Bull Environ Contam Toxicol (2012) 88:89–93
DOI 10.1007/s00128-011-0453-2

Tissue Concentrations of Pesticides, PCBs and Metals Among Ospreys, *Pandion haliaetus*, Collected in France

Charles Lemarchand · René Rosoux · Marie-Eve Pénide · Philippe Berny

Received: 14 June 2011 / Accepted: 24 October 2011 / Published online: 5 November 2011

Abstract In this study, osprey (*Pandion haliaetus*) tissues collected in France were used for contaminants analyses by a non-invasive approach. 53 pesticides (organochlorine, organophosphate, carbamate, pyrethroids, herbicides, anticoagulant rodenticides), 13 PCBs, and 5 metals (mercury, lead, cadmium, copper and arsenic) were quantified in liver of 14 individual samples. PCBs and mercury were frequent (mean 0.5 mg/kg, range < d.l.−2.6 mg/kg and mean 3.4 mg/kg, range < d.l. −16.3 mg/kg wet weight, respectively). Inter-individual variations in contaminant diversity and amounts were noticed. Immediate conservation of the species in the country does not seem to be threatened by global contamination.

Keywords Osprey · pesticides · PCBs · Metals

The osprey (*Pandion haliaetus*), a top predator piscivorous bird of prey once widespread in Europe, has dramatically declined because of earlier eradication efforts, habitat degradation and exposure to persistent pollutants, along with the consecutive decline of the predator's primary prey. Global aquatic contamination by persistent pollutants was considered to be important causative agent in osprey population decline (Dennis 2008). Accumulative organochlorine (OC) compounds (i.e. OC pesticides and PCBs) have been associated with direct toxicity or reproductive failure by eggshell thinning but studies also reported high PCBs content in thriving osprey populations (Henny et al. 2003; Toschik et al. 2005). A paucity of data exists on osprey exposure, persistence and toxicity to other pesticides families (e.g. cholinesterase inhibitors as organophosphate (OP) and carbamate (CA) pesticides, pyrethroids pesticides, herbicides or anticoagulants rodenticides (Chu et al. 2007). Mercury is generally considered as one of the most harmful metals to wild fauna, and particularly concerning aquatic top-predators, due to mercury magnification in aquatic food webs (DesGranges et al. 1998). However, mercury dynamic in osprey was showed to be variable and direct mercury-induced mortality was rarely observed (Hughes et al. 1997; Henny et al. 2008; Rattner et al. 2008). A lot of other metals or metalloids (e.g. Pb, Cu, Cd, Zn, As, Al, Mn) concentrations mesured in ospreys where generally below toxicological thresholds (Henny et al. 1991; Hughes et al. 1997; Rattner et al. 2008). However, knowledge and long-term consequences of metals on osprey remain weak.

C. Lemarchand (✉) · P. Berny
VetAgro-Sup Campus Vétérinaire de Lyon, laboratoire de toxicologie, UMR INRA 1233, 1 avenue Bourgelat, 69280 Marcy l'Etoile, France
e-mail: Charles.LEMARCHAND@univ-bpclermont.fr

R. Rosoux
Muséum des Sciences Naturelles, 6 rue M. Proust, 45000 Orléans, France

M.-E. Pénide
Université Blaise Pascal, 24 avenue des Landais, 63171 Aubière, France

Because of their high trophic level and main ecological characteristics, ospreys are considered as useful sentinels of aquatic systems (Grove et al. 2009). The present study was carried out to evaluate osprey contamination in France by a large spectrum of toxic elements, including 53 pesticides (organochlorine, organophosphate, carbamate and pyrethroids pesticides, herbicides, anticoagulant rodenticides), 13 PCB congeners, and 5 metals.

Materials and Methods

In France, the osprey remains a very rare nesting species (less than 40 pairs; Nadal and Tariel 2008). For ethical and legal reasons, individuals were not killed for analyses and operations were conducted under appropriate authorizations. A non-invasive method was preferred, using young ospreys found dead in nests during ringing (banding) operations. Sample numbers were further augmented with individuals illegally killed, others found dead from power line strikes or electrocution, or accidentally drowned at fish farms. Only freshly dead (24 h maximum) individuals according to the carcass condition were considered for analyses. A network organized and enhanced sampling, under the coordination of the Museum of the city of Orléans. People in charge of osprey ringing and monitoring (CRBPO—MNHN), national authorities for environment (MEEDDM, DREAL, ONCFS, ONEMA, ONF), union of fauna health centres (UFCS) and birds protection league (LPO—French representative of Bird Life International), private land owners and companies, city museums, associations and regional naturalists were contributors. For each carcass, a necropsy was performed; 20 g of liver was sampled and deep-frozen (−40°C) in plastic tubes prior to analyses. Age was defined as "juvenile" (non-flying individual), "subadult" (emancipated individual with characteristic fringe on feathers) and "adult" (adult plumage) (Dennis 2008).

OC pesticides, PCBs, anticoagulant rodenticides and metal analyses and quality control are described in Lemarchand et al. (2010). Organophosphate and carbamates pesticides (Dichlorvos, Carbofuran, Mevinphos, Phorate, Methiocarbe, Terbufos, Diazinon, Disulfoton, Chlorpyriphos methyl and ethyl, Fenitrothion, Pyrimiphos methyl, Malathion, Fenthion, Parathion, Methidathion, Disulfoton sulfone, Triazophos) concentrations were determined by GC/MS after sample preparation using dichloromethane. Pyrethroids pesticides (Tefluthrine, Cyhalothrine, Permethrine, Cifluthrine, Cypermethrine, Fenvelarate, Deltamethrine) concentrations were determined by GC/ECD and confirmed by GC/MS after preparation using ethanol and methanol, according to a modified method of the French Food Safety Authority. Herbicides (Trifluraline, Atrazine, Simazine, Terbuthylazine, Diuron, Alachlor, Metolachlor, Cyanazine) and fungicide Epoxyconazole concentrations were determined by GC/MS spectrometry after preparation using acetone and methanol. Each compound was identified using retention time and 3–4 ions, with pre-defined relative amounts and 20% variability acceptance for each ion. Linearity was confirmed with 5 point calibration curves and $r^2 > 0.99$. Recovery was determined for all spiked samples. Recovery levels were always greater than 92% for pesticides and PCBs, 90% for metals and between 80.1 and 89.2 for rodenticides (Lemarchand et al. 2010). Mann–Whitney or Kruskall-Wallis tests were used to compare independent samples, Spearman rank test to quantify associations between two variables.

Results and Discussion

Since 2007, various samples from 14 different osprey individuals were collected and used for contaminant analysis in France, constituting the first available tissues samples in this part of the species' repartition area in Europe. 4 osprey samples (3 dead downy young in nests and one adult) came from the breeding population. The 10 other birds were collected in France in spring or fall, during north or south migration, respectively, as France is also a major crossing area for ospreys from different European populations (Dennis 2008). 4 of them were ringed in Germany, 1 in Norway. 5 non-ringed birds were from unknown origin (Table 1). Results concerning contamination of ospreys by detected OC compounds (OC pesticides and PCBs) are presented in Table 1. OC pesticides were detected in 10 of the sampled ospreys. Only *p,p'*-DDE and Methoxychlor were found. DDE was detected in only 2 individuals and concentrations remained and comparable to results noted in previous studies (Henny et al. 2008). Methoxychlor was detected in 8 individuals (57%), with low values (range < d.l.−0.72 mg/kg ww, see table 1). General Methoxychlor mean reached 0.13 mg/kg ww, far less than noted in Germany (Weber et al. 2003), where 100% of the sampled ospreys were contaminated by high Methoxychlor values. We did not observe any significant variations in OC pesticides concentrations with osprey age, sex or origin, due to little size of sampling. Lindane, Aldrin, Heptachlor, Heptachlor epoxide and Endosulfan were never found in samples. However these compounds were noted in previous studies concerning ospreys (Toschik et al. 2005). This difference could be related to a more diversified, longer and stronger exposure of American ospreys to OC pesticides when compared to European ones, resulting in a higher OC pesticides accumulation pattern in the whole population. In France, DDT and other OC pesticides were banned before the return of the osprey or at the beginning of population expanding, resulting in a lower and decreasing exposure to contaminants. Further analyses on other ospreys coming from Europe should be performed to assess this hypothesis. Among the highly toxic OP pesticides (cholinesterase inhibitors) analyzed, 7 (Mevinphos, Phorate, Malathion, Parathion, Methidathion, Disulfoton sulfone and Triazophos) were quantified in 7 ospreys (50%, see Table 1). Contamination of ospreys by OP pesticides appeared low and scattered, with only few individuals concerned. OP pesticides were only measured in subadult and adult ospreys, and never found in juvenile during this study (Table 1). None of the individuals coming from the nesting population in France showed any OP pesticides contamination. Concerning subadults and adults, OP pesticides variations with osprey age, sex or origin were not significant. Triazophos, Disulfoton sulfone and

Table 1 Concentrations of organochlorine, organophosphate and pyrethroids pesticides, herbicides, PCBs (mg kg^{-1} wet weight), and metals (mg kg^{-1} dry weight for Pb, Cd, Cu and As, mg kg^{-1} wet weight for Hg for a better comparison with available data) in ospreys (*Pandion haliaetus*) collected in France

Individuals	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sex	Male	Male	–	–	Female	Male	Female	Female	Male	Female	Female	Male	Male	Male
Age	Juv.	Adult	Juv.	Juv.	Subad	Subad.	Adult	Adult	Subad.	Adult	Adult	Subad.	Subad	Adult
Origin	France	France	France	France	Norway	Ger.	Ger.	Ger.	Ger.	Unkn.	Unkn.	Unkn.	Unkn.	Unkn.
OC pesticides (LOD)														
DDT (0.005)	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DDE (0.005)	–	8.2	–	–	–	–	0.4	–	–	–	–	–	–	–
DDD (0.005)	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Metoxychlor (0.005)	–	–	–	–	0.03	0.01	–	0.04	0.01	0.72	0.22	–	0.003	0.01
OP, CA pesticides														
Mevinphos (0.005)	–	–	–	–	–	–	–	0.03	–	0.05	–	0.3	–	–
Phorate (0.005)	–	–	–	–	–	–	–	–	–	–	–	–	0.02	–
Malathion (0.005)	–	–	–	–	–	–	–	–	–	–	–	–	0.03	–
Parathion (0.005)	–	–	–	–	0.4	–	–	–	–	–	–	–	0.8	–
Methidathion (0.005)	–	–	–	–	–	–	–	–	–	0.02	–	–	0.02	–
Disulfoton sulfone (0.005)	–	–	–	–	–	–	–	–	–	0.3	–	0.3	–	0.04
Triazophos (0.005)	–	–	–	–	0.02	0.2	–	–	–	–	0.03	0.03	–	–
Herbicides														
Terbuthylazine (0.005)	–	–	–	–	0.09	0.8	–	–	0.3	–	0.5	–	0.9	–
Alachlor (0.005)	–	–	–	–	0.01	–	–	–	0.01	0.01	0.01	–	0.04	–
Epoxyconazole (0.005)	–	–	–	–	–	–	–	5.6	–	–	–	–	–	–
Total PCBs (0.005)	–	2.6	0.3	0.3	0.04	0.1	0.2	0.08	0.01	0.04	1.2	0.9	0.01	0.05
Metals														
Mercury (0.014)	–	3.1	0.5	0.6	8.3	1.1	0.1	6.8	0.2	4.3	4.5	0.3	16.3	0.4
Lead (0.05)	–	0.4	0.1	0.2	1.2	–	0.5	–	–	0.1	–	–	0.3	–
Cadmium (0.05)	–	0.4	0.2	0.3	0.3	–	0.4	–	–	0.9	–	–	8.7	–
Copper (0.05)	–	0.1	0.01	0.02	134.7	0.001	–	0.004	0.003	42.1	0.001	0.0008	38.8	0.003
Arsenic (0.02)	–	–	–	–	–	–	–	–	–	0.2	–	–	0.1	–

LOD limit of detection, *Juv.* Juvenile, *Subad.* Subadult, *Ger.* Germany, *Unkn.* Unknown, – below detection limit)

Mevinphos were the more frequently detected compounds in ospreys (see Table 1). Phorate and Malathion were detected in only one individual, characterized by the highest diversity (4 compounds with also Parathion and Methidathion) and highest concentrations of total of OP pesticides (0.9 mg/kg ww, see Table 1). As described above, ospreys were generally in good physical conditions (adequate mass and total body fat) and did not show any OP pesticides poisoning sign (e.g. diarrhea, pulmonary oedema, tightened claws) during post-mortem examination. Measured concentrations remained well below toxic doses of total cholinesterase inhibitors (about 5–10 mg/kg ww) and were not death causal agent of these ospreys. Carbamates (Methiocarb and Carbofuran) and pyrethroids pesticides were not quantified in ospreys during this study (data not shown). As observed for OP pesticides, contamination of ospreys by herbicides was generally low and few diversified. Only 6 ospreys (42%) showed detectable herbicides. Terbuthylazine and Alachlor were the only herbicides detected (see Table 1). Herbicides variations with osprey age, sex or origin were not significant. It can be underlined a unique case of contamination by fungicide Epoxyconazole (5.64 mg/kg ww, see Table 1), detected in an osprey from Germany without particular intoxication signs. None of the individuals coming from the nesting population in France showed any herbicide or fungicide contamination. As for OP and CA pesticides, low measured concentrations of herbicides leads to a probable low impact of these compounds on species' conservation. However, sample size is little for a definitive conclusion and few data are available for comparison (Chu et al. 2007). Anticoagulant rodenticides were never found in ospreys during our study (data not shown). These results could be related to osprey general diet in the study area, which is almost exclusively composed of fish (Dennis 2008). Anticoagulant rodenticides are used to control unwanted mammals, and ospreys, as fish-eaters, seem to be of little concerned by such a contamination.

With one exception, PCBs were detected in all of the analyzed samples. Total PCBs mean reached 0.5 mg/kg ww (range < d.l.−2.6 mg/kg wet weight, see table 1). Observed variations between total PCBs values and osprey age or sex were not significant. PCBs values reported here were within the range of those detected in osprey blood, tissues or eggs in previous studies where PCBs were suspected to stress osprey productivity (Toschik et al. 2005). However, osprey productivity in Europe, especially in France is comparable to or higher than reported for American and Canadian populations (Toschik et al. 2005). Considering the natural expansion of the species noted in the study area, OC pesticides and PCBs don't seem to threat the immediate reproductive success and expansion of osprey population. However, osprey population in mainland France remains small and future studies should confirm or infirm these preliminary results.

Values of 5 metals measured in ospreys are presented in Table 1. Mean mercury concentration reached 3.4 mg/kg ww, with very important variations between individuals (range < d.l.−16.3 mg/kg ww, see Table 1). Individual and mean values are higher than those observed in previous studies on osprey tissue in Europe, Canada or US (DesGranges et al. 1998; Rattner et al. 2008). Mercury concentrations of 10 samples (59%, see Table 1) reached or were above thresholds associated with toxicological consequences (e.g. adverse reproduction) in literature (Hughes et al. 1997). In spite of population recovery observed in France and Europe, direct effects of mercury contamination (including direct mortality) should not be excluded. A significant increase of mercury concentrations between juvenile and subadult or adult ospreys, and a significant decrease between subadult and adult ospreys were observed ($p < 0.05$, see Table 1). Total size of the sample in this study remained low for a fine age-dependant evaluation, but results could be related to mercury dynamic in feathers. Indeed, feathers growing of nestling, as well as adult successive moults have been documented as an efficient mercury elimination pathway (Hughes et al. 1997; DesGranges et al. 1998; Anderson et al. 2008). High values observed for subadults could then be related to mercury accumulation in tissues after the end of transfer towards feathers when plumage is fully grown. Decrease of mercury concentrations of adults when compared to subadults could be related to mercury elimination during successive moults. This would confirm postfledging and juvenile risks suggested by DesGranges et al. (1998), especially in highly contaminated environments. Lead was detected in 7 samples (see Table 1). Mean lead concentrations in liver reached 0.2 mg/kg dry weight (dw), with important variations between individuals (range < d.l.−1.2 mg/kg dw, see Table 1). Lead values of this study were higher than those found by Rattner et al. (2008) in blood of nestling ospreys, where lead was apparently eliminated in feathers, but much lower than reported by (Henny et al. 1991) from osprey nestlings living in a contaminated area. Following these authors, measured values of lead in ospreys of this study should not be a threat for species conservation. Cadmium was also detected in 7 ospreys during this study. Maximum cadmium concentrations in liver reached 8.7 mg/kg dw (see Table 1). Cd values of this study were higher than reported in previous studies, where Cd concentrations were often below detection limits (Henny et al. 1991; Anderson et al. 2008; Rattner et al. 2008). Nevertheless, following previously cited authors, Cd concentrations measured in this study do not seem to affect individual survival or population conservation. Measured copper concentrations in livers showed important individual variations, but most measured concentrations were low (see Table 1). 3 ospreys were heavily contaminated with copper, with liver concentrations of 38.8, 42.1 and 134.7 mg/kg dw, respectively. These values are much higher than noted in recent studies concerning ospreys (Rattner et al. 2008). Arsenic was quantifiable in only two samples, with quite lower concentrations (0.1 and 0.2 mg/kg dw, see Table 1) than those reported by Rattner et al. (2008). The size of the sample did not allow any statistical approach concerning lead, cadmium, copper or arsenic contamination with osprey age, sex or origin.

Acknowledgments Authors wish to thank the osprey sampling network members (see text), D. Vey of VetAgro Sup Toxicology unit. This study was financially supported by: European Commission (FEDER), Etablissement Public Loire, Plan Loire Grandeur Nature, VetAgro Sup, MEEDDM, DREAL Centre, ONF, and Ville d'Orléans.

References

Anderson DW, Suchanek TH, Eagles-Smith CA, Cahill TM Jr (2008) Mercury residues and productivity in osprey and grebes from a mine-dominated ecosystem. Ecol Appl 18:227–238

Chu S, Henny CJ, Kaiser JL, Drouillard KG, Haffner GD, Letcher RJ (2007) Dacthal and chlorophenoxy herbicides and chlorothalonil fungicide in eggs of osprey (*Pandion haliaetus*) from the

Duwamish-Lake Washington-Puget Sound area of Washington State, USA. Environ Pollut 145:374–381

Dennis R (2008) A life of ospreys. Whittles Publishing, Dunbeath, Scotland

DesGranges JL, Rodrigue J, Tardif B, Laperle M (1998) Mercury accumulation and Biomagnification in Ospreys (*Pandion haliaetus*) in the James Bay and Hudson Bay Regions of Quebec. Arch Environ Contam Toxicol 35:330–341

Grove R, Henny C, Kaiser J (2009) Ospreys: worldwide sentinel species for assessing and monitoring environmental contamination in rivers, lakes, reservoirs, and estuaries. J Toxicol Environ Health Part B Crit Rev 12:25–44

Henny CJ, Blus LJ, Hoffman DJ, Grove RA, Hatfield JS (1991) Lead accumulation and Osprey production near a mining site on the Coeur d'Alene River, Idaho. Arch Environ Contam Toxicol 21: 415–424

Henny CJ, Kaiser JL, Grove RA, Bentley R, Elliott JE (2003) Biomagnification factors (fish to osprey eggs from Willamette, River, Oregon, USA) for PCDDs, PCDFs, PCBs and OC pesticides. Environ Monit Assess 84:275–315

Henny CJ, Grove RA, Kaiser JL (2008) Osprey distribution, abundance, reproductive success and contaminant burdens along lower Columbia River, 1997/1988 versus 2004. Arch Environ Contam Toxicol 54:525–534

Hughes KD, Ewins PJ, Clark KE (1997) A comparison of mercury levels in feathers and eggs of OSPREY (*Pandion haliaetus*) in the North American Great Lakes. Arch Environ Contam Toxicol 33:441–452

Lemarchand C, Rosoux R, Berny P (2010) Organochlorine pesticides, PCBs heavy metals and anticoagulant rodenticides in tissues of Eurasian otters (*Lutra lutra*) from upper Loire River catchment (France). Chemosphere 80:1120–1124

Nadal R, Tariel Y (2008) Plan national de restauration du Balbuzard pêcheur 2008–2012. Ligue pour la Protection des Oiseaux—Birdlife France—MEEDDM

Rattner BA, Golden NH, Toschik PC, McGowan PC, Custer TW (2008) Concentrations of metals in blood and feathers of nestling ospreys (*Pandion haliaetus*) in Chesapeake and Delaware bays. Arch Environ Contam Toxicol 54:114–122

Toschik PC, Rattner BA, McGowan PC, Christman MC, Carter DB, Hale RC, Matson CW, Ottinger MA (2005) Effects of contaminant exposure on reproductive success of osprey (*Pandion haliaetus*) nesting in Delaware River and Bay, USA. Environ Toxicol Chem 24:617–628

Weber M, Schmidt D, Hädrich J (2003) Chlororganische rückstände in eiern des fischadlers *(Pandion haliaetus)* aus Deutschland. J Ornithol 144:45–58