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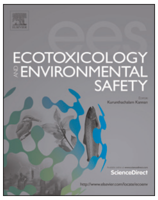

Contaminants in the southern tip of South America: Analysis of organochlorine compounds in feathers of avian scavengers from Argentinean Patagonia

E. Martínez-López [a,*], S. Espín [a,c], F. Barbar [b], S.A. Lambertucci [b], P. Gómez-Ramírez [a], AJ. García-Fernández [a]

[a] *Department of Toxicology, University of Murcia, Spain*
[b] *Laboratorio Ecotono, INIBIOMA (CONICET-Universidad Nacional del Comahue), Bariloche, Argentina*
[c] *Section of Ecology, Department of Biology, University of Turku, 20014 Turku, Finland*

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ABSTRACT

The aim of this study was to assess the exposure to organochlorine compounds (OC) in 91 primary wing feathers of avian scavengers, Turkey vulture (*Cathartes aura*), American black vulture (*Coragyps atratus*) and Southern crested caracaras (*Polyborus plancus*) from the southern tip of South America, in the Argentinean Patagonia. We analyzed for a series of OC including hexachlorocyclohexane (HCH) isomers, endosulfan, aldrin, dieldrin, endrin, dichlorodiphenyltrichloroethane (p,p'-DDT), dichlorodiphenyldichloroethane (p,p'-DDD), dichlorodiphenyldichloroethylene (p,p'-DDE), heptachlor and heptachlor-epoxide. This is the first study on OC in feathers of three terrestrial top carnivores from South America. OC concentrations found in the studied species were much higher than those found in feathers of raptors from Europe and Asia, which likely indicate their high use in the region, specifically in agriculture, and other possible uses of OC in this area. ∑HCH had the highest median concentration, followed by ∑Drins, ∑DDT, ∑Heptachlor, and ∑Endosulfan, similar to those reported in several food samples in Argentina. On the other hand, differences in OC profiles between species and areas may be related to feeding and migratory habits, as well as the molt period. Three individuals showed ∑DDT (DDT, DDD and DDE) concentrations in feathers related to sublethal effects. However, this comparison should be used with caution due to problems with extrapolating such data across tissues and species.

1. Introduction

Persistent organic pollutants (POP) are man-made chemicals that are globally distributed and pose health risks to humans and wildlife (Letcher et al., 2010). One common group of POP is organochlorine pesticides (OC). OC are persistent, lipophilic, and biomagnify through food webs Moreover, these compounds are considered hormone disruptors and immunosuppressive agents, and are known for causing adverse effects on the nervous and reproductive systems of animals (Denneman and Douben, 1993; Furness, 1993). This has led to legal restrictions in most developing countries and the subsequent decrease in pollutant concentrations both in the environment and in wildlife tissues. In spite of the ban in developed countries, these compounds are still frequently found in tissues or fluid samples from several species in these countries (Espín et al., 2010a; Martínez-López et al., 2009; Piqué et al., 2006; van Drooge et al., 2008).

Over the last 20 years, South America has experienced a great development in agriculture and livestock which has resulted in a large increase (9% annually) in the use of pesticides. This development is especially important for Argentina and Brazil (65% of the area), which has led both countries to reach top positions in several agricultural productions worldwide (CASAFE, 2011). Specifically, the Argentine production and use of pesticides has grown continuously since 1989. Endosulfan, malathion and pyrethroids are some of the pesticides used in Argentina (Souza, 2005). Although endosulfan was recently banned (Resolution 511/2011), this and other pesticides use is expected to rise, and reach 116 t by the year 2016 (Pérez Leiva and Anastasio, 2006). Expected increases in pesticide use are a result of poor control of the pesticide market and the fact that farmers often do not respect the period

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[*] Correspondence to: Department of Toxicology, Faculty of Veterinary Medicine, University of Murcia, Campus de Espinardo, 30100 Murcia, Spain. Fax: +34 868 884147.
E-mail address: emmaml@um.es (E. Martínez-López).

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that should lapse between pesticide applications (Souza Casadinho, 2009).

In general, hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), followed by heptachlors, chlordanes, aldrin and endosulfan are the most frequently reported pesticides in food in Argentina (Villaamil Lepori et al., 2013). The high detection frequency and relative abundance of HCHs and DDTs in food (including meats and vegetables) is consistent with the results found in other environmental samples, confirming their widespread distribution. In older reports, the most abundant residues detected in dairy products were DDTs and HCHs (Higa de Landoni, 1978). In subsequent years, they were found in lower concentrations, probably reflecting pesticide restrictions in the 80’s and 90’s (Lenardón et al., 1994; Maitre et al., 1994; Villaamil Lepori, 2000). However, more recent works on infant milk samples confirmed that Heptachlor exceeded current acceptable daily intake (ADI), which is of high concern due to the risk associated with its consumption (i.e. the risk is increased by the high milk intake and low body weight of infants; Ridolfi et al., 2002; Villaamil Lepori et al., 2003, 2006).

Given that OC concentration in humans are already high and the expectations of continued use of OC pesticides in the region, there is a need to better understand OC in top predators in the region. Birds, especially raptor species, have played an important role in documenting human-induced environmental pollution due to their sensitivity to environmental changes and their position in the food chain, thus accumulating high levels of contaminants (Furness, 1993). The first pan-European inventory of contaminant monitoring using raptors has shown that there is an existing monitoring capability across Europe (Gómez-Ramírez et al., 2014). However, there are few studies on environmental contaminants in raptors from South America (Ondarza et al., 2011; 2014; Saggese et al.,2009; Villaamil Lepori et al., 2013).

Feathers have been widely used for assessing the levels of certain contaminants, especially metals, demonstrating that they are very useful as a noninvasive and non-lethal alternative to internal tissues (Espín et al., 2012, 2014; Garitano-Zavala et al., 2010; Martínez-López et al., 2005). Several pesticides have been analysed in feathers, including OC in both terrestrial and aquatic species; however, the scientific literature on this subject is still developing (García-Fernández et al., 2013). Furthermore, studies analyzing these contaminants in feathers have covered species from very few locations such as Belgium, southwest Iran, southeast Spain, the Baltic region and South India (Behrooz et al., 2009a, b; Espín et al., 2012; Falkowska et al., 2013; García-Fernández et al., 2013; Jaspers et al. 2004, 2007; Tanabe et al., 1998) but there is no information on such in the area of this study. Although there is information on trace elements in feathers of Turkey vulture in North America (Cahill et al., 1998; Haskins et al., 2013), to our knowledge, this is the first study on OC in feathers of raptor species from Southern South America.

Based on the acknowledged presence of OC in the Argentinian Patagonia environment, the aim of this study was to estimate the exposure to these OC compounds in top carnivores using non-lethal samples. In order to evaluate the influence of factors such as diet or migratory habits, samples were obtained from three avian scavenger species: Turkey vulture (*Cathartes aura*), American black vulture (*Coragypus atratus*), and Southern crested caracaras (*Polyborus plancus*). Because levels of OC are expected to be highly dependent on land use, samples were collected from two areas with different activities: a rural site with abundant livestock but any agriculture, and a region with predominant agriculture practices.

2. Material and methods

2.1. Study area

The study area was comprised of two zones, 500 km apart, in the Rio Negro Province of Argentina (Fig. 1). The first (near Bariloche city, Rio Negro province; herein, Bariloche) is a rural area with low human density, extensive rearing of livestock, but almost no agriculture. Livestock and exotic species like the red deer (*Cervus elaphus*) and European hare (*Lepus europaeus*), introduced from Europe, have increased their populations, and appear as important sources of food for the scavengers in the area (Lambertucci et al., 2009a,b). Because some of the exotic species are hunted, there is an increase in the risk of lead contamination for raptors (Lambertucci et al., 2011). In contrast, the second study area was the Rio Negro Valley (Fig. 1; herein, Valle). This area covers approximately one hundred thousand hectares. Of these, only about forty thousand acres is used to grow mostly apples and pears for export mainly as fresh fruit and concentrated juice. Pome fruit production is the most important in the valley, followed by grape, produced almost entirely to wine processing, and, to a lesser extent, stone fruit-plums, peaches, nectarines, tomatoes and alfalfa (Blanco, 1999). Intensive agriculture in the area involves massive use of plant protection products, highlighting the use of insecticides, herbicides and miticides.

2.2. Study species and collection of samples

The Turkey vulture, American black vulture and Southern Crested caracaras are carnivores which feed mostly on carrion, including domestic and wild species. The Turkey vulture is the largest in body size (weight: 0.9–2.0 kg) but is similar to the Amercian black vulture (weight: 1.2–1.9 kg), while the Southern crested caracaras is a bit smaller (weight of 1.1–1.6 kg) (Ferguson-Lees and Christie, 2001). Mammals make up the primary diet, although reptile carrion, insect larvae and dead or stranded fish are also consumed (Ferguson-Lees and Christie, 2001). These three species were the most abundant scavengers observed in the study area (Bellati, 2000), all of them are included in the “least concern” criteria by the IUCN Red list (IUCN, 2013).

Fresh-molted flight feathers were collected in roosting sites from Northwestern Patagonia Argentina during austral spring (October–December) of 2011. Each sample taken was kept in individual plastic bag, labeled appropriately (including site, date, and species) and stored at room temperature in a dry place until analysis. In total, 91 primary wing feathers of Turkey vulture ($n=45$; 29 from Bariloche, 16 from Valle), American black vulture ($n=25$; 20 from Bariloche and 5 from Valle), and Crested caracaras ($n=21$; 8 from Bariloche and 11 from Valle) were collected. The area was unknown in two samples of Crested caracaras.

2.3. Organochlorine analysis

Primary feather samples were analysed for a series of organochlorine pollutants including hexachlorocyclohexane (HCH) isomers (α-HCH, β-HCH, γ-HCH or lindane and δ-HCH), endosulfan I, endosulfan II, aldrin, dieldrin, endrin, dichlorodiphenyltrichloroethane (p,p’-DDT), dichlorodiphenyldichloroethane (p,p’-DDD), dichlorodiphenyldichloroethylene (p,p’-DDE), heptachlor and heptachlor-epoxide.

All reagents used for the analysis were of trace analysis grade. Hexane, acetone, petroleum ether and diethyl ether were supplied by Lab-scan Analytical Sciences; anhydrous sodium sulfate by Merck Co. (Darmstadt); SepPak®Classic and Florisil® cartridges were supplied by Waters®; and pesticide standard (EPA Pesticide Mix 48858 dissolved in methanol:methylene chloride 98:2) was

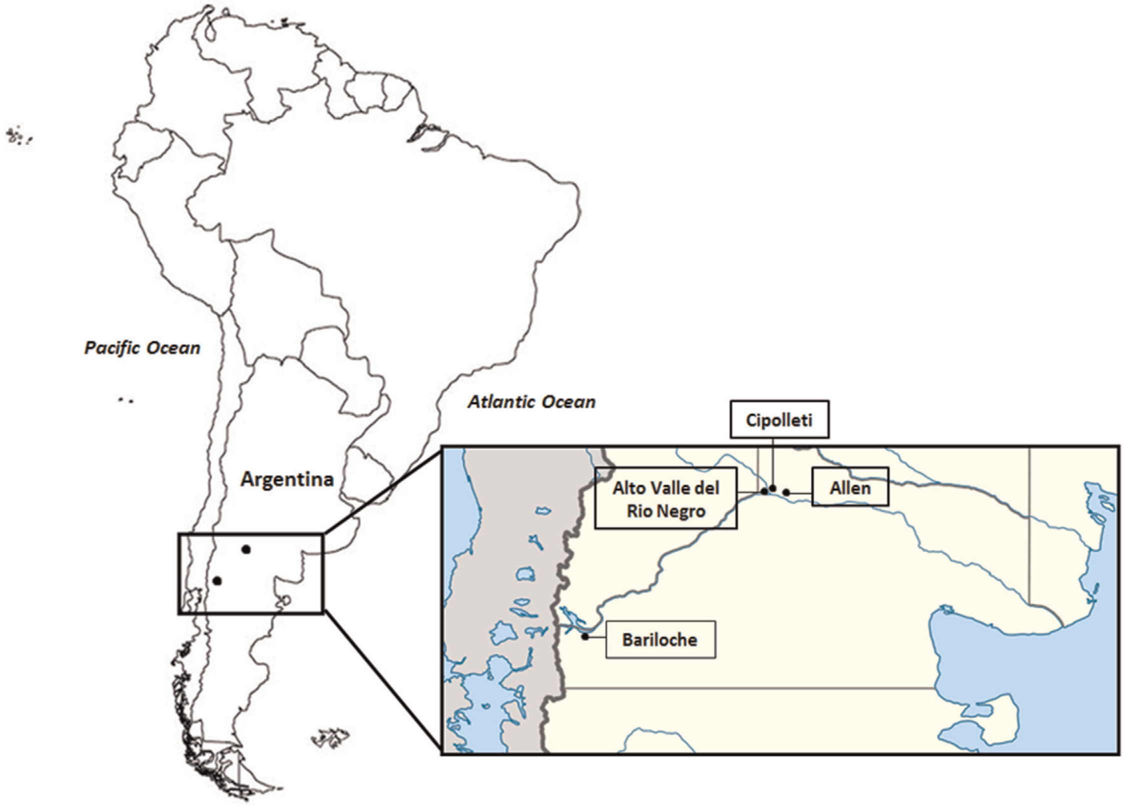

Fig. 1. Map showing the geographical location of the areas studied in the southern tip of South America in 2011.

procured from Supelco (USA). Prior to analytical procedures, all glasswares were rinsed several times with distilled water, hexane and acetone.

2.4. Analytical procedure

The samples were analyzed based on the method described by Espín et al. (2010b, 2012). In order to remove external contamination from the feather surface, prior to the analytical determination, a washing process was performed with tap water, distilled water and Milli-Q water, and two pairs of tweezers were used to separate the barbs of the vane. Thus, efficient washing within the barbs was assured (Jaspers et al., 2007). The feathers were subsequently dried at room temperature.

The feathers (0.2 g) were weighed and incubated overnight at 37 °C in HCl and hexane:acetone (2:1, v/v). Extraction was done with hexane:acetone (3:1, v/v). The samples were homogenized, centrifuged and filtered using anhydrous sodium sulfate and then the solvent collected was evaporated until dryness. After redisolution in 5 ml hexane, samples were cleaned up via Florisil column chromatography (SepPak, Waters®), activated with 2 ml of hexane, using a petroleum ether:diethyl ether mix (21:4, v-v) as elution solvent. The solvent collected was evaporated until dryness.

The final volume was adjusted to 1 ml with n-hexane. One microlitre was injected into a gas chromatograph with electron capture (GC-ECD 17 Shimadzu) for the detection of OC. The SPB-608 capillary column (Supelco®) was 30 m long, 0.25 mm i.d. with a 0.25 μm film thickness, specifically recommended by the EPA for the 15 organochlorine pesticides studied. Helium was used as the carrier gas. The injector was set at the splitless mode; the injector temperature was 290 °C. The column program was: 2 min 50 °C, from 50 to 150 °C at 40 °C/min, 2 min 150 °C, from 150 to 290 °C at 81 °C/min, 10 min 290 °C. The detector temperature was 330 °C and the make-up gas was nitrogen.

Identification and quantification was based on an external standard. The standard solution marked in mixture was prepared by dissolving the reference substances in n-hexane (1:25) at the following concentrations: 10 μg/ml for α-HCH, β-HCH, δ-HCH, lindane, heptachlor, heptachlor epoxide and aldrin; 20 μg/ml for endosulfan I, endosulfan II, DDE, dieldrin and endrin; and 60 μg/ml for DDD, DDT and endosulfan sulfate. Detection limits ranged from 0.03 to 0.41 ng/g. Methoxychlor (1 mg/ml) was used as an internal standard, and was supplied by PolyScience®. A volumen of 10 μl was added to samples and standards in order to compare results and check the repeatability in the chromatograms. Mean recoveries in spiked samples ranged from 46.13% to 146.05%. Concentrations of OC were expressed as ug/g wet weight.

2.5. Statistical analysis

All analyses were carried out using the SPSS v.15.0 statistical package. Reported OC values represent the mean ± standard deviation, median and range. Non-detected values were replaced by the detection limit∗frequency of detection according to Voorspoels et al. (2002). The data were tested for normality using a Kolmogorov–Smirnov test. Since the concentrations of OC were not normally distributed, the data was log-transformed. ANOVA was performed to elucidate significant differences between species and area. Generalized Linear Models (GLMs) with a normal distribution and an identity function were performed to study the effect of area (Valle or Bariloche), species (Southern crested caracara, American turkey vulture and Black vulture), and their interaction, in the concentrations of OC in the feathers. OC concentrations per compound group in feather samples were the response variable, and the explanatory variables considered were area, species and area∗species. We used a backward stepwise procedure to select the final model, and a significance level of $p < 0.05$ for all analyses.

Table 1
Concentrations of organochlorine pesticides (μg/g, wet weight) in feathers of three carnivore scavengers (Southern crested caracara, Turkey vulture and American black vulture) from Northwestern Patagonia, Argentina, in 2011. Values are presented as mean ± standard deviation, median,range and frequency of detection (%).

Organochlorine	**Total** **(*n*=91)**	**Crested caracaras** ***Polyborus plancus*** **(*n*=21)**	**Turkey vulture** ***Cathartes aura*** **(*n*=45)**	**Black vulture** ***Coragyps atratus*** **(*n*=25)**
α-HCH	0.10. ± 0.13 0.06 (nd–0.68) 59	0.10 ± 0.14 0.06 (nd–0.64) 81	0.15 ± 0.14 0.13 (nd–0.68) 82	nd
Lindane	0.45 ± 0.49 0.23 (nd–2.18) 97	0.29 ± 0.43 0.23 (nd–2.04) 95	0.26 ± 0.34 0.14 (nd–1.57) 96	0.94 ± 0.450.80 (0.17–2.18) 100
β-HCH	0.26 ± 0.38 0.13 (nd–2.25) 55	0.23 ± 0.49 0.05 (nd–2.25) 52.4	0.08 ± 0.17 nd (nd–0.75) 31	0.61 ± 0.32 0.51 (0.17–1.38) 100
δ-HCH	0.49 ± 0.88 nd (nd–3.91) 49	0.18 ± 0.15 0.16 (nd–0.49) 71	0.63 ± 0.82 0.11 (nd–2.46) 58	0.52 ± 1.24 nd (nd–3.91) 16
Heptachlor	0.12 ± 0.19 0.07 (nd–1.45) 59	0.12 ± 0.16 0.073 (nd–0.75) 81	0.13 ± 0.22 0.09 (nd–1.45) 67	0.08 ± 0.16 nd (nd–0.57) 28
Heptachlor epoxide	1.66 ± 2.75 0.36 (nd–16.7) 82	0.53 ± 0.84 0.29(0.05–4.02) 100	2.99 ± 3.39 2.32 (nd–16.7) 89	0.22 ± 0.36 0.06 (nd–1.46) 56
Aldrin	0.59 ± 0.68 0.35 (nd–4.66) 96	0.27 ± 0.49 0.17 (0.05–2.42) 100	0.71 ± 0.82 0.45 (nd–4.66) 93	0.63 ± 0.47 0.53 (nd–2.18) 96
Dieldrin	0.30 ± 0.93 0.90 (nd–8.59) 65	0.14 ± 0.26 0.04 (nd–1.09) 81	0.54 ± 1.27 0.32 (nd–8.59) 91	0.01 ± 0.03 nd (nd–0.16) 4
Endrin	0.44 ± 0.86 0.12 (nd–4.19) 82	0.17 ± 0.37 0.08 (nd–1.72) 81	0.17 ± 0.13 0.12 (nd–0.50) 91	1.17 ± 1.37 0.66 (nd–4.19) 68
Endosulfan I	0.06 ± 0.12 nd (nd–0.47) 34	0.02 ± 0.02 nd (nd–0.07) 48	0.11 ± 0.15 nd (nd–0.47) 47	nd
Endosulfan II	0.86 ± 1.83 0.16 (nd–10.8) 87	0.17 ± 0.02 0.13 (nd–1.04) 86	0.19 ± 0.15 0.15 (nd–0.53) 89	2.67 ± 2.78 1.66 (nd–10.8) 84
p.p'-DDT	0.72 ± 1.31 0.43 (nd–10.6) 81	0.65 ± 0.90 0.43 (0.05–4.40) 100	0.84 ± 1.58 0.58 (nd–10.6) 91	0.55 ± 1.05 nd (nd–4.67) 48
p.p'-DDE	0.27 ± 0.32 0.12 (nd–1.57) 81	0.12 ± 0.20 0.07 (nd–0.97) 95	0.39 ± 0.35 0.35 (nd–1.57) 84	0.21 ± 0.29 0.1 (nd–1.07) 64
p.p'-DDD	0.15 ± 0.36 nd (nd–2.92) 50	0.11 ± 0.31 0.02 (nd–1.45) 57	0.19 ± 0.19 0.17 (nd–0.73) 71	0.12 ± 0.58 nd (nd–2.92) 4
∑ HCH	**1.31 ± 1.34** **0.91 (nd–6.53)** **99**	**0.80 ± 1.01** **0.53 (0.15–4.93)** **100**	**1.13 ± 1.11** **0.62 (nd–4.52)** **98**	**2.08 ± 1.65** **1.36 (0.35–6.53)** **100**
∑ DDT	**1.14 ± 1.58**	**0.87 ± 1.40**	**1.41 ± 1.75**	**0.88 ± 1.35**

Table 1 (*continued*)

Organochlorine	**Total** (***n*=91**)	**Crested caracaras** ***Polyborus plancus*** (***n*=21**)	**Turkey vulture** ***Cathartes aura*** (***n*=45**)	**Black vulture** ***Coragyps atratus*** (***n*=25**)
	0.84 (nd–11.7) **92**	**0.55 (0.05–6.83)** **100**	**1.04 (nd–11.7)** **96**	**0.31 (nd-5.17)** **80**
∑ Drins	**1.33 ± 1.52** **0.88 (nd–8.89)** **99**	**0.59 ± 0.87** **0.33 (0.07-4.14)** **100**	**1.42 ± 1.52** **1.06 (0.84–8.89)** **100**	**1.80 ± 1.74** **1.12 (nd–6.01)** **96**
∑ Endosulfan	**0.92 ± 1.81** **0.26 (nd–10.7)** **90**	**0.19 ± 0.23** **0.15 (nd–1.04)** **91**	**0.29 ± 0.21** **0.26 (nd–0.80)** **93**	**2.66 ± 2.79** **1.66 (nd–10.7)** **84**
∑ Heptachlor	**1.78 ± 2.85** **0.51 (nd–18.2)** **90**	**0.65 ± 0.99** **0.36 (0.11–4.78)** **100**	**3.13 ± 3.53** **2.46 (nd–18.2)** **91**	**0.31 ± 0.35** **0.21 (nd–1.46)** **80**
∑ OC	**6.49 ± 5.95** **4.39 (0.35–26.5)** **100**	**3.11 ± 4.39** **2.19 (0.57–21.72)** **100**	**7.38 ± 5.83** **5.92 (0.88–26.5)** **100**	**7.74 ± 6.45** **5.54 (0.35–25.9)** **100**

For GLMs, two samples of Crested caracaras were not used to not knowing the area (*n*=89).

The total concentrations of organochlorine pesticides (ΣOC) were calculated as the sum of individual compound concentrations. The group of DDT and metabolites (ΣDDT) represented the sum of p,p´-DDE, p,p´-DDD and p,p´-DDT, hexaclorocyclohexanes (ΣHCH) included α, β, δ and γ-isomers, the group of heptachlor (ΣHeptachlor) was formed by heptachlor and its epoxide, ΣDrins represented the sum of endrin, aldrin and dieldrin, and finally ΣEndosulfan incorporated endosulfan I and II.

3. Results and discussion

3.1. OC concentrations in feathers and profile.

All the organochlorine pesticides studied were detected in the feathers of the three avian scavengers surveyed (Table 1). The presence of these compounds commonly used in agriculture practices in the study area in the feathers of scavengers suggests that the biota are exposed and, thus, potentially suffering adverse effects. Moreover, this finding coincides with the detection of OC in soils, sediments, suspended particulate matter in water, and water courses in the Rio Negro basin (Miglioranza et al., 2013). When individuals from the three species were pooled together, ∑HCH had the highest median concentration, followed by ∑Drins, ∑DDT, ∑Heptachlor, and ∑Endosulfan (Table 1). This result agrees with the fact that HCHs and DDTs are the pesticides most frequently reported in human food in Argentina, followed by heptachlors, chlordanes, aldrin and endosulfan (Villaamil Lepori et al., 2013). Therefore, the results show that OC feather detection using the analytical method developed by Espín et al. (2010b) is useful to monitor the presence of OC in the environment.

The accumulation pattern of these compounds in the feathers and internal tissues is an important issue to consider when assessing OC exposure. The highest concentrations of lipophilic pesticides are expected to be found in adipose tissue, followed by the liver and the muscles (García-Fernández et al., 2013). However, less persistent or more polar OC are more easily metabolized and can be found at low concentrations in fat tissue or liver, and in higher levels in the bloodstream for a limited period of time. Thus, these compounds could enter feathers during their growth period (García-Fernández et al., 2013). In this sense, some authors have found higher levels of less persistent OC in feathers than in fat, liver or muscle (Dauwe et al., 2005; Espín et al., 2010a, 2012; Rajaei et al., 2011). In this study, the compounds that reached the highest median levels were DDT, heptachlor epoxide, aldrin and lindane. Moreover, lindane, aldrin and endosulfan II were the compounds most frequently detected (Table 1). As aforementioned, recent works carried out on infant milk samples from Argentina, showed that heptachlor exceeded the actual acceptable daily intake (ADI), thus representing the compound of higher risk (Ridolfi et al. 2002, Villaamil Lepori, et al. 2003, 2006). These similar findings in carrion feeders and human food could be explained by their position in the top of their respective food chains. When heptachlor is ingested, it is quickly metabolized to heptachlor epoxide (Melnikov, 1971), which is soluble in lipids and stored in body fat and may be transferred to feathers during the molt period, which explains its presence at higher concentrations in this study.

With regards to the hexachlorocyclohexane isomer γ-HCH (lindane), it has a shorter half-life in the environment compared with other organochlorine compounds, and is metabolized and excreted by organisms relatively rapidly (Blus et al., 1985). Therefore, the high levels of γ -HCH in feathers probably reflect either a direct exposure to lindane or a release into the bloodstream by fat mobilization during feather growth. Moreover, this result shows the capacity of feathers as an excretion route for this compound. Behrooz et al. (2009a,b) and Espín et al. (2012) studied organic compounds in various bird species from Iran and Spain, respectively, and also found that lindane was the most predominant HCH isomer in feathers, which they felt was due to recent exposure of birds to γ-HCH.

Regarding ∑DDT pesticides, p,p’-DDT is rapidly metabolized in the liver, mainly to p,p’-DDE and p,p’-DDD (Gold and Brunk, 1982). Therefore, high concentrations of p,p’-DDT in feathers could indicate exposure to non-degraded DDT, and thus reflect its presence in the environment.

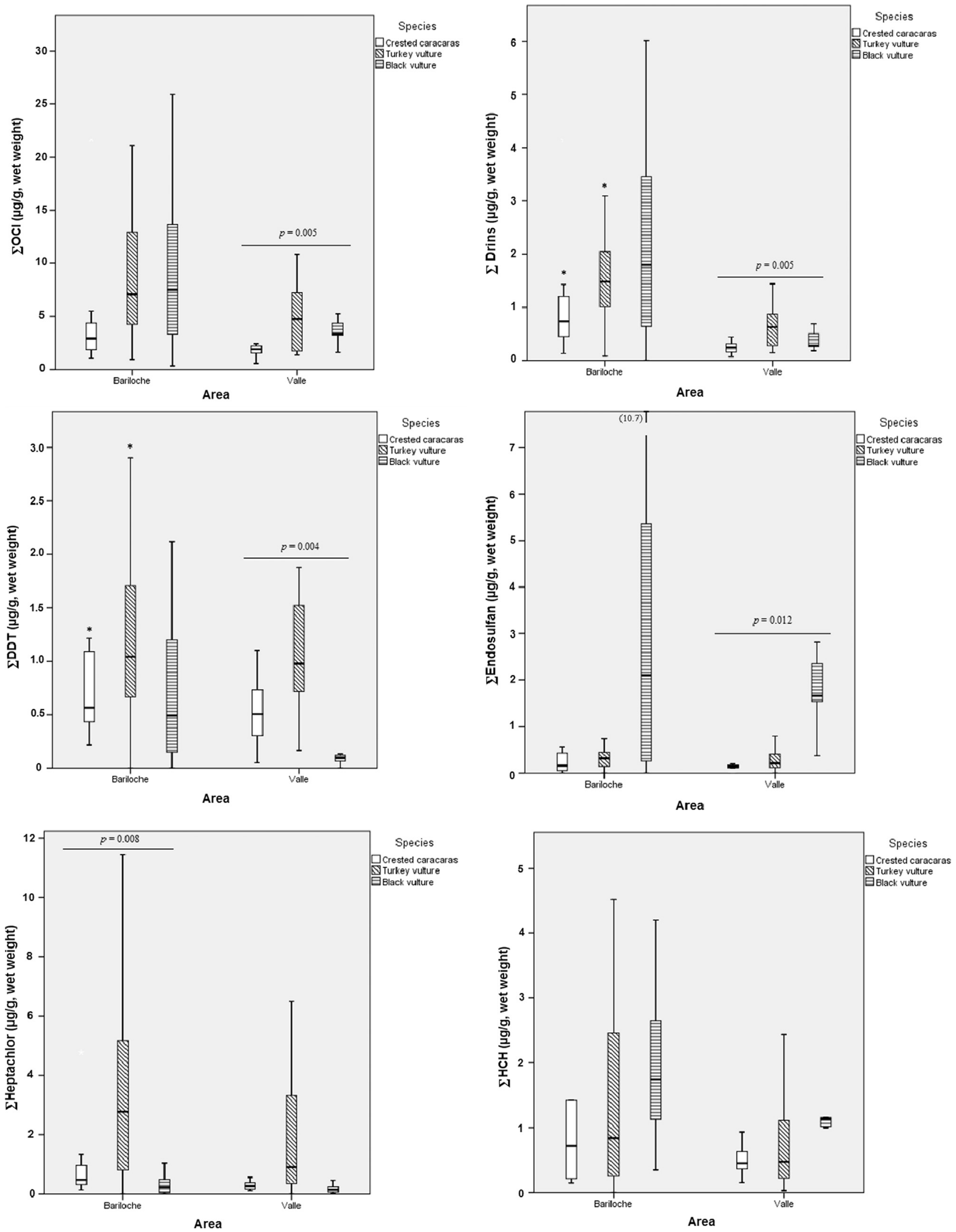

Fig. 2. Boxplots showing organochlorine groups concentrations (µg/g, wet weight) in feathers of three carnivore scavengers (Southern crested caracara, Turkey vulture and American black vulture) in the studied areas in 2011.

Asterisk indicates significant differences between areas in each species ($p < 0.02$). A line above bars indicates significant differences between species in each area. The outliers are removed to represent the data in the figure in order to provide a better overview of boxplot. In the boxplot representing endosulfan concentrations, maximum level corresponding to black vulture in Bariloche was out of the range found for the rest of samples, and the graph was modified so that the maximum value is presented in brackets at the top of the whisker.

The OC exposure in raptors from Argentina found in this study were much higher than those found in feathers of raptors from northern Norway and South-west Iran (Eulaers et al., 2011; Behrooz et al., 2009a), and feathers of seabirds from Spain (Espín et al., 2012) and mongolian plover (*Charadrius mongolus)* from South India (Tanabe et al., 1998). Several factors may have led to the high OC concentrations found in our study. Firstly, the studied species are scavengers that feed mostly on carrion from vertebrates, which put them in a high trophic position. In this sense, Behrooz et al. (2009a,b) investigated the concentrations of organic contaminants in 37 birds with different dietary habits and observed that raptors (carnivores) showed the highest levels of DDTs and PCBs due to the biomagnification process, and herbivores showed the lowest levels. Moreover, an important issue to consider is the regional variations in contamination, since these species inhabit an area in Argentina where OC are frequently reported in spite of pesticide restrictions. In addition, intraspecific factors such as body condition, gender and age can influence contaminant concentrations in feathers (Espín et al., 2012; García-Fernández et al. 2013; Jaspers et al., 2011). Furthermore, other factors such as molt period, collection time, type of feather, and external contamination on the feather surface, could interfere with the results and should be taken into account (Espín et al., 2012; Jaspers et al., 2007, 2011; García-Fernández et al. 2013). However, several of these factors are unknown when feathers are found in the field (García-Fernández et al., 2013), as in this study.

What is clear is that feathers seem to be a promising tool for biomonitoring OC in avian scavengers from Argentinean Patagonia, since these compounds can be quantified in this matrix. In addition, the frequency and abundance profile of OCin this study is similar to those reported in other types of samples in Argentina (Villaamil Lepori et al., 2003, 2006). This suggests that OC concentrations in feathers of scavenger species from Patagonia Argentina may be indicative of OC availability in the environment. As cited above, carrion feeders and humans are in the top of their food chains, and considering the obvious differences, we suggest that feathers of these species be considered complementary tools in toxicological and environmental risks assessments, especially in exposure assessment.

3.1.1. *Differences among species*

Significant differences in OC concentrations were found among the three species studied in el Valle (Fig. 2). Indeed, “species” was included in all the models to explain organochlorine group concentrations, except for ΣDrins (Table 2). In general, Southern crested caracara showed significantly lower OC concentrations than the other species (Table 1, Fig. 2). Although, the three species feed primarily on a wide variety of carrion (Dabbs and Martin, 2013; Haskins et al., 2013) the smaller size and lesser weight of the Southern crested caracara in comparison with the other two species of Cathartidae may explain these differences.

Although the ∑OC were similar between turkey vulture and black vulture, the distribution pattern was different in both species (Table 1). In Turkey vulture, heptachlor epoxide reached the highest concentrations, with levels ranging between non detectable values ($n=5$) and 16.7 ug/g, and median concentration of 2.32 ug/g; followed by *p.p'*-DDT with a median concentration of 0.58 ug/g (Table 1). Furthermore, ∑DDT was one of the most frequently detected OC insecticides (> 95%; Table 1). However, in American black vulture the highest levels registered precisely reflected the most widely used OC in the study area, endosulfan. Specifically, a median of 1.66 ug/g was registered for ∑endosulfan (endosulfan I and II), due solely to endosulfan II. The information regarding endosulfan and its metabolites in samples of wildlife is limited. However it is known that the half-life of endosulfan I is much shorter than that of endosulfan II, 30 days and 900 days respectively (Cairos and Stewart 1974). Endosulfan is a compound considered as non-persistent in warm-blooded organisms and is rapidly metabolized and easily excreted (Dorough et al., 1978), and partially oxidized to endosulfan sulfate (Gorbach, 1966). This could explain why only endosulfan II was detected in our samples. The samples were collected in spring 2011, before a new resolution was passed in Argentina in June 2011 announcing restrictions on and banning the import of the active ingredient of endosulfan, starting later in 2013 (Resolution 511/2011, SENASA). With the exception of α-HCH and endosulfan I, which were not detected in any of the samples analyzed, all compounds were detected in feathers of American black vulture. Compounds detected more frequently were β-HCH and lindane with 100% of detection, aldrin with 96%, and endosulfan II with 84% detection frequency (Table 1).

Table 2
Generalized Linear Models for organochlorine groups.

Response	Model	X^2	*p*	*n*
Log ΣHCH	Species	12.6	0.002	89
Log ΣHeptachlor	Species	14.3	0.001	89
Log ΣDrins	Area	16.7	< 0.001	89
Log ΣEndosulfan	Species	6.76	0.034	89
Log ΣDDT	Species ($p=0.012$)+Area ($p=0.024$)	16.7	0.001	89
Log ΣOCl	Species (p=0.004)+Area (p=0.003)	25.5	< 0.001	89

An important factor probably involved in these OC profile is the differences in diet between species, which has been reported as a cause for changes in organochlorine loads in raptors (Gervais and Anthony, 2003; Gómez-Ramírez et al., 2012; Jaspers et al., 2006a; Mañosa et al., 2003; van Drooge et al., 2008). Thus, it is clear that different species with different dietary habits accumulate OC in feathers in different manners (García-Fernández et al., 2013). In the study area, Turkey vultures live and search for food in more open areas (Sibley and Monroe, 1990; Hoyo et al., 1994) incorporating several food items (eg., livestock, fish, reptiles, carnivores, mice and a great number of birds in their diets). However, the trophic niche breadth of the black vultures is more restricted than the turkey vulture feeding mainly on ungulates and arthropods (Ballejo et al., 2013). Besides, in in recent years, black vultures have increased in numbers and become increasingly associated with urban developments and have been observed feeding at garbage dumps, and on road kills (Lambertucci et al., 2009a, b; Carrete et al., 2010) in larger numbers than the other species. These differences in feeding habits between the three study species could be producing differences in OC profile. Birds are generally less able to metabolize OC relative to other species; therefore a higher proportion of birds in the diet may result in higher organochlorine levels in predatory birds (van Drooge et al., 2008). Also, migratory habits and molt periods must also be considered when evaluating the exposure and distribution of contaminants in the body and when making comparisons between species (Espín et al., 2012; García-Fernández et al., 2013), since birds may accumulate OC while spending summer or winter in areas with higher levels of OC (García-Fernández et al., 2013). Importantly in the study area, only Turkey vulture is considered a migratory species (Dodge et al., 2014). It is known that black vultures also fly large distances, but the information is poor on the patterns of movement of the three species for the study area and further studies are recommended in this sense.

3.1.2. *Differences between study areas*

Regional variations in contamination should also be reflected in the OC levels in feathers, thus spatial differences need to be considered (García-Fernández et al., 2013). We observed statistical differences among studied areas in the concentration of ∑DDT and

∑Drins for Crested caracaras and Turkey vulture (Fig. 2). "Area" was included in the models for ∑OC, ∑Drins and ΣDDT (Table 2). On the contrary to our prediction, the highest levels of OC were found in feathers from the area with lower human disturbances (Bariloche area). As explained before, Bariloche is a city (with 140,000 inhabitants) immersed in a rural area with low human density and extensive livestock farming; while the Valle has several cities and is an intensive agricultural area, which is why we expected to find higher OC concentrations. Organic pollutants can reach feathers through the bloodstream only during their growth in a certain period of time, the molt, thus reflecting internal contamination (García-Fernández et al., 2013). As feathers mature, vascular connections undergo atrophy and compound concentrations remain stable (García-Fernández et al., 2013). Therefore, feathers can provide information on concentrations in the blood circulation at the time of growth. Thus, an important factor to consider is the molt period regarding the pattern of movement of birds (García-Fernández et al. 2013). However, it may be complex to interpret feather concentrations taking into account the molt strategy, especially if there is scarce literature available on feather molting and movement behavior for the bird species studied. Although we collected molted feathers during austral spring (October–December), we cannot be totally sure where the feather grew. When statistical models were done, we found that both "Species" and "Area" had an effect on ∑OC and ∑Drins (Table 2). One possible explanation to this unexpected result could be that the birds in this study gathered food outside of the sampling area before their last molt. It is known that migratory habits influence in the levels of contaminants in birds (García-Fernández et al., 2013). This is especially possible in the particular case of the Turkey vulture which is a migratory species, and may accumulate higher OC in areas to which it migrates, as explained above. However, another explanation could be that birds from Bariloche area feed on unexpected food resources containing OC. In this regard, the scavengers may be eating in rubbish dumps with OC residues from the Bariloche area. In addition, it is notable that most of the feathers from Bariloche were collected close to an area with fish farms and the colonies feed on the fish. In this sense, the levels of OC have been found to be high in farm fish (Hites et al., 2004). It is also possible that these species, particularly the black vultures, feed on both rubbish dumps and fish discards containing OC. In this sense, Ondarza et al. (2014) found that OC and other organic pollutants are ubiquitous contaminants in Patagonian fish tissues in Negro River in the Valle region. However, OC were also found in brown trout (*Salmo trutta*) in the Andean Patagonia closer to the Bariloche area (Ondarza et al.,2011). In view of these results, as a precautionary principle, it may be useful to carry out detailed study on OC concentrations in fish and dumps from the Bariloche area due to the potential risk to wildlife and human health.

3.2. Effect assessment

Few data are available on the relationship between OC in feathers and their effects on birds. In an experimental study, concentrations of 48 ppm (4.80 μg/g) of DDTs (DDT, DDD and DDE) in feathers of nestling white pelicans showed several sublethal effects evident in the vitamin A levels in the liver, as well as in the potassium, calcium and protein in serum but were not associated with signs of intoxication (Greichus et al.,1975). Thus, the threshold value associated with sublethal effects is probably less than 4.80 μg/g of ΣDDT in feathers (García-Fernández et al., 2013). In this study, three individuals showed concentrations above said threshold. However, the possible interspecific variability which may render the threshold different for every species should be considered.

Few studies provide information on concentrations of OC in feathers and internal tissues of the same individuals, and fewer still, dispute the importance of OC concentrations in feathers, on the estimation of adverse effects (Behrooz et al. 2009a,b; Espin et al. 2010a,b, 2012). Espín et al. (2010a, 2012) and Jaspers et al. (2006b) analyzed OC in feathers and internal tissues of the same population of adults Razorbills and Common Buzzard, respectively. In these studies, the ΣDDT (DDT and DDE) liver to feather ratio ranged from seven to eight. Using this relationship, theoretical hepatic concentrations of ΣDDT (DDT+DDE) in the species in this study would be 5.33 μg/g in American black vulture, 5.35 μg/g in Southern crested caracara and 8.70 μg/g in Turkey vulture. DDE levels of 124 μg/g in the livers of some bird species (Ardeidae) were associated with broken eggshell (Pratt, 1972), while levels of 569 μg/g were associated with deaths of birds (Call et al., 1976). These levels are much higher than those estimated in this study; however, we cannot discard sublethal effects since the values found are far from normal at least for these birds. This comparison should be used with caution due to problems with extrapolating such data across tissues and species. Therefore, further experimental and field studies are required in order to determine a nonadverse-effect threshold value in feathers from different species (García-Fernández et al., 2013).

4. Conclusion

This is the first study on OC in feathers of three terrestrial top carnivores from South America. OC concentrations found in the three study species were much higher than those found in feathers of raptors from Europe and Asia, and in feathers of seabirds from Spain, which probably indicate the impact of agriculture, and other possible uses of OCs in the area. The pesticides most frequently found in this study and at high concentrations are similar to those reported in several food samples in Argentina. This suggests that OC concentrations in feathers of scavenger species from the Argentinean Patagonia reflect OC in the environment. Moreover, taking into account the obvious differences with humans, their feathers can be considered as complementary tools for exposure assessment in toxicological and environmental risks assessment processes. On the other hand, differences in OC profiles between species and areas seem to be related to molt period, as well as to feeding and migratory habits. Feathers appear to be a promising tool for OC biomonitoring also in avian scavengers. Three individuals showed ∑DDT concentrations (DDT, DDD and DDE) related to sublethal effects, although this comparison should be used with caution due to problems with extrapolating such data across tissues and species.

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