Bull. Environ. Contam. Toxicol. (1995) 55:886–892

Environmental Contamination and Toxicology

PCB Burden and Pattern in Eggs of the Curlew (*Numenius arquata*) and the Black-Tailed Godwit (*Limosa limosa*) from Northwest Germany

E. Denker, A. Büthe

Chemisches Institut, Tierärztliche Hochschule Hannover, Bischofsholer Damm 15, Haus 123, 30173 Hannover, Federal Republic of Germany

Received: 4 March 1995/Accepted: 12 June 1995

In recent decades the number of breedingpairs of the curlew has decreased in Westfalen (North-West Germany) as well as in the whole Federal Republic of Germany caused by permanent change or destruction of the environment (Kipp 1977, Nicolai 1993, Flade 1994). The hatching success decreased because of breeding in subideal habitats like fields resulting in starvation and reduced mobility to escape predators (Kipp 1977).
In the District of Steinfurt (Westfalen, Germany), members of the „Workinggroup Wetmeadows" recognized decreasing hatching success of individually marked birds during several years. The burden of PCBs or other chlorinated compounds was hypothesized as a possible cause of this decrease.

This paper deals with the PCB burden and pattern of the two cited bird species, which have relatively low PCB levels. In spite of their similar diet and their low position in the food chain, distinct species-specific differences in PCB burden as well as in pattern occur. These differences give indications on varying enzyme-systems of these species. An important point is the intraspecific difference among the females. Furthermore none of the coplanar PCBs was found.

MATERIALS AND METHODS

In 1993 21 eggs of the curlew (*Numenius arquata*) and 9 eggs of the black-tailed godwit (*Limosa limosa*) were collected in the district of Steinfurt in North-West Germany. The eggs originate from deserted or destroyed clutches or were unfertile and collected after the other chicks had hatched.

Correspondence to: E. Denker

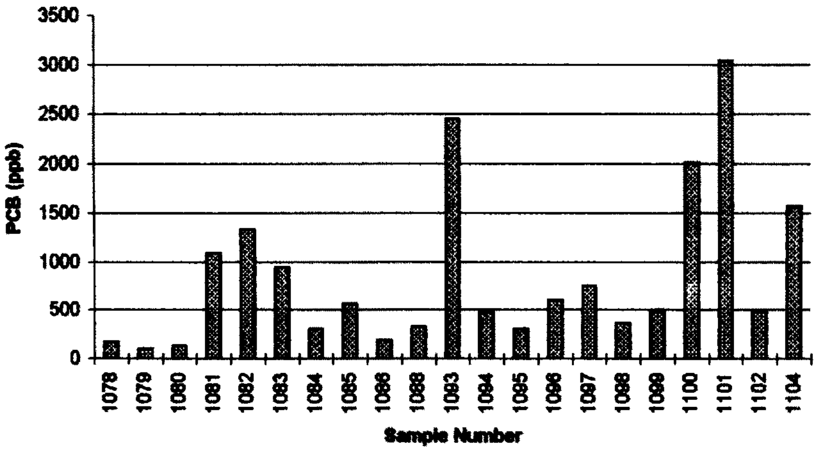

Figure 1. PCB values of the curlews' eggs

Due to this, some eggs were decayed while others contained nearly fully developed embryos. The curlew eggs originate from 13 different females; from one female each are the eggs Nos.1078-1080, 1081-1083, 1085-1086, 1094-1095 and 1097-1099. The eggs of the black-tailed godwit are from 4 females; from the same clutch are Nos.1089-1092 and 1105-1107. The eggs were stored in sample glasses and frozen at -18°C until further treatment.

The preparation of the samples was described by Heidmann (1986). The determination of the PCB congeners was carried out with a HT-5 GC column and a Finnigan MAT SSQ 710 MS; the precise method was already published (Büthe & Denker 1995). The results are given in ppb (µg/kg) fresh weight egg without shell. The single PCBs are numbered according to Ballschmitter and Zell (1980), revised by Ballschmitter et al. (1992).

RESULTS AND DISCUSSION

The sum PCB values of the eggs of the curlew vary between 99.3 and 3035 ppb (Fig.1) with a mean of 839 ppb. For the black-tailed godwits' eggs the sum PCB values vary between 30.2 and 2286 ppb (Fig.2) with a mean of 412 ppb.

For interpretation the values of the single PCB congeners were comprised in eight groups according to the degree of chlorination. The PCB pattern with reference to the degrees of chlorination is very different in the two species (Fig.3).

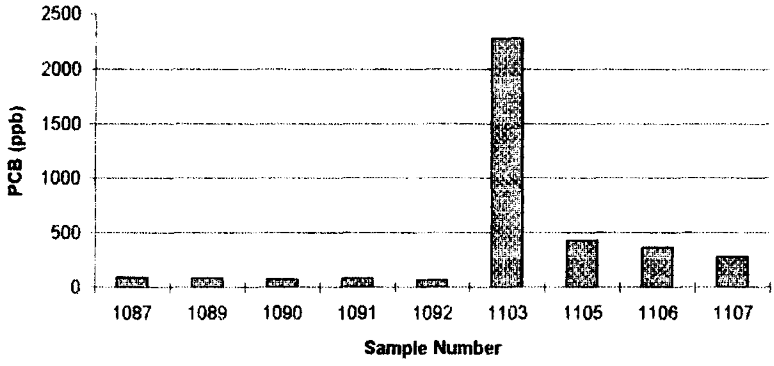

Figure 2. PCB values of the black-tailed godwits' eggs

The low chlorinated PCBs with 3 and 4 Cl as well as the high chlorinated PCBs with 7, 8, 9 or 10 Cl are in higher values in the PCB mixture of the black-tailed godwit. Only the penta- and hexa-CBs have higher values in the PCB mixture of the curlew.

The investigated populations of the curlew and the black-tailed godwit have only relatively low levels of PCBs, the levels of the godwit are distinctly lower. This result could be expected because both species are in a relatively low position in the food-chain. The diet of the two species is quite similar; both feed on worms, snails, molluscs and insects and their larvae like beetles, dragonflies or locusts. In addition the curlew feeds on small frogs and, in the autumn, berrys and seeds (Flade 1994, Glutz v. Blotzheim 1977).

Regarding these similar feeding habits of the two species with a probable similar uptake of PCB, we get an indication of a different enzyme-system, causing the godwit to metabolize PCBs more than the curlew. The mean of 412 ppb sum PCB for the godwit is very low compared to the curlew (839 ppb sum PCB) and is additionally strongly influenced by the one higher contaminated egg No.1103 (Fig.2). The aspect of a possible different uptake of PCB in the winter quarters can not be answered sufficiently. The winter quarters of the North-West German curlew populations are located mostly at the British and French coasts (Schlenker 1982). For the black-tailed godwit the same winter quarters are given (Glutz v. Blotzheim 1977), but also African coasts down to the Sahel Zone are possible (Flade 1994).

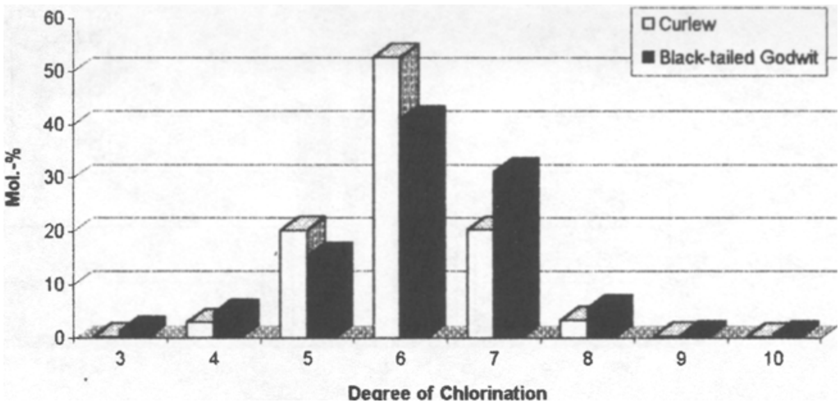

Figure 3. Comparison of the molar parts of the single degrees of chlorination

So an uptake of PCB at a higher contaminated coast can not be excluded and might be the reason for the higher contamination of the female that laid egg No.1103.
A second indication for a better metabolism of PCB through the enzyme-system of the black-tailed godwit is the PCB pattern of the two species. It is remarkable that only the values for penta- and hexa-CBs are higher in the curlews' eggs. That means a better metabolism of the penta- and hexa-CBs by the godwit and automatically a higher percentage part of the other degrees of chlorination. A point of view that supports this statement is that the penta- and hexa-CBs are the major parts of the PCBs released into the environment. These are, following two authors, 1:1 mixes of the technical PCB mixtures Clophen A60 and Aroclor 1254 (Heidmann 1986) or 2.2:1 mixes of Clophen A60 and Clophen A50 (Zell et al. 1978).

Concerning the PCB pattern, there are two higher contaminated eggs, one of each species, with conspicuous differences compared to all others. The curlew egg No.1093 (Fig.1) shows shifting to higher chlorinated PCBs: penta-CBs 4.08% (mean 20.06%), hexa-CBs 40.15% (52.65%), hepta-CBs 42.09% (20.22%), octa-CBs 11.96% (3.37%). A distinct increase of the hepta- and octa-CBs is visible.
In the godwit's egg No.1103, the only higher contaminated one, we found a distinct decrease of penta-CBs: 7.48% (mean 15.19%) and an increase of hexa-CBs: 52.17% (41.01%). Such differences from the mean may indicate a relatively new uptake of a highly chlorinated PCB mixture, a fact further indicated by

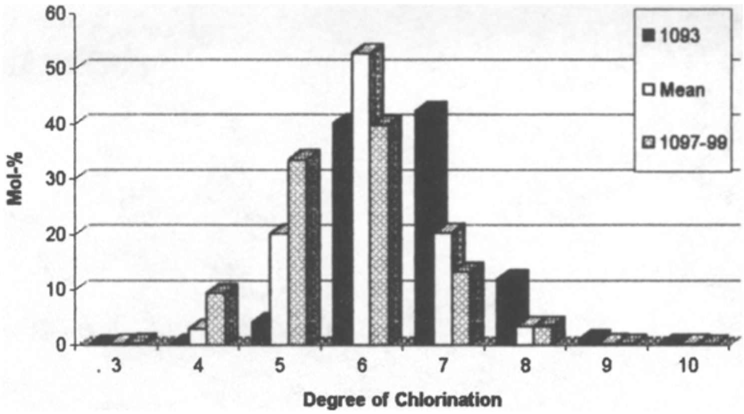

Figure 4. Comparison between PCB pattern of eggs from two single curlew females and the mean

the higher sum PCB value. A possible explanation might be deviating winter quarters of these two females on contaminated coasts.
One more reason could be a modified enzyme-system of these two birds, a point of view that is supported by the curlews eggs Nos.1097-1099 which originate all from one female and deviate in their PCB distribution also distinctly from the mean. Concerning all clutches, the interclutch differences with reference to sum PCB and PCB pattern are always higher than the intraclutch differences and can reach high deviations in the same species. Fig. 4 shows a comparison between two single females and the mean supporting our statement. This is an important point that is unfortunately mostly neglected when results are published and whose importance surely increases in highly contaminated species like predators.
In our investigation we considered also the age of the females as possible reason for differences. From six curlew females the age was known; five of them were between 13 and 16 years old, one more was at least 16 years old. The age of the other birds was unknown. No relation between age and PCB burden or pattern was visible among the eggs from known-age birds.
None of the coplanar PCBs Nos.77, 126 and 169 was found. In recent years those congeners have been intensively investigated (Harrad et al. 1992, Schwartz et al. 1993, Safe 1990), but they may not be important for species with low levels of PCBs.

Compared to samples from curlews from 1978, which were collected at the same sample sites, a decrease in PCB burden was found.

The maximum value of the 1993 samples (3035 ppb) is only slightly higher than the mean value from 1978 (*2650 ppb, n=53, unpublished data*). Though these values were determined by another method (Heidmann & Büthe in Rüssel 1986) this difference seems real.

The few other studies on species of the family Scolopacidae show also a low contamination of these birds. In eggs of the redshank (*Tringa totanus*) Denker et al. (1994) found a mean of 0.93 ppm sum PCB, which was the lowest value of all investigated 11 waterbird species. For an egg of the woodcock (*Scolopax rusticola*) Presst et al. (1970) did not find PCBs, which is surely a result of the determination method of this year, but which is an indication of low contamination of this species. Values for two further species of related bird families with similar feeding habits were published. Beyerbach et al. (1988) found values between 0.3 and 0.468 ppm sum PCB for the lapwing (*Vanellus vanellus*). Nipkow (1989) gave a value of 3.8 ppm egg/dry weight for the stone curlew (*Burhinus oedicnemus*) with a conversion factor of 5, so that a value of 0.95 ppm fresh weight is calculated.

Acknowledgments. Our study was supported by the District of Steinfurt. We thank R. Tüllinghoff, M. Kipp and C. Kipp from the „Workinggroup Wetmeadows" for the collection of the samples and I. Denker for revising the manuscript.

REFERENCES

Ballschmitter, K., Zell, M. (1980) Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography-composition of technical Aroclor- and Clophen-PCB mixtures. Fres Z Anal Chem 302: 20-31.

Ballschmitter, K., Bacher, R., Mennel, A., Fischer, R., Riehle, U., Swerev, M. (1992) The determination of chlorinated biphenyls, chlorinated dibenzodioxins and chlorinated dibenzofurans by GC-MS. J High Res Chromatogr 15: 260-270.

Beyerbach, M., Büthe, A., Heidmann, W.A., Knüwer, H., Rüssel-Sinn, H.A. (1988) Belastung des Kiebitzes (*Vanellus vanellus*) mit Dieldrin und anderen chlorierten Kohlenwasserstoffen. J Orn 129: 353-361.

Büthe, A., Denker, E. (1995) Qualitative and quantitative determination of PCB congeners by using a HT-5 GC column and an efficient quadrupole MS. Chemosph Vol.30, No.4, 753-771.

Denker, E., Becker, P.H., Beyerbach, M., Büthe, A., Heidmann, W.A., Staats de Yanes, G. (1994) Concentrations and metabolism of PCBs in eggs of waterbirds on the German North Sea coast. Bull Environm Contam Toxicol 52: 220-225.

Flade, M. (1994) Die Brutvogelgemeinschaften Mittel- und Norddeutschlands, IHW Verlag.

Glutz v. Blotzheim (1977) Handbuch der Vögel Mitteleuropas, Band 7: Charadriiformes 2.Teil, Aula Verlag Wiesbaden.

Harrad, S.J. Sewart, A.S., Boumphrey, R., Duarte-Davidson, R., Jones, K.C. (1992) A method for the determination of PCB congeners 77, 126 and 169 in biotic and abiotic matrices. Chemosph Vol.24, No.8: 1147-1154.

Heidmann, W.A. (1986) Isomer specific determination of polychlorinated biphenyls in animal tissues by gas chromatography mass spectrometry. Chromatographia Vol.22, No.7-12: 363-369.

Heidmann, W.A., Büthe, A. (1986) Chlorpestizide und chlorhaltige Industriechemikalien. In: Rüssel, H.A.: Rückstandsanalytik von Wirkstoffen in tierischen Produkten. G.Thieme Verlag, Stuttg.

Kipp, M (1977) Artenschutzprojekt Brachvogel (*Numenius arquata*). Ber Deutsch Sekt Int R Vogels, Ber Nr. 17: 33-38.

Nicolai, B. (1993) Atlas der Brutvögel Ostdeutschlands. G. Fischer Verlag, Jena.

Nipkow, M. (1989) Rückstände chlororganischer Verbindungen in Gelegen des Triels (*Burhinus oedicnemus*) im Elsaß. J Orn 130: 79-82.

Presst, I., Jefferies, D.J., Moore, N.W. (1970) Polychlorinated biphenyls in wild birds in Britain and their avian toxicity. Environm Poll 1: 3-26

Safe, S. (1990) Development of toxic equivalency factors for polychlorinated biphenyls (PCBs). Short paper of Dioxin 90, E.-Sem. 2: 55-59.

Schlenker, R. (1982) Vom Zug süd- und nordwestdeutscher Brachvögel (*Numenius arquata*) nach Ringfunden. Beih Veröff Naturs Landschaftspfl Bad-Württ 25: 109-112.

Schwartz, T.R., Tillitt, D.E., Feltz, K.P., Peterman, P.H. (1993) Determination of mono and non-o,o' chlorine substituted polychlorinated biphenyls in Aroclors and environmental samples. Chemosph Vol.26, No.8: 1443-1460.

Zell, M., Neu, H.J., Ballschmitter, K. (1978) Single component analysis of polychlorinated biphenyl (PCB)- and chlorinated pesticide residues in marine fish samples. Fres Z Anal Chem 292: 97-107.