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Concentrations of persistent organic pollutants in California women's serum and residential dust

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ABSTRACT

Background: Humans are exposed to persistent organic pollutants (POPs) through various routes, including consumption of contaminated food and accidental ingestion of settled dust.
Objectives: We aimed to identify key routes of exposure to organochlorine pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in California women of reproductive age.
Methods: Blood was collected from 48 mothers participating in the California Childhood Leukemia Study from 2006 to 2007 and analyzed for POPs using gas chromatography–mass spectrometry. Multivariable linear regression models of natural-log transformed serum concentrations were used to identify determinants of exposure from available questionnaire information on dietary habits, reproductive history, and demographic characteristics, as well as vacuum cleaner dust-POP levels.
Results: After adjusting for blood lipid levels, age, body mass index, cumulative lactation, and sampling date, serum concentrations of multiple major PCBs were positively associated with fish consumption, but not dust-PCB levels. After adjusting for blood lipid levels, Hispanic ethnicity, country of origin, and household annual income, serum concentrations of multiple major PBDEs were positively associated with dust-PBDE levels.
Conclusions: Our findings suggest that the relative contribution of specific exposure routes to total POP intake varies by chemical class, with dust being a relatively important source of PBDEs and diet being a relatively important source of PCBs.

1. Introduction

Persistent organic pollutants (POPs) are stable and widespread in the environment, they accumulate in fatty tissue of biota, and they are toxic to humans and wildlife. Three important classes of POPs are organochlorine (OC) pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Chemicals from each of these classes were produced globally in large volumes, but the time period of peak production varied by chemical. For example, DDT [*i.e.*, *p,p′*-1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] has been used extensively to control insects on agricultural crops and to control insect-borne diseases, with perhaps as much as four million metric tons produced worldwide since 1945; however, DDT use peaked circa 1970 and all uses of DDT in the U.S. have been banned since 1973 (Li and Macdonald, 2005). Likewise, as components of electrical, heat transfer, and hydraulic equipment, PCBs had a similar production history to DDT, with over 1 million metric tons produced worldwide since 1929 and peak production in 1970, followed shortly thereafter by a ban of U.S. production and distribution (Breivik et al., 2004). At the same time that DDT and PCBs were being phased out, PBDEs began to be used as chemical flame retardants to treat plastics and textiles in consumer products, and an estimated global market demand of 67,000 metric tons in 1999 suggests that peak PBDE production was on the same order of magnitude as peak PCB production (Breivik et al., 2004). In the U.S., the manufacture and import of the commercial mixtures, Penta-BDE (composed primarily of BDEs 47, 99, 100, 153, and 154) and Octa-BDE (composed primarily of BDEs 153, 183, 196, 197, and 207) were phased out, as of January 1, 2005, and the Deca-BDE mixture (composed primarily of BDE-209) was subsequently phased out, as of December 31, 2013 (U.S. EPA, 2014).

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Adults are exposed to POPs through various routes, including consumption of contaminated food, accidental ingestion of settled dust, dermal contact with settled dust, and inhalation of contaminated air. The relative contribution of each exposure route to total POP intake may vary by chemical class and by chemicals within the same class. For example, because consumer goods that have been treated with PBDEs can still be found readily in U.S. homes (Stapleton et al., 2012b), PBDE levels in settled dust remain high [*e.g.*, median concentrations >1 ppm for BDEs 47, 99, and 209 in 2010 (Whitehead et al., 2013)]. Accordingly, it has been suggested that dust ingestion is a major route of exposure to PBDEs for U.S. adults (Lorber, 2008) and positive relationships have been observed between levels of PBDEs in dust and levels of PBDEs in matched samples of serum (Johnson et al., 2010; Watkins et al., 2012) and milk (Wu et al., 2007) in U.S. adults. However, due to small sample sizes [*i.e.*, $N=12$ (Johnson et al., 2010; Wu et al., 2007) and 31 (Watkins et al., 2012)], these previous studies had limited capacity to use multivariable regression to adjust for other factors, such as diet, that may influence serum PBDE concentrations. As such, the true role of dust ingestion in adults' exposure to PBDEs remains a topic of interest.

In contrast, dust ingestion is hypothesized to be a relatively minor contributor to total PCB intake for U.S. adults compared to inhalation or diet (Harrad et al., 2009). All PCB-containing consumer products in the U.S. are at least 35 years old and their presence in U.S. homes is increasingly rare; as a result, PCB levels in settled dust are relatively low compared to PBDE levels [*e.g.*, median concentrations <5 ppb for PCBs 138 and 153 in 2010 (Whitehead et al., 2014)]. However, one study of 20 Wisconsin households did observe a relationship between dust-PCB concentrations and serum-PCB concentrations, after adjusting for fish consumption (Knobeloch et al., 2012). To our knowledge, no other previous studies have evaluated the relationship between PCB levels in matched dust and biological samples in U.S. adults.

Given that women exposed to POPs may experience various adverse reproductive effects, including decreased birth weight (Govarts et al., 2012; Harley et al., 2011), increased time to pregnancy (Chevrier et al., 2013; Harley et al., 2010), increased risk of spontaneous abortion (Korrick et al., 2001), and increased risk of leukemia (Bailey et al., 2014) and other cancers (Infante-Rivard and Weichenthal, 2007; Vinson et al., 2011) in their offspring, we sought to identify key routes of exposure to OC pesticides, PCBs, and PBDEs in California mothers of reproductive age participating in the California Childhood Leukemia Study.

2. Material and methods

2.1. Study population

The California Childhood Leukemia Study (CCLS) is a case–control study of childhood leukemia conducted in the San Francisco Bay area and California Central Valley that seeks to identify genetic and environmental risk factors for childhood leukemia. Cases 0–14 years of age were ascertained from pediatric clinical centers; controls, matched to cases on date of birth, sex, Hispanic ethnicity, and mother's race were selected from the California birth registry. We have employed several strategies to characterize the children's exposure to chemicals, including the measurement of POPs in serum collected from the children's mothers and in dust samples collected from the children's homes. Mothers of case and control participants who were initially interviewed from 2005 to 2007 were eligible for blood collection if the participating child was 0–7 years old. Households of case and control participants who were enrolled in the study from December 1999 through November 2007 were eligible for dust collection if the participating child was 0–7 years old and living in the same home occupied at the time of diagnosis (or a similar reference date for controls). Among 112 mothers who provided a blood sample and had a vacuum-bag-dust sample analyzed for PBDEs, we selected a group of 50 mothers for POP analysis. Because we previously observed that Hispanic families, families with annual income below $75,000, and families residing in the Sacramento Valley and Sierra Mountains had higher PBDE-dust concentrations compared to other CCLS families (Whitehead et al., 2013), we prioritized samples from these groups for POP analysis. Of the 50 blood samples analyzed for POPs, two did not pass quality control and were excluded from further analyses. Fig. S1 shows a complete flow diagram of the 48 mothers comprising the study population.

2.2. POPs analysis in serum

Blood samples were collected from the mothers at their homes from January 2006 to October 2007 by a physician's assistant. Blood samples were collected in red-top vacutainer tubes without anticoagulant, shipped or hand delivered on ice packs for receipt at the laboratory no more than one day after collection, centrifuged, and the separated serum was stored at -20 °C or colder prior to analysis.

The serum sample preparation protocol (see Fig. S2 and Table S1) was adapted from Sjodin et al. (2004b). After thawing, 1-mL serum samples were diluted to 2 mL with HPLC-grade water, spiked with internal standards (tetrachloro-m-xylene, PCB-14, PCB-65, PCB-165, and BDE-139), denatured with formic acid, and extracted *via* an automated sample extraction system (RapidTrace, Biotage; Uppsala Sweden) that used a 540-mg Oasis HLB solid phase extraction cartridge (Waters Corp.; Milford, MA) and 12 mL of 1:1 hexane:methylene chloride for elution. After extraction, samples were concentrated to 1 mL using an automated nitrogen evaporation system (TurboVap LV, Biotage; Uppsala, Sweden). Subsequently, concentrated extracts were cleaned using manually packed acid–silica chromatography columns, followed by a further concentration to 80 μL, and a solvent exchange into isooctane. Finally, $^{13}C_{12}$-labeled PCB-209 was added as an injection standard.

Samples (1-μL injections) were analyzed for 17 PCBs (PCBs 28, 66, 74, 99, 101, 105, 118, 138, 153, 156, 167, 170, 180, 183, 187, 194, 203), 5 PBDEs (BDEs 47, 99, 100, 153, 154, major components of the Penta-BDE commercial mixture), and 7 OC pesticides or metabolites thereof, including β-hexachlorocyclohexane (β-HCH, the major metabolite of the insecticide HCH), *o,p′*-DDT (a minor component of the insecticide DDT), *p,p′*-DDT (the major component of DDT), *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE, the major metabolite of DDT), hexachlorobenzene (HCB, a fungicide), *trans*-nonachlor (a minor component of the insecticide chlordane), and oxychlordane (the major metabolite of chlordane) using gas chromatography (7890 GC, Agilent Technologies; Sunnyvale, CA)-triple quadrupole mass spectrometry (7000B Series, Agilent Technologies; Sunnyvale, CA). Chromatographic conditions included pulsed splitless injection at 250 °C, helium carrier gas at 1 mL/min, and a 30-m DB-5 ms column with 0.25-mm diameter and 0.25-μm film thickness (Agilent Technologies; Sunnyvale, CA). The GC temperature program was initiated at 90 °C, held for 1 min, ramped at 50 °C/min to 150 °C, held for 1 min, ramped at 8 °C/min to 225 °C, held for 6.5 min, ramped at 14 °C/min to 310 °C, and finally held for 6 min. The mass spectrometer was operated in electron impact ionization mode using multiple ion detection, source temperature of 275 °C, ionization energy of 70 eV, and mass resolution of 1.2 amu (see Table S2).

Serum samples were analyzed in batches of 20 including 14 field samples, two bovine serum (HyClone bovine serum, Thermo Fisher Scientific, Inc.; Waltham, MA) blanks as negative laboratory controls, two bovine serum blanks spiked with each target analyte