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TEMPORAL TRENDS OF POLYCHLORINATED BIPHENYLS, ORGANOCHLORINE PESTICIDES AND POLYBROMINATED DIPHENYL ETHERS IN OSPREY EGGS IN SWEDEN OVER THE YEARS 1966 – 2013

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Introduction

Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) are three groups of persistent organic compounds, all with different chemical structure and applications. PCBs were extensively used as plasticizers, in electrical transformers and as additives to paints and lubricants since 1930s to mid-1970s [1]. OCPs, such as dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB) and chlordanes, were mostly used in agriculture or disease control. DDT is still in use in some parts of the world [2]. Moreover, PBDEs have been used mainly as flame retardants since the 1960s. Due to the toxic effects observed for PCBs, OCPs [3] and some brominated flame retardants (BFRs), in particular PBDE [4], these compounds have been banned and are now regulated by the Stockholm Convention [5, 6].

POPs accumulate in biological tissues and their concentrations increase when moving up the food chain [8, 9]. Osprey (Pandion haliaetus) is a fish eating raptor having a nearly worldwide distribution, living by the coast, lakes, along large rivers or other habitats with enough prey. Sweden was estimated as one of the countries with the largest populations of osprey within Europe [7]. Normally ospreys occupy high trophic levels and accumulate relatively high concentrations of persistent organic pollutants. Consequently, ospreys suffered a decline related to exposure to DDT and other pesticides [10, 11]. The relation between nesting success and DDT residues in the eggs of osprey was discussed [12, 13] with the focus on eggshell thinning and effects of chlorinated hydrocarbon and mercury pollutants. Thus, ospreys can be used as an indicator on environmental health and exposure to POPs in Sweden. Currently there is limited information on the POPs exposure to ospreys in Sweden [14] or even in Northern Europe.

The aim of this study was to investigate the patterns and temporal trends of PCBs, OCPs and PBDEs in osprey eggs collected in Sweden over five decades.

Materials and methods

Samples

Unhatched (dead) eggs from osprey (Pandion haliaetus) have been collected since 1970s to mid-2013. Approximately 3 grams of each egg was homogenized for chemical analyses while the rest is stored frozen in the Swedish Environmental Specimen Bank, at Swedish Museum of Natural History for future studies. A certified reference material (CRM) (Wellington Laboratories Ontario, Canada), freeze-dried fish (Oncorhynchus tshawytscha) was used for quality control. The samples were stored in amber glass bottles at −20°C before extraction and analysis.

Chemicals

PCBs congeners (PCB#28, #52, #74, #66, #101, #99, #110, #118, # 105, #153, #138, #128, #167, #156, #187, #180, #170, #189, #194, #206, #209) were supplied from Cambridge Isotope Laboratories (Tewksbury, MA, United States). The native OCPs (HCB, trans-Nonachlor, cis-Heptachlorepoxide, trans-Chlordane, cis-Chlordane, o,p'-DDE, p,p'-DDE, p,p'-DDD, p,p'-DDT) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A 13C-labeled internal standard mixture consisted of the following 12 PCBs; #70, #101, #105, #118, #138, #153, #156, #170, #180, #194, #206 and #209, was used as the internal standard for PCBs and OCPs. A dilution stock (13C-labled PCB #81, #114 and #178) was used as recovery standards. While the PBDEs analytes and standards (BDE#47, #100, #99, #154, #153, #183) were purchased from Wellington Laboratories (Ontario, Canada). A 13C-labeled solution containing BDE#28, 47, 99, 100, 153, 154, 183 and 209 was used as internal quantification standards for PBDEs, 13C-labeled PBDE#77 and #138 were used as recovery standard.

Gas chromatography/mass spectrometry

An Agilent 7890A gas chromatograph (Agilent Technologies, Atlanta, GA, USA) was coupled to an Agilent 5975C inert MSD mass spectrometer (Agilent Technologies, Atlanta, GA, USA) equipped with an electron ionization source was used for the analysis of PCBs and OCPs.
PBDEs were analyzed on a high resolution mass spectrometer (GC/HRMS). Experiments were performed on a Micromass AutoSpec Ultima (Waters Corporation, UK) operating at >10,000 resolving power using EI ionization at 35 eV.
Stable isotope ratio mass spectrometry
Stable isotopes of carbon and nitrogen were analyzed using an EuroEA3024 elemental analyzer (Eurovector, Milan, Italy) coupled on line to an Isoprime isotope-ratio mass spectrometer (VGInstruments, Manchester, UK).

Results and discussion:
Results
All twelve PCBs were detected in the samples. The concentrations of all the individual PCB congeners ranged from 0.00 010 to 3.2 ng/g wet weight, while the sum of 7 indicator PCBs (PCB#28, 52, 101, 105, 118, 153, 180) ranged from 0.078 to 8.1 ng/g ww, median 1.0 ng/g ww. The most abundant congener was PCB#153 (28-43% of ∑7PCB), followed by PCB#180 (15-39% of ∑7PCB). The highest concentration of lower substituted (Cl<5) PCBs was found in a sample collected from southern Sweden (Lessebo) in 1966. But for higher Cl substituted PCBs, the highest concentrations were detected in the samples collected from the west coast of Sweden in 1978.
Among all the OCPs, the detection rates of HCB, trans-Nonachlor, cis-Heptachlorepoxide, trans-Chlordane, cis-Chlordane, o,p'-DDE , p,p'-DDE, p,p'-DDD were 100% in the samples analysed. The cis-Heptachlorepoxide and p,p'-DDT were found in approximately 50% of the samples. The most prominant compound was p,p'-DDE, ranging from 39 to 31000 ng/g ww (median 540 ng/g ww), followed by p,p'-DDD (between 1.5 and 2100 ng/g ww, median 25 ng/g ww). The sample collected in southern Sweden (Lessebo) in 1966 showed the highest concentrations for most of the OCPs, but o,p'-DDE and p,p'-DDD were found in highest concentrations in the sample from central Sweden within the same year 1966. The highest concentration of p,p'-DDT was detected in the sample from the west coast of Sweden in 1978.
All the PBDEs were detected in each sample, except BDE#183 having a 49% detection rate. The most abundant congener was BDE#47, ranging from 0.31 to 190 ng/g ww, median 16 ng/g ww, followed by BDE#100 and BDE#154. The contribution of BDE#47 to ∑PBDEs was between 50% and 82%. The highest concentration levels of PBDEs were detected in southern Sweden (Helgasjön) in the year of 2002.
Correlation of compounds
Principal component analysis (PCA) was performed on the data set to further study the correlation of the compounds and other variables (stable isotope ratios, sample location and sampling year). The values of the two first components added up to 66% of the total variance. As can be seen in Figure 1, the chlorinated compounds show different patterns compared to the PBDEs. The sum ∑7PCB, ∑4Chlordane and ∑7PBDE correlated with their individual congeners, respectively. p,p'-DDT, cis-Heptachlorepoxide and BDE#183 are separate from the other compounds, this may be due to the low level and low detection rate in the samples. There were no connections between sampling year and other variables. Stable isotope ratios could be used to evaluate the dietary patterns of the ospreys and the trophic levels among different animal species. Within this data set, PCB#209, cis-Heptachlorepoxide and p,p'-DDT were related with the dietary δ13. However no significant correlations could be found between the trophic level δ15N and the compounds.
Spearman's rank analysis was used to assess the correlation between individual compounds. Strong correlations were observed between PCBs, HCB and OCPs (o,p-DDE, p,p'-DDE and p,p'-DDD), but not for the rest of OCPs. Cis-Chlordane was correlated with trans-Nonachlor, cis-Heptachlorepoxide and trans-Chlordane. Trans-Chlordane was correlated with trans-Nonachlor, cis-Heptachlorepoxide and Cis-Chlordane. Correlation was also found between p,p'-DDT and three OCPs, Cis-Chlordane, trans-Nonachlor and cis-Heptachlorepoxide. Between individual PBDEs only week correlations were found and no correlation was found between PBDEs and the chlorinated compounds.
Temporal trends of POPs in osprey eggs
The POPs were divided into five groups to investigate the temporal trends in osprey eggs. PCBs, DDX (o,p-DDE, p,p'-DDE and p,p'-DDD and p,p'-DDT), Chlordanes (trans-Nonachlor, cis-Heptachlorepoxide, trans-Chlordane and cis-Chlordane), HCB and PBDEs, as illustrated in Figure 2.
During the whole monitoring period, median concentrations of ∑4DDX decreased with a higher rate than other chlorinated compounds in osprey eggs from the year 1966 to 2013. PCBs and other OCPs

showed similiar temporal trends with DDX. However ∑7PBDE increased 21 fold from the year 1966 to 1978. PBDEs showed an increasing trend until 2002. After 2002 the concentrations started decreasing.

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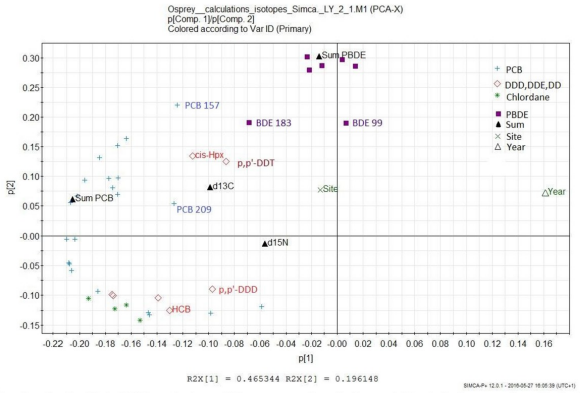

Figure 1. Loading Scatter Plot of PCA analysis on all the compounds and other variables including sampling site, isotope ratio as well as year.

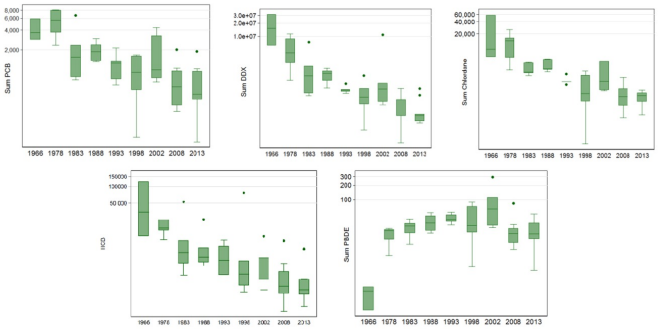

Figure 2. Temporal trends of Sum $\sum_7$PCB, $\sum_4$Chlordane, HCB and $\sum_7$PBDE in osprey eggs. Boxes display median, 2nd quartile, and 3rd quartile. Whiskers display minimum and maximum values, outliers defined as >1.5 interquartile range excluded. Y-axis is in logarithmic scale.