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Polybrominated diphenyl ethers and perfluorinated alkyl substances in blood serum of New Zealand adults, 2011–2013

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HIGHLIGHTS

- This is the first New Zealand survey of brominated flame retardants (BFRs) and perfluorinated alkyl substances (PFASs).
- BFRs and PFASs were measured in pooled serum samples from 734 adult New Zealanders.
- 20 BFRs and 4 PFASs were detected in at least 50% of the pooled serum samples..
- In agreement with previous studies, age is an important determinant of BFRs and PFASs.
- Gender is a determinant of BFRs and PFAS in the study population.

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ABSTRACT

A national survey was conducted in 2011–2013 to assess serum concentrations of brominated flame retardants (BFRs) and perfluorinated alkyl substances (PFASs) in adult New Zealanders. Participants were randomly selected from the 2010 Electoral Roll within 64 demographic strata according to 4 age groups, 4 geographic regions, 2 ethnic groups (Māori/non-Māori) and sex. Eligible participants (n = 734; response rate of contacted individuals = 37%) donated up to 30 mL of blood, after which serum was pooled (49 pools for BFRs, 63 pools for PFASs) according to demographic strata. BFRs were analysed by GC-HRMS and PFASs by LC-MS/MS. Associations between serum BFRs and PFASs and demographic variables (age, region, ethnicity, sex) were assessed using regression analysis. The weighted geometric mean (GM) serum concentrations of BDE47, BDE99, BDE100, and BDE153 were 2.0, 0.66, 0.43, and 1.2 ng/g lipid, respectively. The weighted geometric mean (GM) serum concentrations of PFOS, PFOA, PFHxS, and PFNA were 3.4, 2.4, 1.0, and 0.66 ng/mL, respectively. The majority of BFRs showed higher serum concentrations in younger age groups. Conversely, the four PFASs showed higher serum concentrations in older age groups. Concentrations of BFRs and PFASs were generally lower in females compared to males. In New Zealand, both age and sex are important determinants of BFR and PFAS serum concentrations.

1. Introduction

Brominated flame retardants (BFRs) and perfluorinated alkyl substances (PFASs) are synthetic chemicals that can be present in a wide range of products, including consumer goods, electronics, textiles, surface treatments, adhesives and building materials. Due to their wide use and persistence in the environment, exposure to BFRs and PFASs has become universal in humans and wildlife over the past decades. There is evidence that these chemicals adversely affect a range of physiological processes, including disruption of the endocrine system (Costa et al., 2008; Darnerud, 2003; Fromme et al., 2016a; Fromme et al., 2009). National surveys that have investigated levels of BFRs and PFASs in humans have been carried out in relatively few countries (Porta et al., 2008), and questions remain about differences in population levels for a range of chemicals between countries and demographic groups based on age, gender, and ethnicity (Fromme et al., 2016a; Hermann Fromme et al., 2009).

The manufacture and use of BFRs has been subject to strict regulatory controls, including outright bans in many countries on

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common BFR formulations. Tetra-to hepta-brominated diphenyl ether (PBDE) formulations are included in the Stockholm Convention on Persistent Organic Pollutants (POPs), and there is a proposal to also include the commonly used deca-brominated formulation (i.e. BDE209) (UNEP, 2009). Internationally, PBDE use has largely been switched to alternative flame retardants such as tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), and organophosphate flame retardants (OPFRs) (Dodson et al., 2012). The import, use and manufacture of BFRs included in the Stockholm Convention are currently not permitted under New Zealand legislation, but estimates suggest annual imports of 15 tonnes prior to this ban mostly for manufacturing of export goods (Keet et al., 2010). Human biological monitoring studies of BFRs in New Zealand include a small study of PBDEs in serum collected in 2001 from 23 adult blood donors in Wellington (Harrad and Porter, 2007) and a study of PBDEs in human milk (Mannetje et al., 2013). The results of these studies show that BFR concentrations in New Zealand were comparable to Europe, and lower than the USA and Australia. However, given the small size of these previous studies, levels of BFRs in the general New Zealand adult population are unclear.

Less is known in New Zealand about human exposure to PFASs. Similar to BFRs, the import and use of PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) have been controlled under New Zealand legislation since 2011, but PFOS and PFOA have been previously used in applications such as fire-fighting foams on defence force bases (MfE, 2017). PFOS and PFOA have been detected in New Zealand wastewater, soil, and sewage sludge (Stewart et al., 2016). However, there have been no previous New Zealand studies of PFAS levels in humans.

This paper reports the results of the first national survey of BFRs and PFASs in the serum of adult New Zealanders. The results of the survey are compared with human serum concentrations of BFRs and PFASs reported for other countries, and we investigate the significance of demographic determinants of exposure (i.e. age, sex, ethnicity, and geographic region) to BFRs and PFASs.

2. Methods

This cross-sectional survey assessed serum concentrations of BFRs and PFASs, 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), sex, geographic region (Northland/Auckland, Waikato/Bay of Plenty, Lower North Island, South Island), and ethnicity (Māori, non-Māori. Māori are a distinct indigenous Polynesian group within New Zealand, making up approximately 15% of the total population). 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. Chlorinated POPs (i.e. dioxins, furans, PCBs, and organochlorine pesticides) were included in the survey (Coakley et al., 2018), therefore the exclusion criteria covered current or previous employment in occupations with high exposure to chlorinated POPs, specifically timber treatment, manufacture and repair of electrical equipment, and pesticide application. In addition, participants were not eligible if they had medical conditions that 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 samples were collected during 2011 and 2012. Blood was allowed to clot (30–45 min) at room temperature then centrifuged and serum was collected using cleaned glass pipettes. Serum samples and quality-control (QC) samples (bovine serum method blanks, replicate samples, duplicate samples) were stored in amber glass vials (for BFR analyses) and polypropylene vials (for PFAS analyses) at −20 °C. Polypropylene vials were used to avoid potential PFAS contamination from polytetrafluoroethylene (PTFE) lined seals in glass vials, and to avoid adsorption of PFAS to glass vials. One duplicate sample for BFRs, and two duplicate samples for PFASs, were sent to an overseas laboratory (Axys Analytical Laboratories, Canada) for inter-laboratory analysis.

2.1. Sample pooling and laboratory analysis

A pooling strategy was applied to ensure sufficient serum volume in each pool to achieve suitable laboratory detection limits for BFRs to and reduce analytical costs. The pooled serum samples were also tested for chlorinated POPs so the required sample volume was relatively large (50 mL). We did not have sufficient participants in all demographic strata to create pools using equal volume aliquots, while still achieving the required volume 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 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. The selected analytical method for PFASs (LC-MS/MS) requires considerably less serum therefore separate pools comprised of equal volumetric aliquots (0.5–1.0 mL) were made for this analysis.

The pooled serum samples were analysed using isotope dilution methods; GC-HRMS for BFRs (based on USEPA Method 1614) and LC-MS/MS for PFASs (in-house developed method). For BFRs we extracted 40 mL of serum, however there wasn't enough volume for 13 of the 49 samples so in those cases we extracted what was available (range 19–38 mL). For PFAS we extracted 0.5 mL of serum from all pooled samples.

For BFRs analysis a matrix spike (human serum) and reagent blank (deionised water) was included with each batch of samples to serve as laboratory QC samples. Each sample was spiked with ^{13}C labelled internal standards (Wellington Laboratories, Canada, Cat # BFR-LCS) prior to extraction using C18 SPE (Grace, C18-HC 10000 mg). Extraction tubes were conditioned with methanol followed by deionised water before applying the sample, and the analytes eluted with hexane. Clean-up and fractionation was achieved using acid silica, basic alumina, and florisil column chromatography. The cleaned extracts were spiked with recovery standards (Wellington Laboratories, Canada, Cat # BFR-ISS) before being reduced to a final volume of 50 μL. BFRs were analysed by GC-HRMS (Agilent 6890/7890 GC, Waters Ultima/Premier HRMS at 5000 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. Limit of detection (LOD) for BFRs was calculated for each analyte, for each sample, based on a signal-to-noise ratio (S/N) of 3:1.