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Chlorinated persistent organic pollutants in serum of New Zealand adults, 2011–2013

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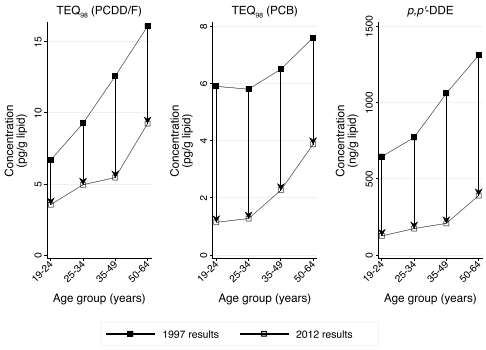
HIGHLIGHTS

- Chlorinated persistent organic pollutants (POPs) have decreased in the serum of New Zealand adults since 1997.
- Age is the most important determinant of chlorinated POPs in the New Zealand general adult population.
- Concentrations of chlorinated POPs in adult New Zealanders are low compared to international results.

GRAPHICAL ABSTRACT



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ABSTRACT

A national survey was conducted in 2011–2013 to assess serum concentrations of persistent organic pollutants (POPs) in adult New Zealanders. Participants were randomly selected from the 2010 Electoral Roll within 64 demographic strata according to 4 age groups, 4 regions, 2 ethnic groups (Māori/non-Māori) and gender. Eligible subjects ($n = 734$) donated up to 30 ml of blood, after which serum was pooled ($n = 49$) according to demographic strata prior to analysis by GC-HRMS. Associations between demographic variables (age, region, ethnicity, gender) and serum POPs were assessed using linear regression. The weighted geometric mean (GM) of PCDD/Fs was 5.3 pg/g lipid toxic equivalents using the WHO 2005 toxic equivalence factors (TEQ_{05}), which increased by age (3.2, 4.4, 4.8, and 8.1 pg/g lipid for the 19–24, 25–34, 35–49, and 50–64 year age groups, respectively). The weighted GM of dioxin-like PCBs was 1.4 pg TEQ_{05}/g lipid which also increased by age (0.82, 0.86, 1.4, and 2.3 pg/g lipid for the same age groups, respectively). Of the detected OCPs, the highest concentration was observed for *p,p′*-DDE (weighted GM, 220 ng/g lipid) followed by hexachlorobenzene (HCB; 7.3 ng/g lipid), *beta*-HCH (7.0 ng/g lipid), and dieldrin (4.7 ng/g lipid). For most Cl-POPs, concentrations were lowest in the youngest age group, and were similar for men and women and Māori and non-Māori. Serum Cl-POPs were, on average, 50% lower than those measured 15 years earlier in 1997. This survey provides evidence of declining serum concentrations of chlorinated POPs in the New Zealand adult population. Age was the most important determinant of POPs concentrations. Body burdens of PCDD/Fs and PCBs in New Zealand are relatively low by international comparison, while for OCPs they are similar or lower compared to those reported for other developed countries.

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1. Introduction

Chlorinated persistent organic pollutants (POPs) are ubiquitous environmental contaminants which are toxic, resistant to degradation, bio-accumulative, and transported by air, water and migratory species across international boundaries (Jones and de Voogt, 1999; Loganathan and Kannan, 1994; UNEP, 2009; Wania and Mackay, 1996). Humans in non-occupational settings are primarily exposed to POPs through diet, particularly from foods of animal origin (Smith and Lopipero, 2001). Health effects associated with human exposure include cancer, allergies and sensitisation, and disorders of the nervous, reproductive, and immune systems (Li et al., 2006). The most studied POPs are polychlorinated-*p*-dibenzodioxins (PCDDs), polychlorinated-*p*-dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) including the historically used dichlorodiphenyltrichloroethane (DDT), and its degradation products dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE). Other OCPs historically used in New Zealand (and many other countries) are hexachlorocyclohexane (HCH), dieldrin, pentachlorobenzene (PeCB), and hexachlorobenzene (HCB).

The Stockholm Convention embodies the commitment of member countries to reduce the effects of POPs on human health and the environment, and makes recommendations for member states to monitor POPs in people and the environment (UNEP, 2009). A number of countries have carried out biological monitoring of POPs in the general population in order to establish reference levels and assess temporal trends (Consonni et al., 2012; Fång et al., 2015; Porta et al., 2008). New Zealand conducted its first national study of serum Cl-POPs in non-occupationally exposed adults in 1997 (Buckland et al., 2001). In addition, three surveys of POPs in human milk were carried out in 1988 (Bates et al., 1994), 1998 (Bates et al., 2001), and 2008 (Mannetje et al., 2013; Mannetje et al., 2010). These studies showed that intakes of POPs and associated body burdens in human serum and milk in New Zealand are relatively low compared to other developed countries (Buckland et al., 2001; Buckland et al., 1998; Mannetje et al., 2010). In addition, they showed that levels of chlorinated POPs in human milk have declined between 1988 and 2008 (Mannetje et al., 2013), but there is currently no information on temporal trends of POPs representative for the New Zealand general adult population, including men and older age groups.

The aim of this study was to assess concentrations and demographic determinants of chlorinated POPs in non-occupationally exposed adults in the New Zealand general population. We also assessed temporal trends of chlorinated POPs since the previous New Zealand study conducted in 1997.

2. Methods

This cross-sectional survey assessed serum concentrations of chlorinated POPs in the adult New Zealand population, using a stratified sampling method. Participants were recruited using the 2010 Electoral Roll from the New Zealand Electoral Commission (www.elections.org.nz). Potential study participants were randomly selected with equal proportions based on age (19–24, 25–34, 35–49, 50–64 years), gender, geographic region (Northland/Auckland, Waikato/Bay of Plenty, Lower North Island, South Island), and ethnicity (Māori, non-Māori). The survey sample was therefore based on 64 strata consistent with the previous New Zealand POPs serum survey conducted in 1997 (Bates et al., 2005), except for the exclusion of the 15–18 years and 65 + years age groups which were included in the 1997 survey. Ethics approval was obtained from the Upper South A Regional Ethics Committee (reference URA/10/07/054 11 August 2010).

Mailed invitation letters, along with an information sheet and reply form, were sent in 6 separate mail-out events between February 2011 and June 2012 to 14,310 people. For those who replied positively we conducted a short telephone interview to determine eligibility. Exclusion criteria included: current or previous employment in occupations with high exposure to POPs, specifically timber treatment, manufacture and repair of electrical equipment, and application of organochlorine pesticides; medical conditions which would prohibit giving blood (e.g. exposure to certain blood-borne pathogens or other conditions specified by the respondent); or non-residency in New Zealand at the time of the survey.

Eligible participants provided written consent and were asked to visit a local private pathology laboratory to have up to 30 ml of whole blood taken (using BD Diagnostics Systems 10 ml glass Vacutainer®, no additives). Blood was allowed to clot (30–45 min) at room temperature, then centrifuged and serum was collected using cleaned glass pipettes. Serum samples and bovine serum quality assurance (QA) samples were stored in amber glass vials at −20 °C. Duplicate and replicate samples were included to assess laboratory precision. Duplicate samples from four strata were sent to an accredited overseas laboratory for inter-laboratory comparison.

2.1. Sample pooling and laboratory analysis

A pooling strategy was developed to ensure sufficient serum volume in each pool to achieve suitable laboratory detection limits (i.e. 50 ml), and reduce analytical costs. We did not have sufficient participants in all demographic strata to create pools using equal aliquots, while still achieving a minimum of 50 ml of serum per pool. We estimated the pool-specific 75th percentile volume for the individual samples within each pool and used this figure as the maximum volume that would be aliquoted to the pool from any participant. If a participant's sample serum volume was less than the pool-specific 75th percentile volume, the complete serum sample was aliquoted to the pool. For age strata with very low numbers of participants (i.e., males aged 19–34, Māori females aged 19–24), the samples from the four geographic regions were combined together into one pool.

A 40 ml aliquot of each pooled serum sample was analysed for PCDDs, PCDFs, and PCBs while a 10 m aliquot was analysed for OCPs. Lab methods were based on USEPA methods for PCDD/Fs (USEPA, 1994), PCBs (USEPA, 2003), and OCPs (USEPA, 2007). A matrix spike and reagent blank was included with each batch of samples. Each sample was spiked with ^{13}C labelled internal standards prior to extraction using either C18 SPE (PCDD/Fs, PCBs) or soxhlet extraction (OCPs, after dehydration with sodium sulfate). Clean-up and fractionation was achieved using acid silica, basic alumina, florisil, carbon column chromatography, and gel permeation chromatography. The cleaned extracts were spiked with recovery standards before being reduced to a final volume of 10 μl (PCDD/Fs), 50 μl (PCBs), and 25 μl (OCPs). PCDD/Fs, PCBs, and OCPs were analysed by GC-HRMS using Agilent 6890/7890 GC coupled with Waters Ultima/Premier HRMS. PCDD/Fs were analysed at 10,000 mass resolution. Quantification was performed using Waters QuanLynx software. Internal standards were used for quantification of the target analytes, thus results were recovery corrected. The recovery standard was used for quantification of the internal standards to determine the percent recovery. Testing results from bovine serum QA samples showed no evidence of sample contamination during storage and handling. Mean coefficient of variation (CV) (Reed et al., 2002) results for duplicate and replicate QA samples were 8% and 22%, respectively, which is acceptable considering that some of the measured POPs were at concentrations near laboratory detection limits. Results from testing of inter-laboratory duplicate samples were also acceptable, with normalised difference (ND) values within 50% for the majority of congeners.

Triglycerides and HDL-cholesterol levels were determined using Roche P800 GPO-PAP and P800 Direct Enzymatic methods, respectively. Serum lipid concentrations were calculated using the formula of Phillips et al. (1989). Results were reported on a lipid adjusted basis as pg/g lipid (for PCDD/F and PCBs) and ng/g lipid (for OCPs). Analyses of OCPs