Levels of PCBs in wild bird eggs: Considering toxicity through enzyme induction potential and molecular structure


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Highlights
- The metabolic potential of the PCBs showed agreement with biodegradability.
- Phenobarbital-type inducer and metabolic group I PCBs were prevalent.
- 88% of PCB congeners measured was found in more than 80% of samples.
- PCB levels, including dioxin-like PCBs, were highest in piscivore species.
- The high prevalence of CB-138, -153 and -180 make them ideal for monitoring PCBs.

Abstract
Polychlorinated biphenyls (PCBs) were analysed in wild bird eggs from industrialised areas in South Africa. The concentration, congener profile, feeding guild, potential associated risk and biology were investigated. PCBs were detected in all eggs with 30 congeners present in more than 80% of the samples. \(34\) PCB concentrations ranged between 0.9 and 296 ng g\(^{-1}\) wet weight (ww). The metabolic potential of the PCB metabolic groups showed good agreement with the biodegradability of the individual congeners. Phenobarbital-type (PB-type) inducer PCBs were prevalent, indicating the predominance of less toxic PCB congeners. However, non-ortho PCBs which were not included in the current analyses, could affect the toxic potential of the PCBs in the eggs requiring more investigation. Although the current levels of PCBs measured do not indicate a health risk to the birds assessed, the presence of mono-ortho PCBs at appreciable levels motivates for the assessment of dioxin-like chemicals in wild bird eggs.

1. Introduction
Polychlorinated biphenyls (PCBs), apart from some natural sources, entered the environment from extensive use in industrial applications. However, due to the hydrophobicity and biological recalcitrance of PCBs concern over the possible adverse health effects and long-range transport led to restricted use and eventual banning during the 1970s (Takasuga et al., 2006). Although, PCBs are banned or controlled on a global and regional scale they are still formed as unintended industrial by-products. Additionally, legacy sources of PCBs are still present and can contribute to the current PCB loading into the environment through leaching and re-volatilisation processes (UNEP Chemicals, 1999).

PCBs exhibit congener-specific toxicity where the structural specificity of PCBs for enzyme induction is a well-recognised indicator of potential toxicity (McFarland and Clarke, 1989). The presence of vicinal H-atoms in the \textit{meta–para} position increases the susceptibility of the PCB-molecule to metabolism through enzymatic activity of the P450 system (Warner et al., 2005).

A group of microsomal cytochrome P450-dependent enzyme systems, known as mixed-function oxidase (MFO), is responsible for catalysing biotransformation processes of xenobiotics (McFarland and Clarke, 1989; Denison and Whitlock, 1995). The presence and activity of the cytochrome P450-enzymes determines an organism's ability to metabolise compounds such as PCBs and therefore influence the occurrence of these chemicals in biological tissue (Borgå et al., 2005). PCBs are metabolised via the MFO system, specifically the CYP1A and CYP2B subfamilies, which are sensitive to the level and position of chlorination (Warner et al., 2005). CYP1A metabolises PCB congeners lacking \textit{ortho-}, but containing \textit{para-} and \textit{meta}-chlorines with adjacent, unsubstituted \textit{ortho–meta...
Assignment of PCBs to different metabolic groups, inducer types and structure, as well as WHO/IPCS toxic equivalency factors (TEFs) for DL-PCBs (McFarland and Clarke, 1989; Warner et al., 2012). PCBs can therefore be characterised into three groups, each inducing a separate MFO:

1. phenobarbital-type (PB-type) PCBs, which induce P450-CYP2B1 and P450-CYP2B2, are generally less toxic and more readily excreted,
2. 3-methylcholoranthene-type PCBs (3-MC-type) are inducers of P450-CYP1A1. 3-MC-type PCBs are planar molecules with conformational hindrance at the sites for oxygen. This leads to increased stability and decreased detoxification potential, and
3. PCBs that induce both PB and 3-MC, known as mixed-type PCBs (McFarland and Clarke, 1989; Warner et al., 2012).

The most toxic PCB isomers, due to their co-planar structure, have toxic effect similar to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) (Lemieux et al., 2001), and are known as dioxin-like chemicals (DLCs). As with PCDD/Fs, coplanar PCBs bind to the aryl hydrocarbon receptor (AhR) and elicit AhR-mediated biochemical and toxic responses (Behnisch et al., 2001) in birds, Ah-mediated toxicity is suspected to cause reproductive and embryonic effects (Barron et al., 1995), including effects on the size of eggs (Fernie et al., 2000).

**Table 1** Assignment of PCBs to different metabolic groups, inducer types and structure, as well as WHO/IPCS toxic equivalency factors (TEFs) for DL-PCBs (McFarland and Clarke, 1989; Boon et al., 1997; Van den Berg et al., 1998; Borgå et al., 2005; Van den Berg et al., 2006).

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*a* As listed in the WHO/IUPAC interim toxic equivalency factors.  
*b* Dioxin-like PCB congeners.
Very little is known about the current levels of PCBs in biota from Africa, and even less in wild birds. The main aim of this study was to assess the occurrence of PCBs in wild bird eggs of various species from different trophic positions. To facilitate the study of different trophic positions, the feeding guild approach was followed. As described by Root (1967), guilds define a group of species that exploit similar environmental resources, in this case focussing on diet. The congener profiles and possible toxicological impact of PCBs in the eggs were then assessed.

2. Materials and methods

The present study was approved by the North–West University Ethics Committee (NWU-EC) (NWU-00055-07-S3) with the necessary permits obtained from provincial governmental departments (HK/P1/08760/001; CPF6 1340). Between October 2008 and January 2009, 77 wild bird eggs, representing 12 different non-migratory, non-endangered species (Table S1), were collected from four sampling areas within the Gauteng and Free State provinces (Fig. 1).

2.1. Sample collection and treatment

The study area was the Gauteng Province (Pretoria, Kempton Park and Soweto) and Vaal Triangle (Vanderbijlpark, Vaalpark and Sasolburg; Fig. 1), which constitutes the major industrial centre of South Africa. Industries include iron and steel works, electricity generation from coal, petrochemical industries, manufacturing of consumer goods, as well as the historic production of organo-chlorine pesticides (Osibanjo et al., 2002; Quinn et al., 2009). Eggs were hand-collected and wrapped in aluminium foil pre-cleaned with acetone and hexane. In the laboratory, egg contents (yolk and albumin), were homogenised with an ultrasonic homogeniser (Misonix sonicator 3000, Farmingdale, NY, USA). Eggs were homogenised individually, except for the small eggs of the Cape Turtle Dove, Cape Sparrow and Southern Masked Weaver that had to be pooled. The frozen samples and blank controls were couriered frozen to the Norwegian School of Veterinary Science (NVH) with the necessary export and import permits.

2.2. Analysis

Sample extraction and gas chromatography (GC) analysis were done in the Laboratory of Environmental Toxicology at the NVH, Norway. The egg homogenates were analysed for 34 PCBs (CB-28, -31, -47, -52, -56, -66, -74, -99, -101, 105, -110, -114, -118, -123, -128, -137, -138, -141, -149, -151, -153, -156, -157, -167, -170, -180, -183, -187, -189, -194, -196, -199,-206 and -209). The mono-ortho, dioxin-like (DL) PCBs are marked with ‘\*’. The liquid–liquid extraction and clean-up procedures were based on the method of Brevik, 1978, modified as described by Bouwman et al. (2008), Polder et al. (2008a), and Helgason et al. (2008). In short, internal standards (CB-29, -112 and -207; Cambridge Isotope laboratories Inc., Andover, MA, USA), together with 10 ml distilled water, 15 mL aceton, 20 mL cyclohexane and 2 mL NaCl (2% solution) were added to between 2 and 3 g of accurately weighed homogenised egg.

The lipid extraction was performed by ultrasonic homogenisation (4710 Series; Cole Parmer Instruments, Chicago, IL, USA) for 2 min and centrifugation (10 min at 1 643 g). The supernatant was removed and the lipid extraction was repeated with 15 mL aceton: cyclohexane (1:2). The supernatants of both extractions were combined and the volume was adjusted to 5 mL with cyclohexane in a volumetric flask. A 1 ml aliquot of the extract was used for gravimetric lipid determination. Sample extracts were treated twice with concentrated sulphuric acid (purity 96%; Scapure, Chemscan AS, Elverum, Norway) to remove lipids. The final extracts were concentrated to 0.5 mL for analysis.

A complete description of the GC analysis is given in Murvoll et al., 2006 and Polder et al. (2008b). Briefly, the separation and detection of the non-dioxin-like-PCBs (NDL-PCBs) was performed by high resolution gas chromatography (GC: Agilent 6890 Series gas chromatography system; Agilent Technologies, PA, USA) equipped with an auto sampler (Agilent 7683 Series; Agilent Technologies) and coupled to two 63Ni electron capture detectors (Agilent 6890 µ-ECD). The separation and detection of the dioxin like PCBs (DL-PCBs) was performed by GC (Agilent 6890) equipped with a SPB-5 column (60 m, 0.25 mm, i.d., 0.25 µm film, Supelco) and connected to a low resolution mass spectrometer (LR-MS, Agilent 5973N) operated in selected ion monitoring mode with negative chemical ionisation. The target ions used were: m/z 325.8 for CB-112, -123, -118, -114, -105; m/z 359.7 for CB-156, -157, -167 and m/z 395.7 for CB-189. Limits of detection (LOD) for individual compounds were defined as three times the noise level. To compensate for positive blank values of CB-209 the detection limit for this compound was increased by the mean of the blank values plus two standard deviations.

2.3. Analytical quality control

The laboratory is accredited by the Norwegian Accreditation for testing biological material of animal origin according the requirements of the NS-EN ISO/IEC 17025 (Test 137). The laboratory’s analytical quality was successfully approved through international...
inter-calibration and proficiency testing including CRL EUPT-AO 03 pesticides in chicken eggs (2009).

Each sample series included one chicken egg blank, two recovery samples (homogenised chicken eggs, spiked with recovery standards) and three solvent blanks. The repeatability of the GC was confirmed by running a standard after every ten samples while reproducibility of the method was tested through analyses of the laboratory’s in-house reference material (seal blubber).

2.4. Data analysis

Calculations were done based on five- or eight-point linear calibration curves with quantification in the linear range for each component. All concentrations are given as ng g\(^{-1}\) wet weight (ww) except for comparisons with other studies where lipid-based values were used as lipid weight (ng g\(^{-1}\) lw). To assess the influence of trophic levels, birds were divided into five trophic guilds: piscivores (fish eating birds), scavengers (opportunist feeders), omnivores, herbivores, and granivores (Table S1).

Concentrations below the LOD were assigned the value of half the LOD. Statistical analysis was done using STATISTICA (version 8) and Canoco for Windows (version 4.5). PCAs were performed to elucidate differences in pollution patterns. Log-ratio transformation was applied to the dataset prior to the PCA analysis as described in Howel (2007). In short, the log-ratio of each proportion (p) was determined by dividing each proportion by the geometric mean across the sample (Howel, 2007; Quinn et al., 2009): \(\log \left(\frac{p_j}{\bar{g}(p)}\right)\) where \(g(p) = (p_1, p_2, p_3 \ldots p_d)^{1/d}\).

3. Results and discussion

3.1. PCB congener profiles

PCBs were quantified in all eggs (Tables S2 and S3). Eleven PCB congeners (CB-52, -101, -105, -138, -153, -167, -180, -187, -194, -196, and 206) were present in all samples, 22 congeners (CB-28, -31, -47, -66, -74, -99, -110, -114, -118, -123, -128, -137, -141, -149, -151, -156, -157, -170, -183, -189, and -199 and -209) in greater than 70–80% of samples, while CB-56 was quantified in only 19%.

The dominant congeners in all species were CB-138 (group II), -153 (group III), and -180 (group III), together contributing 25–75% of 34PCB. This pattern has been seen in many biological matrices including bird tissues worldwide (Boumphrey et al., 1996; Mora, 1996; Humphrey et al., 2000; Dip et al., 2003). The relatively higher levels of these congeners are usually attributed to their recalcitrant and bioaccumulative nature in the environment, as well as their low metabolic degradation potential (McFarland and Clarke, 1989; Borgå et al., 2005; Antoniadou et al., 2007; Luo et al., 2009).

Median PCBs values ranged between 0.92 and 300 ng g\(^{-1}\) ww. The White-breasted Cormorant had the highest concentration (415 ng g\(^{-1}\) ww), followed by the African Darter (250 ng g\(^{-1}\) ww). A higher concentration in piscivores was expected due to bioaccumulation in higher trophic levels (Zimmerman et al., 1997).

Although the industrial uses of PCBs have been phased out since the 1970s, PCBs remain ubiquitous in almost all environmental compartments. In general, it is assumed that levels that are skewed to higher chlorinated PCB congeners are linked to historic applications, whereas the presence of lower chlorinated PCB congeners are more likely from recent or current releases (Breivik et al., 2002). Therefore, the presence of measurable levels of almost all PCB-congeners indicates the presence of current sources in the areas that were sampled. Because of their high prevalence and persistence, PCB-138, -153 and -180 are ideal PCB congeners for monitoring purposes in wild life from South Africa.

3.2. PCA analysis to investigate the distribution of PCB congeners

In the PCA-biplot (Fig. 2A; factor scores and loadings given in supplementary data Table S4), Factor 1 explained 32% of the variance and was mainly a contrast between the higher chlorinated (CB-138, -153, -156, -157, -170, -180, and -183), with negative scores, and the lower chlorinated PCBs (CB-47, -52, -56, -101, and -110) with positive scores. Piscivores were associated with higher chlorinated PCBs, while insectivores/omnivores and granivores were associated with lower chlorinated PCBs. Birds on a higher trophic level would be expected to have higher chlorinated PCBs (Ólafsdóttir et al., 2001) since lower chlorinated PCBs are more readily metabolised and higher PCBs are more likely to be transferred from prey to predators (Antoniadou et al., 2007). Lower chlorinated PCBs are predominant in non-point source areas through deposition on vegetation and soil (Konstantinou et al., 2000), where granivores, and insectivores are exposed to these congeners.

For further data analysis, PCBs were divided into eight groups according to level of chlorination (Table 1; tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca- PCB). There was a statistically significant difference between species, feeding guilds, and habitats (one-way ANOVA; p < 0.05; Fig. 2B). As with previous studies concerning wild bird eggs, hexa-PCB (28–71%) and hepta-PCB (9–32%) were predominant, likely due to their high persistence (Luo et al., 2009). The order of PCB abundance that followed hexa-PCB differed between species. The resistance of PCBs to degradation increases with higher chlorination. However, the extent to which PCBs are metabolised seems to be species-specific (Henry and De Vito, 2003).

There was an increase in PCB concentrations with higher trophic level. Piscivores had the highest levels, followed by scavengers and insectivores/omnivores (Fig. 2B). Due to the physicochemical nature of PCBs, birds will accumulate PCBs from their environment that in turn leads to biomagnification with higher concentrations in higher trophic levels (Warner et al., 2005).

Factor 2 (Fig. 2A) explained 22% of the variance in the data and was a contrast between the less metabolically active group I PCBs with negative scores (PCB-189, -194, -196, -199, -206, and -209) against the more metabolically active group III PCBs which are more readily degraded through CYP 1A enzyme linked reactions (PCB-28, -31, -66, -74, -99, -105, and -123) with positive scores (Borgå et al., 2005). The Southern Masked Weavers and Red-knobbed Coots with positive loadings were separated from the Ardea spp. (Black-headed and Grey Heron) with negative loadings on the second axes of the PCA-biplot. This indicates that the Ardea spp. eggs contained more persistent PCB congeners when compared to Southern Masked Weaver and Red-knobbed Coot.

3.3. Metabolic and MFO-induction

Metabolic groups as well as PB-type, mixed type inducers (Table 1) and DL-PCBs differed significantly between species, guild and feeding habitat types (one-way ANOVA log transformed data, p < 0.05). Group I PCBs were predominant in all eggs with the exception of the Red-knobbed Coot where Group III PCBs were dominant (Fig. 3). In most species, the concentrations of Group V and IV in eggs were negligible compared with Groups I, II and III (Fig. 3). In addition, levels of group V and IV PCBs did not differ significantly between species (one-way ANOVA, p > 0.05). The significant difference in the concentration of the various metabolic groups was likely due to differences in trophic level, diet, as well as species specific responses to the individual congeners (Antoniadou et al., 2007).

PB-type, PCBs that induce P450-CYP2B and are generally less toxic and more readily excreted, were predominant in all species.
PB inducible enzymes catalyse the biotransformation of PCBs by inserting oxygen into the molecule (McFarland and Clarke, 1989) and are classified as less toxic. In general, there were higher levels of mixed-type inducers as well as DL-PCBs in piscivores and...
scavengers, indicating increased potential risk to these bird species (Fig. 3).

3.4. Comparisons

In general, PCB concentrations in wild bird eggs studied were lower than that in reviewed literature (Table 2). Concentrations here were comparable with those reported by Bouwman et al. (2008). Concentrations in eggs of piscivore species were approximately half of those measured in the European Shag from Norway (2008). Concentrations in eggs of piscivore species were approximately half of those measured in the European Shag from Norway (2008). Concentrations in eggs of piscivore species were approximately half of those measured in the European Shag from Norway (2008). Concentrations in eggs of piscivore species were approximately half of those measured in the European Shag from Norway (2008).
range or order of magnitude as the present study. Levels in insec-
tivores were in the same range as those measured in the Kentish
Plover from China (Gao et al., 2009), but between 3% and 53% lower
than all other literature reviewed. For the scavengers, levels were
in the same range as the Mediterranean Gull from Belgium (Dauwe
et al., 2009), but 3–10% less than in other studies.

3.5. Toxicity assessment

Although PCBs were one of the first chemical classes directly
linked to decreases in wildlife populations (Jensen, 1966), there is still a lack of data on the relative importance of non-dioxin like
PCBs in wild bird populations (Henry and De Vito, 2003). Reproductive failures have been linked to PCBs concentration of
1.6–10 μg g⁻¹ ww in cormorant and heron species (Antoniadou et al., 2007). Decreased hatching success has been reported at
concentrations of 1–25 μg g⁻¹ ww for chickens, cormorants, and
eagles (Brustrøm and Halldin, 2000). Mortality in birds has been
associated with concentrations of 90 and 470 μg g⁻¹ 1 ww
(Guruge et al., 1997).

The “no observed effects level” (NOEL) of 4 μg g⁻¹ 1 ww in eggs as
proposed by Brustrøm and Halldin (2000), was used to assess the
risk of PCBs in the current study. In the present study, the highest
34PCB concentration was in a White-Breasted Cormorant egg
(290 ng g⁻¹, Table S7), 13 times lower than the NOEL, indicating
low risk of reproductive failure or mortality from the current level
of PCBs. Birds with increased levels of PCBs have been linked with
behavioural (hatching and rearing) impairment (Bustnes et al.,
2001), altered hormone function and increased stress responses
(Fry, 1995; Dawson, 2000). These effects all indicate possible neg-
ative health effects on wild birds exposed to PCBs. However since
these effects are at a sub-lethal level they cannot easily be quanti-
fied, an aspect that needs urgent research in African conditions.

4. Conclusions and recommendations

All species had quantifiable levels of PCBs, with 88% of the con-
geners measured being found in more than 80% of samples. PCB lev-
els were highest in piscivore species that also had the highest
percentage of DL-PCBs. Metabolic group I PCBs were more prevalent, likely due to resistance to degradation, whereas the
more biodegradable group IV and V PCBs were present in low
levels. The PB-type inducer PCBs were more prevalent than mixed-type PCBs, indicating a prevalence of less toxic PCBs in wild
bird eggs. Higher chlorinated congeners were more prevalent in
higher trophic levels while lower chlorinated congeners were
associated with lower trophic levels.

The high prevalence of CB-138, -153 and -180 found in this
study make them ideal candidates for monitoring PCBs in the
South African environment specifically. The difference between
the higher and lower chlorinated PCBs according to trophic posi-
tion, requires further research. The presence of mono-ortho PCBs
at appreciable levels motivates for the continued assessment of di-
oxin-like chemicals in wild bird eggs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in
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