TEMPORAL TREND OF ORGANOCHLORINE PESTICIDES IN AUSTRALIA

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Introduction

Persistent, lipophilic organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), dieldrin, chlordanes, hexachlorobenzene (HCB) and mirex are known to accumulate in human samples [1, 2]. Persistent OCPs are among the chemicals that are covered under the Stockholm Convention on persistent organic pollutants [3]. Exceptions to this include relatively less lipophillic compounds like HCH ($K_{OW}<10^5$). In Australia, OCPs such as DDT and HCHs were introduced in the 1940s. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Mirex, however, remained in very restricted use in Northern Australia for treatment of one species of termites (the Giant Termite (*Mastotermes darwinensis*)) but this use was phased out in 2007.

OCPs have been monitored in numerous countries, however a review of monitoring data on OCPs internationally has reported knowledge gaps including the interplay of age, gender as well as period and cohort effects [4]. The most recent OCP monitoring in Australia from 2002/03 found the highest concentrations of p,p'-DDE (mean ± standard deviation; median concentration 311 ± 174; 279 ng g^{-1} lipid) followed by β-HCH (80 ± 173; 21 ng g^{-1} lipid). Other OCPs consistently detected included dieldrin, HCB, transnonachlor and p,p'-DDT. The results of this study provided valuable monitoring data and showed following a substantial decline of OCP concentrations from the early 1980s to the 1990s the levels have plateaued.. As human milk samples were used, only females of child-bearing age (15-45years) were included and no assessment of age or gender trends could be made.

This study aimed to expand our assessment of human body burden of OCPs in the Australian population. The specific aims of this study were to use samples representative of the Australian population to:

- Assess age and gender differences in the concentration of OCPs in human blood sera
- Investigate temporal trends by comparing results from samples collected in 2002/03, 2006/07 and 2008/09
- Compare findings with other Australian and international data.

Materials and methods

Pooled samples of human blood serum from males and females collected in South East Queensland, Australia in 2002/03, 2006/07 and 2008/09 were used for determination of OCPs in human blood serum. This provided us with robust serum data from three time points over the past 7 years. All samples were obtained in collaboration with Sullivan Nicolaides Pathology from de-identified surplus pathology samples. Stratification criteria included age and gender as follows: cord blood; 0 – 0.5; 0.6 – 1; 1.1 – 1.5; 1.6 – 2; 2.1 – 2.5; 2.6 – 3; 3.1 – 3.5; 3.6 – 4; 4.1 – 6; 6.1 – 9; 9.1 – 12; 12.1 – 15 (06/07 samples only); 0-4 (08/09 samples only); 5-15 (06/07 and 08/09 samples only); < 16 (2002/03); 16-30; 31-45; 46-60; and >60 years. Individual serum samples were pooled and for 2002/03 and 2008/09 samples, each pool consisted of up to 100 samples, see Harden et al. [5] for further details. For 2006/07 samples, each pool consisted of approximately 30 samples, see Toms et al. [6] for details. It was not possible to determine if any one donor contributed to more than one collection period. Ethics approval for this study was granted by The University of Queensland Medical Research Ethics Committee.

Chemicals targeted for analysis were hexachlorobenzene (HCB), β-Hexachlorocyclohexane (β_HCCH), γ-Hexachlorocyclohexane (Lindane) (γ_HCCH), Oxychlordane (OXYCHLOR), Trans-Nonachlor (T_NONA), 2,2-Bis(4-chlorophenyl)-1,1-dichloroethene (PP_DDE), 2-(4-chlorophenyl)-2-

(2-chlorophenyl)-1,1,1-trichloroethan (OP_DDT), 2,2-Bis(4-chlorophenyl-1,1,1-trichloroethan (PP_DDT), mirex The samples were analysed at the Center for Disease Control (CDC) in Atlanta as described previously [7]. Briefly, samples were analysed by gas chromatography high resolution mass spectrometry (MAT95XP ThermoFinnigan, Bremen, Germany) The chromatographic separations were carried out on an 6890 gas chromatograph (Agilent Technologies, Atlanta, GA) fitted with a DB5HT capillary column [(15m, 0.25mm inner diameter, and 0.10 μm thickness)].

Results and discussion

Hexachlorobenzene (HCB), β-Hexachlorocyclohexane (β_HCCH), γ-Hexachlorocyclohexane (Lindane) (γ_HCCH), Oxychlordane (OXYCHLOR), Trans-Nonachlor (T_NONA), 2,2-Bis(4-chlorophenyl)-1,1-dichloroethene (PP_DDE), 2-(4-chlorophenyl)-2-(2-chlorophenyl)-1,1,1-trichloroethan (OP_DDT) and 2,2-Bis(4-chlorophenyl-1,1,1-trichloroethan (PP_DDT) were detected in some of the pools from all collection periods while Mirex was not detected in any pools except at a low concentration in one pool from 2006/07, 9-12 years, females. Trans-nonachlor and pp-DDE were the only pesticides detected in all pools from 2002/03 while in 2008/09, this was the case for pp-DDE. Examples of temporal, age and gender trends are listed for HCB and pp-DDE only as these chemicals were detected in most pools.

For adults > 16 years, the mean and median HCB concentrations for all pooled samples were 51 ± 63 ng/g lipid and 35 ng/g lipid for 2002/03; 25 ± 33 and 8.4 ng/g lipid for 2006/07; and 21 ± 30 ng/g lipid and 6.7 ng/g lipid for 2008/09. For children < 16 years, the mean and median HCB concentrations for all pooled samples were 6.3 ± 2.1 ng/g lipid and 6.1 ng/g lipid for 2002/03; 5.3 ± 1.9 and 5.1 ng/g lipid for 2006/07 (excluding cord blood); and 3.3 ± 1.6 ng/g lipid and 3.5 ng/g lipid for 2008/09. For adults > 16 years, the mean and median pp-DDE concentrations for all pooled samples were 610 ± 478 ng/g lipid and 612 ng/g lipid for 2002/03; 538 ± 509 and 292 ng/g lipid for 2006/07; and 353 ± 307 ng/g lipid and 220 ng/g lipid for 2008/09. For children < 16 years, the mean and median pp-DDE concentrations for all pooled samples were 111 ± 16 ng/g lipid and 115 ng/g lipid for 2002/03; 161 ± 77 and 147 ng/g lipid for 2006/07 (excluding cord blood); and 153 ± 105 ng/g lipid and 93 ng/g lipid for 2008/09.

To evaluate the effect of age on the concentration of OCPs in the population, the blood samples were pooled into 6 age groups: 0-4 years (2008/09 only), 5-15 years (2008/09 only), <16 years (2002/03 only), 16-30 years, 31-45 years, 46-60 years and > 60 years. Overall, OCP concentrations increased with age and were highest in the oldest age groups. This can be related to the history of exposure of these chemicals with the oldest age groups receiving greatest exposure and the elimination of the use of these chemicals resulting in reduced exposure in the youngest age groups. The elevated concentrations of pp-DDE and trans-nonachlor observed in the 0-4 years groups in 2008/09 is likely related to placental transfer and exposure through breast feeding as previously demonstrated (Mueller et al. 2008).

When the results are separated by age group to assess a difference between male and female OCP concentrations, the sample size becomes too small to carry out a statistical evaluation of the difference. However, the mean concentration of HCB for females was consistently higher compared to males for all age groups, with the exception of the 16-30 and 31-45 year old groups in the 2002/03 pools and the 0-4 and 5-15 year age groups in the 2008/09 pools. Concentrations of pp-DDE were higher in females compared to males across all age groups (Figure 1).

Temporal trend analysis for adult pools showed, concentrations of HCB and pp-DDE are lower in the 2008/09 pools compared to the 2002/03 pools by 35 – 70 % and 30 – 50 %, respectively (Figure 2 and 3). In the > 60s age group, the average concentration of pp-DDE was marginally higher than in 2002 which may have been caused by one or a few higher contaminated individuals within the pool.

The mean concentrations of HCB and pp-DDE in these Australian pooled samples are lower than that observed in Spain [8, 9] but higher than that found in pregnant women in the USA [10] and also in data from the NHANES (USA) [11]. Concentrations from the Australian data were similar to that observed in Korea [12] and

Japan [13]. It should be noted that there is limited recent literature on OCPs in human blood serum which makes international comparisons difficult.

In summary, concentrations of OCPs in Australia are highest in the older age groups and in females. This data confirms the expected result that concentrations of OCPs have decreased over time and is consistent with the now restricted use of these chemicals

Acknowledgements
The authors thank: all laboratory staff at Sullivan Nicolaides Pathology and the CDC. The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the Centers for Disease Control and Prevention. LMLT is funded by an ARC DECRA (DE120100161). The National Research Centre for Environmental Toxicology is co-funded by Queensland Health.

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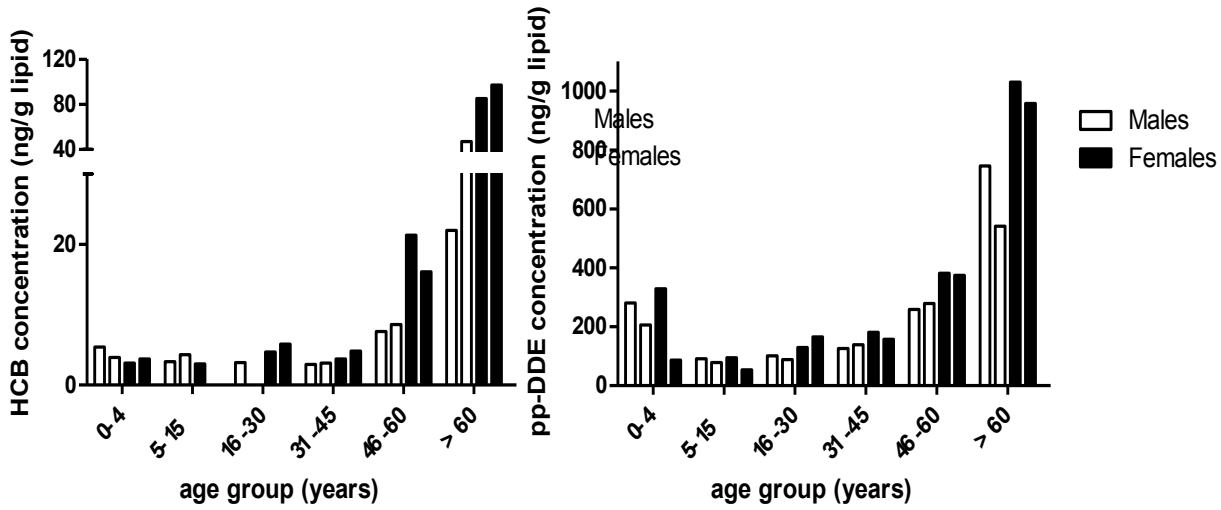


Figure 1. Mean HCB (A) and pp-DDE (B) concentrations (ng/g lipid) by gender and age for the 2008/09 samples.

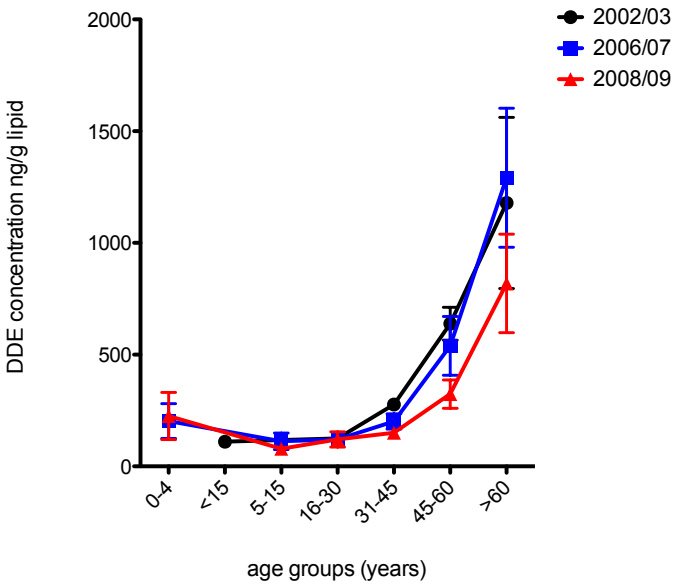
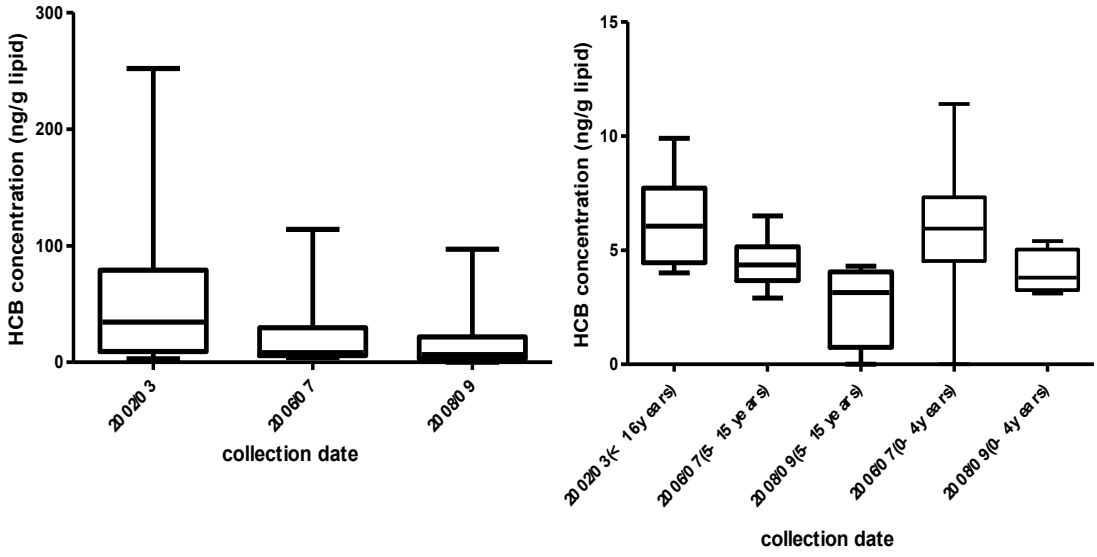


Figure 2. Concentrations of pp-DDE (ng/g lipid) by age group (years) and year of collection



(A) **(B)**

Figure 3. Box and whisker plot with median, minimum and maximum data for HCB combined by gender and age for adults (> 16 years) (A) and children (< 16 years and 0-4 years) (B) by collection date.