PERFLUORINATED COMPOUNDS (PFC) IN PEREGRINE FALCON EGGS FROM SOUTHWESTERN GERMANY – LEVELS, PATTERNS AND TEMPORAL CONCENTRATION VARIATIONS

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Introduction

As a top predator, the peregrine falcon (Falco peregrinus) is capable of accumulating a wide range of persistent pollutants and therefore represents a valuable object for observation and chemical analysis. In the past, peregrine falcons became almost extinct in Germany and elsewhere due to excessive burdens of organochlorine substances such as DDE[1]. Recently, poly- and perfluorinated compounds (PFCs) were identified as compounds of increasing environmental concern. They are almost irreplaceable for industry and commerce[2], but several PFCs such as perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) are persistent[5], globally distributed, toxic and partly bioaccumulative[3,4,5]. Because of these properties, wildlife samples from all around the globe were analysed to determine PFC contamination. The objective of this study was to evaluate the PFC presence in peregrine falcon eggs from Baden-Württemberg (SW Germany) as part of an existing monitoring programme.

Materials and Methods

Sampling: 20-30 eggs per year were collected from 2008-2011 by a private organization for the protection of birds (AGW, see *Acknowledgement*). Only unhatched or abandoned eggs were collected. About half of the egg samples were analysed for 11 PFCs: 4 sulfonates (PFBS, PFHxS, PFOS, PFDS,), 6 carboxylates (PFHxA, PFHpA, PFOA, PFDA, PFDoA) and perfluorooctane sulfonamide (PFOSA).

Figure 1: Peregrine Falcon (photo: Reinhard Lodzig)

An amount of 0.1-0.2 g homogenised dried sample have been extracted using ultrasonic extraction with methanol. Before extraction, a set of mass-labelled internal standard substances were applied for quantification/recoveries. The extract was evaporated and cleaned with ion exchange-SPE (STRATA XAW) followed by application of Envicarb if necessary.
Detection was performed on a Varian 1200 LC-MS/MS system. With respect to sample conditions, calculation based on dry weight (dw); for comparison to wet weight (ww), divide by 5 (cfr. Table 1) at limits of quantification of typically 0.5 ng g^{-1} dw.

Results and Discussion

The substance spectrum was clearly dominated by PFOS with mean values of 327 ng g^{-1} dw in 2008 decreasing to 208 ng g^{-1} dw in 2011. Other PFCs were present only to a minor degree with long-chain PFCs (PFDA, PFDoA) being observed at higher concentrations (1-30 ng g^{-1} dw); PFHxA, PFHpA and PFOSA were not detected.
The general pattern of PFSA and PFCA in P. falcon eggs is consistent with published findings[6]. Average PFC-concentrations (yearly mean conc. 152-330 ng g^{-1} dw) were in the same order of magnitude as other published results[6] and as those of PBDEs (annual mean 122-428 ng g^{-1} dw) in the same samples[7].

Maximum PFOS concentration observed in one of this study's eggs was 801 ng PFOS g^{-1} dw [corresponds to 163 ng g-1 ww]. This is lower than results observed for N German (550 ng g^{-1} ww) or Californian (>1000 ng g^{-1} ww) cormorant eggs[8].

		dry matter					fat content				
Year	samples n	average %	median %	rel. SD %	min %	max %	average %	median %	rel. SD %	min %	max %
2008	6	22,1	20,5	15,1%	19,1	26,6	6,7	6,7	7,8%	5,8	7,3
2009	13	19,2	18,5	11,8%	16,1	25,4	5,4	5,4	19,9%	3,3	7,1
2010	14	21,7	21,1	19,1%	17,5	34,7	7,4	7,0	33,2%	3,5	14,3
2011	8	20,8	20,0	12,5%	18,1	26,9	6,2	6,1	17,0%	4,4	8,1

		total egg mass				
Year	samples n	average g	median g	rel. SD %	min g	max g
2008	6	38,6	37,3	11,5%	35,0	46,5
2009	13	34,7	36,0	23,1%	9,0	40,2
2010	14	36,2	37,0	17,8%	18,3	46,3
2011	8	35,8	37,0	17,4%	22,2	42,3

Table 1: Sample characteristics

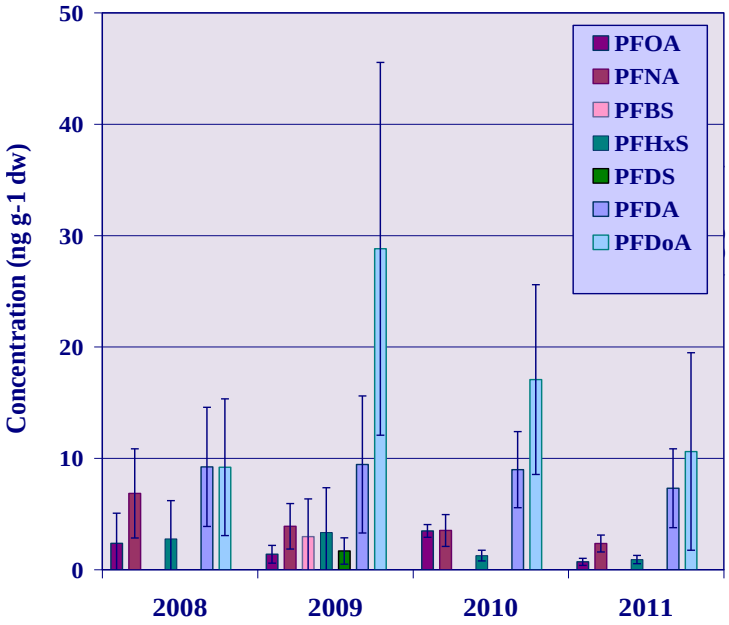

Figure 1: Mean PFC profiles over time (ng g-1 dw)

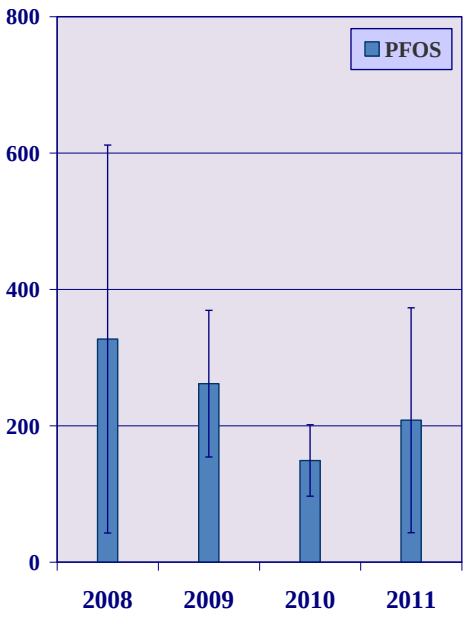

Figure 2: Mean PFOS profiles over time (ng g-1 dw)

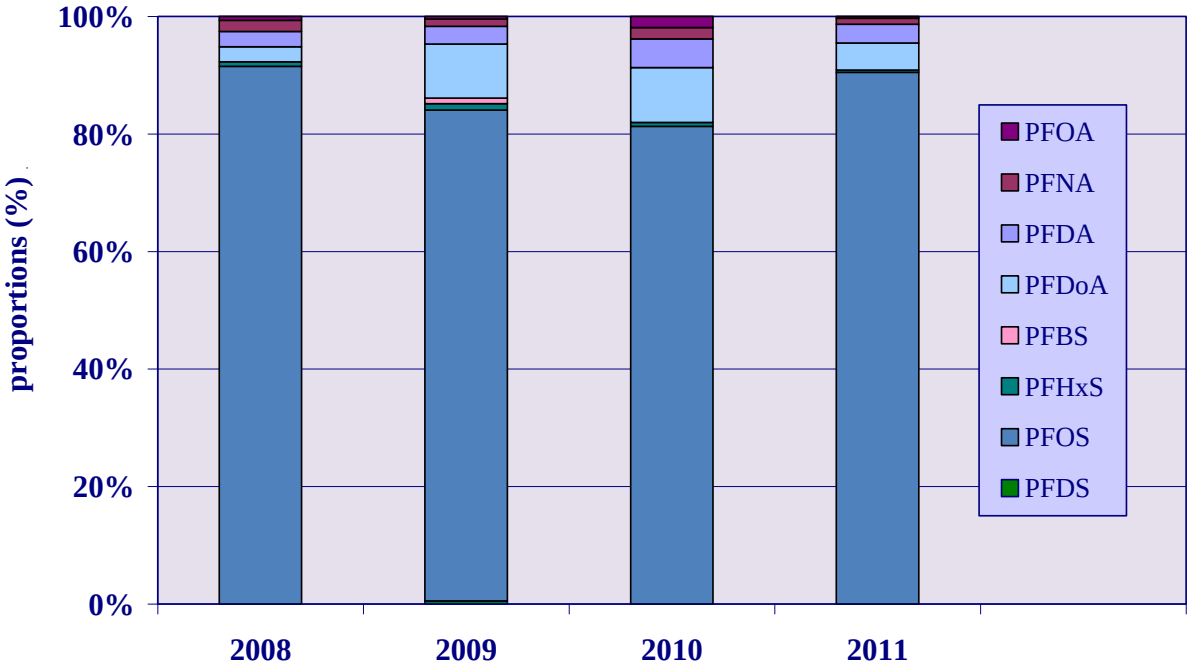

Figure 3:Mean PFC composition (%) in Peregrine Falcon eggs between 2008 and 2011

Conclusions

The PFC-contamination of peregrine falcon eggs adds more evidence to the notion that the spectrum of P. falcon egg pollutants mirrors the Stockholm POPs list. The PFOS concentration approaches the toxicity threshold (NOAEL: 500 ng g^{-1} dw) for PFOS established for chicken eggs[9]. Therefore toxicologically relevant effects for peregrine falcons cannot be excluded, given this species is similarly sensitive to PFOS effects.

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