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Current concentrations, temporal trends and determinants of persistent organic pollutants in breast milk of New Zealand women

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HIGHLIGHTS

- New Zealand breast milk concentrations of PCDD/Fs and PCBs were low internationally
- Breast milk concentrations of PBDEs, dieldrin and DDTs were in the mid-range
- Age, urban/rural residency and BMI were determinants of POPs concentrations
- Between 1998 and 2008 POPs body burdens decreased by half in nursing women

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ABSTRACT

Breast milk samples of 39 first time mothers aged 20–30 were collected in 2007–2010 from rural and urban areas of New Zealand, following the fourth World Health Organization coordinated survey protocol. Samples were individually analysed for persistent organic pollutants (POPs) including dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). The lipid adjusted concentrations of PCDD/Fs (mean toxic equivalent (TEQ): 3.54 pg/g) and PCBs (mean TEQ 1.29 pg/g) were low in comparison to those reported for other countries, and concentrations of dieldrin (10 ng/g) and *p,p′*-DDE (379 ng/g) and PBDEs were in the mid-range. Breast milk concentrations of PCDD/F-TEQ, PCB-TEQ, dieldrin and *p,p′*-DDE were significantly higher in rural compared to urban areas (+23%, 33%, 59%, and 44% respectively), while concentrations of several PBDEs and lindane were higher in urban areas. Concentrations of PCDD/Fs, PCBs and OCPs, but not PBDEs, increased with age, and higher body mass index was associated with lower concentrations of PCBs. Despite New Zealand's low body burdens of many chlorinated POPs in comparison to other countries, breast milk concentrations continued to decrease over time, with a decrease by half over the last 10 years for PCDD/F-TEQ (−40%), PCB-TEQ (−54%) and OCPs −34 to −90%), indicating that regulatory measures continue to have beneficial effects. Continued monitoring is needed particularly for the brominated POPs for which little New Zealand specific data is available.

1. Introduction

Persistent Organic Pollutants (POPs) are a range of organic chemicals that enter the environment as a result of human activities, are persistent in the environment, and become widely distributed via long range transport through air and water. Due to their stability and lipophilic properties, POPs are stored in fat tissues and bio-accumulate in the food chain. Exposure to POPs has been associated with a range of toxic effects in wildlife (Tanabe, 2002) and humans (Li et al., 2006) and it has been recognised for several decades that concerted action is needed to reduce environmental levels of POPs.

In 2004 New Zealand ratified the Stockholm Convention (www.pops.int), which requires parties to take measures to eliminate or reduce the release of POPs into the environment. The Stockholm Convention's 2001 list of POPs consisted of 12 chlorinated compounds including: Aldrin; Chlordane; Dieldrin; Endrin; Heptachlor; Hexachlorobenzene (HCB); Mirex; Toxaphene; Polychlorinated biphenyls (PCBs); DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane); PCDDs (polychlorinated dibenzo-p-dioxins); and PCDFs (polychlorinated

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dibenzofurans). In 2009, nine additional compounds were added to the Stockholm Convention, including certain brominated and fluorinated compounds. Articles 11 and 16 of the Convention require the collection of comparable human monitoring data of POPs, and WHO/UNEP has coordinated a series of exposure studies on concentrations of POPs in human milk, facilitating parties to meet this requirement and maintaining comparability of study results through unified protocols.

Background body burdens of chlorinated POPs have been estimated for the New Zealand population during two previous breast milk surveys in 1988 (Bates et al., 1994) and 1998 (Bates et al., 2002) and a serum survey in 1996–1997 (Bates et al., 2004). These studies indicated that New Zealand has relatively low background (non-occupational) body burdens of chlorinated POPs, and that between 1988 and 1998 a two-thirds decline in breast-milk concentrations had occurred. Here we present the results of the third New Zealand breast milk survey of POPs, which followed the WHO/UNEP protocol of the fourth round (WHO, 2007) and was conducted during 2007–2010, hereafter referred to as the 2008 survey. In this study, we determined individual breast milk concentrations of chlorinated POPs as well as selected brominated flame retardants (BFR) not previously measured in New Zealand breast milk samples.

2. Material and methods

2.1. Survey methods

The design of the survey was modelled on the fourth WHO-Coordinated Survey of human milk for persistent organic pollutants (WHO, 2007). The selection criteria for participating mothers included: (1) primiparous, with singleton pregnancy; (2) ages 20–30 years; (3) apparently healthy mother and child, and 'normal' pregnancy (i.e. gestation >37 weeks, birth weight >2500 g); (4) exclusively breastfeeding; (5) resident within the study area for the last five years. Having ever worked with pentachlorophenol (PCP), polychlorinated biphenyls (PCBs) or organochlorine pesticides was used as exclusion criteria. Participants were recruited from 4 study areas in New Zealand: Wellington (urban North Island), Wairarapa (rural North Island), Christchurch (urban South Island) and North Canterbury (rural South Island). Living in a rural area was defined as living more than 3 km from any town with a population of more than 2500 people. Living in an urban area was defined as living within the city boundaries of Wellington (2006 population: 179,000) or Christchurch (348,000).

Participants were recruited through midwives, medical doctors and breast feeding consultants, depending on what was most practicable in each area, who approached potential participants after which interested participants could contact the research nurse for more information and to check eligibility. After birth, the eligibility criteria and the mother's willingness to participate in the study were verified again after which a research nurse visited the mother 3 to 6 weeks after birth. During this first visit, the research nurse provided the women with a breast milk sample collection kit (a laboratory cleaned 250 ml glass storage container with Teflon lined lid for the storage of the samples and eight smaller glass collection containers to directly collect the expressed breast milk), explained the use of the collection containers, and administered the study questionnaire, which was based on the WHO protocol (WHO, 2007).

Breast milk samples were collected, usually during the second and sometimes into the third month after birth, through hand expression by the mother directly into the provided collection containers. The mother contacted the research nurse when a total of up to 250 ml of breast milk was collected or all of the eight collection containers had been used. The milk was stored in the freezer at home until collected by the research nurse. Samples were transported using ice packs and kept in a −20 °C freezer at the Centre for Public Health Research in Wellington until transport to the laboratory.

2.2. Laboratory analyses

All individual samples were analysed at AsureQuality (Lower Hutt, New Zealand) for PCDD/Fs, PCBs, OCPs and BFRs (the specific analytes are listed in the tables). Concentrations of all analytes were determined through High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS). For PCDD/Fs Method 1613B Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (U.S. Environmental Protection Agency, October 1994) was used. For PCBs Method 1668B Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS (U.S. Environmental Protection Agency, November 2008) was used. For Organochlorine pesticides methods were based on 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS (U.S. Environmental Protection Agency, December 2007) was used. For BFRs, Method 1614 Brominated Diphenyl Ethers in Water, Soil, Sediment and Tissue by HRGC/HRMS (U.S. Environmental Protection Agency, August 2007) was used.

For the purpose of quality assurance, prior to extraction each milk sample was fortified with internal standards containing isotopically-labelled ^{13}C analogs of most target analytes. Clean-up was performed using a combination of gel permeation chromatography and solid-phase chromatography to remove interfering components. Immediately prior to injection, a labelled injection standard was added to each extract and an aliquot of the extract was injected into the gas chromatograph (GC). The analytes were separated by the GC and detected by a high-resolution (≥10,000 for PCDD/Fs; ≥8000 for PCBs and OCPs; ≥5000 for BFRs) mass spectrometer. Two exact mass-to-charge ratios (m/z's) for each analyte were monitored throughout a pre-determined retention time window. An individual analyte was identified by comparing the GC retention time and ion abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

Quantitative analysis was performed in one of two ways using selected ion current profile (SICP) areas: for analytes for which a labelled analog was available, the GC/HRMS was multi-point calibrated and the concentration was determined using the isotope dilution technique. For analytes for which a labelled analog was not available, the GC/HRMS was multi-point calibrated and the concentration was determined using the internal standard technique. The labelled compounds were used as internal standards, affording recovery correction for all pesticides.

The quality of the analysis was assured through reproducible calibration and testing of the extraction, clean-up, and HRGC/HRMS systems. Each batch of 10–15 samples included the analysis of one laboratory blank, which provided information on laboratory background concentrations of the target analytes. A spiked QA sample was also included with each batch of samples to confirm compliant method performance.

The lipid determination was performed on the PCDD + F/PCB/BFR extract before clean-up, and the concentrations of all POPs were expressed as picogram per gram lipid (or nanogram per gram lipid).

2.3. Analysis of the pooled sample

For the purpose of inclusion into the fourth WHO round, pooled samples of individuals were also analysed by the WHO reference laboratory (State Laboratory for Chemical and Veterinary Analysis of Food, Freiburg, Germany). Aliquots (10 ml) of individual samples of sufficient volumes (n = 37) were combined into a pooled sample in a glass container and couriered frozen on icepacks to the WHO accredited laboratory in Freiburg, Germany. The lipid content of the pooled sample was determined and the concentrations of a range of basic POPs. The WHO Reference Laboratory analytical methods have been described elsewhere (Hui et al., 2008). Agreement between the