	5.82	6.90	25.74
Gamma-chlordane	0.202	0.237	0.363	0.382
Alpha-chlordane	0.263	1.03	0.620	1.52
cis-Nonachlor	5.40	10.00	9.23	10.42
trans-Nonachlor	17.32	28.82	43.66	57.11
op-DDE	<0.27	<0.15	2.23	0.370
pp-DDE	10438	55908	197887	49510
op-DDD	0.114	<0.07	0.711	<0.06
pp-DDD	27.25	47.55	426	350
op-DDT	0.333	<0.14	2.58	<0.18
pp-DDT	43.55	37.75	750	277
Dieldrin	314	354	1504	441
Endrin	0.180	0.363	0.944	0.870
Mirex	7.27	15.48	10.39	10.39
Parlar-26	1.02	1.23	<0.24	3.77
Parlar-50	0.655	0.553	0.302	10.98
Parlar-62	<0.12	<0.78	<0.16	1.42
Parlar 40+41	0.148	0.186	<0.11	3.85
Parlar-44	0.083	<0.10	<0.11	2.41

[1]Not detected in any sample: α-BHC (<0.24 ng/g lw), δ-BHC (<0.28 ng/g lw), Heptachlor (<0.13 ng/g lw), Aldrin (<0.18 ng/g lw), Endosulfan-A (<1.7 ng/g lw), Endosulfan-B (<1.4 ng/g lw) , Endrin-aldehyde (1.8 ng/g lw), Endosulfan sulfate (<0.33 ng/g lw), Endrin-ketone (<1.2 ng/g lw), Methoxychlor (<0.16 ng/g lw).
Recovery of ^{13}C recovery standards typically ranged between 70-100%, with the exception of HCB (21%-56%), gamma-BHC (30-53%) and mirex (43%-56%).

Table S4. Individual PCB congener concentrations (ng/g lw) in Australasian harriers collected from the Canterbury Region, New Zealand.[1]

Analyte	Harrier 1	Harrier 2	Harrier 3	Harrier 4
PCB77	0.174	0.801	1.00	1.45
PCB81	0.038	0.115	0.171	0.358
PCB126	0.401	0.813	1.35	1.82
PCB169	0.304	1.03	0.905	0.716
PCB105	5.57	16.25	28.27	38.24
PCB114	0.375	1.10	1.93	3.01
PCB118	14.67	49.86	84.15	129.66
PCB123	0.287	0.769	1.36	1.62
PCB156	17.66	23.80	58.10	72.30
PCB157	2.68	4.18	9.58	10.91
PCB167	11.22	15.85	28.49	31.37
PCB189	3.72	3.83	9.15	10.25
Sum of dioxin-like PCBs	**57.10**	**118.40**	**224.46**	**301.70**
PCB1	0.002	0.003	7.54	0.003
PCB3	0.002	0.005	<0.005	<0.003
PCB4/10	<0.002	0.003	<0.037	<0.002
PCB15	0.016	0.013	<0.051	0.0095
PCB18	0.774	1.45	2.70	1.38
PCB37	0.063	0.331	0.514	0.219
PCB44	0.0367	0.0210	0.0630	0.132
PCB49	0.0635	0.284	0.458	0.819
PCB52	0.184	0.360	0.725	2.37
PCB70	0.122	0.775	0.609	3.80
PCB74	1.17	6.14	7.36	12.23
PCB99	6.08	17.26	29.01	44.61
PCB101	1.75	7.46	14.30	23.38
PCB104	<0.001	<0.001	<0.001	<0.001
PCB110	0.552	3.11	2.31	8.01
PCB138	107	176	479	618
PCB153	207	297	806	926
PCB155	0.0307	0.0545	0.107	0.0748
PCB170	60.83	69.45	179	195
PCB180	142	173	415	485
PCB183	20.54	26.86	70.42	93.63
PCB187	37.96	48.99	175	190

PCB188	0.056	0.055	0.062	0.089
PCB194	20.39	27.67	47.54	62.01
PCB196/203	18.64	29.39	54.93	70.34
PCB200	<0.001	<0.001	0.0327	<0.001
PCB202	1.59	1.73	4.19	3.48
PCB205	0.985	1.20	2.57	2.87
PCB206	4.67	7.32	7.04	9.75
PCB208	0.594	1.35	1.19	1.73
PCB209	0.922	2.88	1.70	2.14

[1]Not detected in any sample: PCB19 (<0.001 ng/g lw), PCB54 (<0.001 ng/g lw).
Recovery of ^{13}C recovery standards typically ranged between 70-105%, with the exception of PCB1 (20%-54%), and PCB3 (30-56%).

Table S5. Individual PCDD/PCDF concentrations (pg/g lw) in Australasian harriers collected from the Canterbury Region, New Zealand.

Analyte	Harrier 1	Harrier 2	Harrier 3	Harrier 4
PCDDs				
2,3,7,8-TCDD	5.18	10.78	12.99	11.10
1,2,3,7,8-PeCDD	13.60	16.89	28.87	20.22
1,2,3,4,7,8-HxCDD	8.25	4.84	14.33	5.66
1,2,3,6,7,8-HxCDD	36.25	23.46	142.25	27.94
1,2,3,7,8,9-HxCDD	5.84	2.18	7.82	0.67
1,2,3,4,6,7,8-HpCDD	38.93	2.70	49.30	5.07
OCDD	7.37	0.7	17.39	1.45
2,3,7,8-TCDF	7.08	5.01	11.76	9.88
1,2,3,7,8-PeCDF	4.48	2.63	7.04	4.26
2,3,4,7,8-PeCDF	12.77	10.23	26.73	24.75
1,2,3,4,7,8-HxCDF	13.43	1.84	11.27	4.78
1,2,3,6,7,8-HxCDF	9.32	2.42	10.14	4.93
2,3,4,6,7,8-HxCDF	5.52	1.08	11.87	4.98
1,2,3,7,8,9-HxCDF	<0.38	<0.27	<0.80	<0.54
1,2,3,4,6,7,8-HpCDF	3.24	<0.33	12.4	1.45
1,2,3,4,7,8,9-HpCDF	<0.62	<0.60	<1.4	<1.18
OCDF	<0.85	<0.41	2.46	<0.66

Recovery of ^{13}C recovery standards typically ranged between 82-105%.

Table S6. Brominated flame retardant concentrations (ng/g lw) in Australasian harriers collected from the Canterbury Region, New Zealand.[1]

Analyte	Harrier 1	Harrier 2	Harrier 3	Harrier 4
BDE-15	0.029	0.010	0.027	<0.04
BDE-30	0.155	0.323	0.290	0.218
BDE-17	0.036	<0.002	<0.001	<0.003
BDE-28/33	0.574	0.115	0.186	0.165
BDE-49	0.032	0.591	0.275	0.163
BDE-71	0.628	<0.005	0.199	0.319
BDE-47	17.1	7.3	15.3	20.9
BDE-66	0.188	0.112	0.401	0.348
BDE-77	0.046	0.032	0.129	0.087
BDE-100	2.433	1.04	4.47	5.9
BDE-119/120	<0.02	0.094	<0.058	0.146
BDE-99	10.7	8.9	22.9	41.2
BDE-85	0.178	0.297	0.401	0.574
BDE-126	0.021	0.025	0.080	0.038
BDE-154	0.720	0.571	1.592	2.745
BDE-153	10.9	20.7	20.6	27.2
BDE-139	0.063	0.216	0.243	0.341
BDE-140	0.060	0.061	0.169	0.226
BDE-138/166	0.401	1.16	0.993	1.434
BDE-183/175	1.056	3.69	2.067	5.809
BDE-191	<0.011	<0.021	<0.054	0.036
BDE-180	0.104	0.320	0.326	0.510
BDE-184	<0.005	<0.010	<0.024	0.021
BDE-171	0.013	0.036	0.240	0.069
BDE-201	0.169	0.663	0.437	1.480
BDE-197	0.229	0.272	0.451	1.640
BDE-203	0.187	0.991	0.430	1.105
BDE-196	0.192	0.778	0.440	1.409
BDE-208	0.043	0.127	0.114	0.449
BDE-207	0.075	0.118	0.198	0.850
BDE-206	0.011	0.019	0.020	0.022
BDE-209	0.355	0.406	0.458	1.032
HBB	0.007	<0.007	<0.013	0.007
BB-153	280	4.380	2.6	3.333
PBEB	<0.001	<0.001	<0.001	0.011
DBDPE	1.98	2.14	1.63	0.892

[1]Not detected in any sample: BDE 7 (<0.06 ng/g lw), 156/169 (<0.03 ng/g lw), 204 (<0.03 ng/g lw), 205 (<0.07 ng/g lw). Recovery of ^{13}C recovery standards typically ranged between 82-130%, with the exception of BDE100 (42%-46%), and BDE209 (32%-41%).