TEMPORAL TRENDS OF PCBs, DDE, POLYBROMINATED BIPHENYL ETHERS (PBDEs), HBCDD AND PERFLUORINATED ALKYL ACIDS (PFAAs) IN OTTERS (*LUTRA LUTRA*) IN SWEDEN WITH A FOCUS ON TRANSFER FROM MOTHER TO CUB

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Introduction

Otters (*Lutra lutra*) can be used as indicator species for water quality. The population in Sweden as well as in large parts of Europe decreased between the 1950s-1980s, probably due to elevated concentrations of PCBs[1]. Now that PCBs have been banned for more than 4 decades, we wanted to compare the temporal trends and concentrations of PCBs in otters with other contaminants, such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and perfluorinated alkyl acids (PFAAs). Several of the PBDEs have been found in increasing concentrations in fish from the Swedish environment up to the end of 1990s when the concentrations started to decrease[2], and similar trends have been seen for PFAAs in other parts of the world[3]. Also, we studied possible transfer of these contaminants from mother to suckling cubs.

Materials and methods

Muscle from 66 otters, found dead between 1983 and 2012, were analyzed for five PBDEs (BDE-47, -99, -100, -153 and -154) and 64 of them were analyzed for HBCDD. Also, muscle from 138 otters collected between 1968 and 2010 were analyzed for total-PCB and p,p'-DDE, and finally, liver from 99 otters collected between 1972 and 2011 were analyzed for PFAAs (PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxS and PFOS). Most of the otters were either killed in traffic accidents or drowned in fishing gear and all of them originated from southern Sweden. Total-PCB, p,p'-DDE, the PBDEs and HBCDD were analyzed in muscle and results are presented on a lipid weight basis (l.w.). The PFAAs were analyzed in liver and results are presented on a wet weight basis (w.w.). Parts of this material has been published before, including the analytical methods for the different chemicals.[1,2,4,5,6]

Also, an additional twelve otters were chemically analyzed for the PCBs, p,p'-DDE and PBDEs as well as hexachlorobenzene (HCB), and alpha-, beta- and gamma-hexachlorocyclohexane (α-HCH, β-HCH and lindane): six mothers and their suckling cubs (all killed in traffic) in order to study transfer of contaminants from mother to cub. Also, one mother and her subadult offspring were analyzed.

In this study, we wanted to investigate and compare large scale patterns and concentrations, so instead of reporting individual congeners, we have chosen to present data on total-PCB, DDE, sum of PBDEs, sum of perfluoroalkyl carboxylic acids (PFCAs, *i.e.* PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFTeDA) and PFOS.

Contaminant data was log transformed to meet assumptions for normal distribution before the statistical analyses. A log-linear regression was applied to the annual median concentrations. As an alternative to the regression a 3-point running smoother was also fitted and the significance tested by analysis of variance, where the variance explained by the smoother and by the regression is compared to the total variance[7]. In no cases was the 3-point running smoother significantly better to explain the trend than the log-linear regression.

Results and discussion

Chlorinated chemicals

Total-PCB and DDE were found in all otters, with significant annual decreases of 7.2% and 7.8% during the period from 1968 to 2010, respectively ($p<0.001$) (Figure 1). However, after approximately 2000 the concentrations have ceased to decrease. Annual decreasing rate after 2000 for total-PCB was only 0.6% and for DDE 3.8%, but none are statistically significant ($p=0.89$ and $p=0.31$, respectively).

The otter population started to increase in numbers around 1990 in Sweden but in southern Sweden it was most notably after 2000. Mean concentration for total-PCB in otters was 19.5 mg/kg l.w. in 2000-2010. Laboratory studies on several species showed reproductive failure when the animals were exposed to PCBs, for example the American mink[8,9,10]. Brunström *et al*. found reproductive impairment in mink treated with PCB at 12.5 mg/kg l.w. in muscle[8]. In 2000-2010 the majority of otters had concentrations below 12.5 mg/kg l.w. (70% of the analyzed otters) compared to only 38% in the 1990s. The decrease of PCB and sDDT in otter coincided with an increasing population[4].

In a laboratory study on mink given a combination of DDT and PCBs, it was shown that it was PCB that gave a negative effect on reproduction, and not DDT[11]. The ratio DDE/PCB in the present study on otters did not change over the study period (mean ratio=0.044 SD=0.077) ($p=0.38$), in contrast to what has been seen in fish from Sweden[1]. This ratio is more than 20 times lower compared to sDDT/PCB in pike from southern Sweden (recalculated from Nyberg 2013). It has been shown that mink, exposed to a combined dose of PCB and DDT, biomagnified PCB but not DDT[11], which is in accordance with the present study of otters.

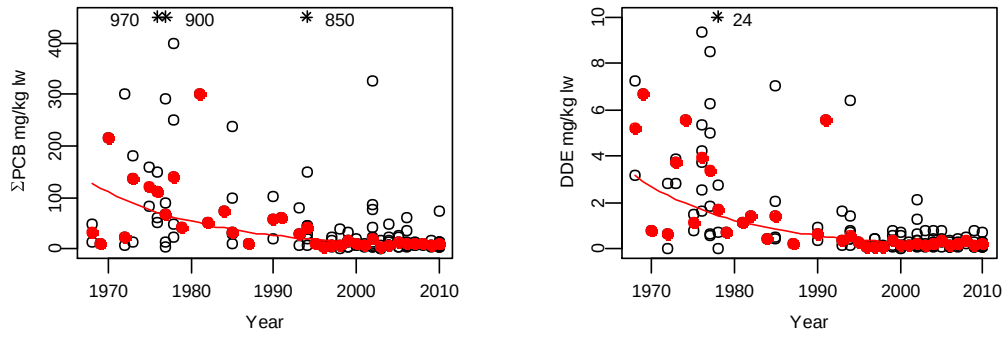

Figure 1. Total-PCB (left) and DDE (right) in otters from southern Sweden (n=138). Filled circles are annual medians and lines are log-linear regressions. Asterisks together with numbers are concentrations outside the shown range.

Brominated chemicals

Concentrations of BDE-154 were below quantification limit in 43 of 66 otters (65%), and excluded from the sum of PBDE. BDE-99 was under quantification limit in three otters and was in those cases replaced with the quantification limit for that particular analysis, divided by square root two prior to the statistical analysis. BDE-47, BDE-100 and BDE-153 were all above quantification limit in all samples.

∑PBDE decreased 10% annually during the study period ($p=0.01$) (Figure 2). Mean concentration for the period 2000 to 2010 was 0.1 mg/kg l.w. and is considerably lower compared to that of total-PCB (19.5 mg/kg l.w.), despite the fact that PCBs have been banned for more than 4 decades in Sweden.

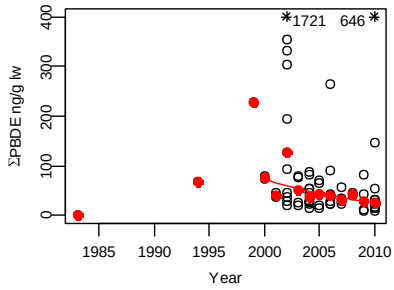

Figure 2. ∑PBDE (BDE-47, - 99, -100 and -153, n=66) in otters from southern Sweden (muscle, ng/g l.w.). Filled circles are annual medians and the line is the log-linear regression. Asterisks together with numbers are concentrations outside the range.

HBCDD was below quantification limit in 57 of 64 samples (89%) hence no temporal trend analysis was performed. However, it should be noted that it was only in samples between 2002 and 2010 that concentrations above the quantification limit were obseved (2,3-20 ng/g l.w.).

Perfluorinated alkyl acids

The PFAAs showed different trends compared to the chlorinated and brominated compounds. The ∑PFCAs increased 11.6% yearly during the whole study period ($p<0.001$) (Figure 3). The increase for many of the PFCAs was more pronounced during the last ten years, as seen in a decreased doubling time for PFOA, PFNA, PFDA, PFDoDA and PFTeDA post 2000 compared to the whole time period[6]. PFOS was the dominating PFAA. It showed an annual increase of 6.8% ($p<0.001$) since the beginning of the 1970s and was found in concentrations up to 16 003 ng/g w.w.

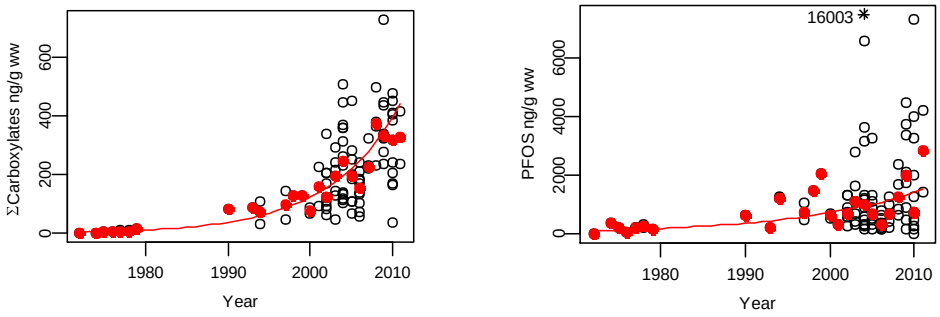

Figure 3. Left: ∑PFCAs in otters (liver, ng/g w.w.) from southern Sweden (n=99). Right: PFOS in otters (liver, ng/g w.w.) from southern Sweden. Filled circles are annual medians and lines are log-linear regressions. Asterisks together with numbers are concentrations outside the shown range. Note the different scales on the y-axis.

Transfer from mother to cub

Little is known about the effects of early life exposure to environmental contaminants, even though fetus and very young specimen usually are more susceptible to contaminants than adults. Here we analyzed 6 pairs, mother and cubs, to compare concentrations in suckling cubs with concentrations in their mother (muscle tissue). As shown in table 1, the concentration ratios cub/mother of chlorinated and brominated chemicals is above 1 in most cases. The highest ratio was found for CB-105 (82) *i.e.* the cub had 82 times higher concentration of this coplanar congener compared to its mother. However, only one pair was analyzed for CB-105. The lower chlorinated CBs (CB-28, 52, 101) showed mostly ratios close to 1. CB-118 had ratios up to 63, and other higher chlorinated CBs (CB-138+163, 153, 156 and 180) had ratios up to 56. Only one pair cub/mother was analyzed for PFAAs (pair no 5) and for no cases compounds did the ratio exceed 1[6]. The age of the cubs could not be determined accurately, it was not possible to even measure total length or weight since they were traffic killed. However, they were all small and up to approximately 3.5 months old and still dependent on their mother's milk. Two of them were smaller than the others, and they had much higher ratios (pair no 1 and 6, Table 1). The PBDEs show ratios above 1, but not as high as for the chlorinated analytes.

These high ratios raise questions on the impact of contaminants in early life. Once the cubs start eating fish the body burden decreases, probably because fish is less contaminant by the fatty soluble contaminants compared to mother's milk, in combination with dilution effects (growth). This was indicated in yet another pair killed in traffic, a mother and her subadult offspring (approximately 10 months old, indicated from size). Here, the ratios of PCBs were below 1 for all congeners, and just above one for most of the brominated compounds.

Pair no.	**1**	2	3	4	5	**6**	subadult
HCB	8.3	2.0	3.5	2.7	1.2	3.2	0,7
α-HCH	<QL	1.2	0.7	0.8	0.9	0.8	<QL
β-HCH	40	1.1	0.7	0.9	0.9	25	<QL
LINDAN	NA	1.1	0.7	0.9	0.9	0.8	<QL
CB-28	NA	1.2	0.7	0.8	0.9		<QL
CB-52	NA	1.2	0.7	0.8	0.9	0.9	<QL
CB-101	<QL	1.2	<QL	<QL	0.9	1.1	0.8
CB-105	82						
CB-118	64	7.4	6.5	9.5	5.9	11	0.4
CB-(138+163)	56	5.7	4.9	11	4.2	14	0.5
CB-153	50	6.2	5.5	9.3	4.7	13	0.5
CB-156	56	NA	NA	NA	NA	NA	NA
CB-180	32	6.1	3.7	6.5	4.7	10	0.5
p,p'-DDE	0.1	1.8	4.6	6.4	1.4	2.9	1.3
BDE-47	13	1.8	3.5	5.9	1.5	4.3	1.2
BDE-99	4.2	1.0	1.6	4.5	1.0	2.1	1.2
BDE-100	6.4	1.1	2.4	5.7	1.2	2.3	1.6
BDE-153	19	3.8	2.1	4.1	4.0	6.9	0.7
BDE-154	<QL	<QL	<QL	<QL	<QL	0.6	0.8
HBCDD	<QL	<QL	<QL	<QL	0.9	3.4	0.8

Table 1. Ratio cub/mother of concentrations of chlorinated and brominated compounds. The otter cubs were up to 3.5 months old approximately, still dependent on mother's milk. Cubs in pairs no 1 and 6 were smaller compared to cubs in pairs 2-5. Also, a subadult male and its mother were analyzed, and here the ratios were much lower. NA=not analyzed and <QL = below limit of quantification.

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