OCCURRENCE OF SELECTED PESTICIDES IN CANADIAN HOUSE DUST

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Introduction

The indoor environment has increasingly gained attention as an important source of human exposure to environmental contaminants, and house dust is known to be a sink for semi-volatile organic compounds and particle-bound organic matter and thus may be a significant route of human exposure to the environmental pollutants. A survey of US indoor environments showed that most floors in occupied homes have measurable levels of organochlorine, organophosphate, and pyrethroid pesticides that may serve as sources of exposure to occupants[1]. Pesticides in house dust may arise from indoor use, or they may enter the home from outdoors as constituents of soil and airborne particles. Owing to their persistent and bio-accumulative nature, many legacy pesticides that have not been registered for use in Canada for decades are still detected in the environment as well as in the food chain[2,3]. Moreover, certain pesticides that were banned in some countries including Canada (e.g., DDTs, HCHs, aldrin, dieldrin, heptachlor and hexachlorobenzene) continue to be used in other countries[4]. These pesticides may exhibit endocrine disrupting activity and have been implicated in diabetic nephropathy[2,5]. Exposure to commonly used pesticides in the US and Canada has been reviewed in the context of cancer incidence[6] and a recent prospective human study linked measured DDT exposure *in utero* to risk of breast cancer[7]. A wide range of potential toxic effects (neurotoxicity, immunotoxicity, cardiotoxicity, hepatotoxicity, cytotoxicity, etc.) have been suggested in relation to exposure, although no causative link to human disease has been established[8,9]. Currently, a synthetic Type I pyrethroid (permethrin) is the most frequently used insecticide, to control pests in residential areas, the textile industry and agricultural settings because of its high activity as an insecticide and its assumed low mammalian toxicity. However, a number of studies have suggested that exposure to permethrin may exhibit toxic effects[10] similar as seen with exposure to other groups of commonly studied pesticides (e.g., DDT, malathion). Recently, transformation products such as DDE, DDD, and dieldrin have also gained attention worldwide owing to their higher concentrations in the environment and higher toxicity than the parent compounds[11]. The objective of this study is to determine concentrations of permethrin (PER), 14 organochlorine (OC) and 8 organophosphate (OP) compounds in nationally representative house dust samples collected over a four-year period (2007 to 2010) under the Canadian House Dust Study[12].

Materials and methods

Chemicals

Target compounds included phorate, hexachlorobenzene (HCB), terbufos, diazinon, methyl parathion, heptachlor, aldrin, malathion, chlorpyrifos, parathion, heptachlor epoxide, *o,p'*-dichlorodiphenyl dichloroethylene (o,p'-DDE), *cis*-chlordane, *trans*-nonachlor, dieldrin, p,p'-dichlorodiphenyl dichloroethylene (*p,p'*-DDE), o,p'-dichlorodiphenyl dichloroethane (*o,p'*-DDD), p,p'-dichlorodiphenyl dichloroethane (*p,p'*-DDD), *cis*-nonachlor, *o,p'*-dichlorodiphenyl trichloroethane (*o,p'*-DDT), *p,p'*-dichlorodiphenyl trichloroethane (*p,p'*-DDT), azinphos methyl, and permethrin. Individual standards were purchased from Sigma-Aldrich (Oakville, ON, Canada), and labeled internal standards were from Cambridge Isotopes Laboratories (Tewksbury, MA, USA).

Sample collection

Dust samples were collected from 2007 to 2010 according to the Canadian House Dust Study protocol. The detailed procedures (e.g., sampling, shipping, drying, sieving, and storage) have been described elsewhere[12]. Briefly, single family homes were randomly selected from thirteen cities across Canada. Trained technicians used a Pullman Holt (model 102 ASB-12PD) vacuum sampler to collect fresh or 'active' dust samples from floors in living areas, including family rooms, hallways, bedrooms, and study areas. Samples were shipped to Health Canada laboratory, where they were dried and sieved. The fractions with particle sizes less than 80 µm were collected for analysis.

Sample preparation

Sieved house dust samples (75 mg) were spiked with 10 µL of a 1 mg/L mixture of labeled internal standards. The dust samples were then extracted twice, by shaking with 2 mL 20% acetone in hexane for 20 minutes. For sample cleanup, the extracts were loaded to an SPE cartridge (Florisil, 12 mL, 2000 mg) preconditioned with 5 mL hexane/acetone (80:20). The analytes were then eluted with 20 mL hexane/acetone (80:20). The extracts were concentrated under a gentle stream of nitrogen to a volume of 250 µL. The final 250 µL extract was analyzed using GC/EI-MS/MS.

GC-MS/MS analysis

Chromatography	*Mass spectrometry*
Gas chromatograph: Trace GC Ultra equipped with the Triplus autosampler Column: 30 m Zebron ZB-5HT (30 m x 0.25 mm x 0.1 µm) GC oven temperature program: 80°C (hold 1 min) to 180°C at 20°C/min, to 280°C at 5°C/min Injection volume: 1 µL, splitless mode Flow rate: 1.2 mL/min, helium constant flow mode	Mass spectrometer: TSQ Quantum GC Ionization mode: electron impact (EI) Emission current: 25 µA Ion Source temperature: 180°C Scan type: Selected reaction monitoring (SRM); Scan width: 0.4 amu; Scan time: 25 ms Collision gas: 1.5 mtorr, argon

Results and discussion

The Canadian House Dust Study (CHDS) is a multi-year study, which was designed to provide statistically robust national estimate of concentrations of selected chemicals in urban homes[12]. For the present study on pesticides, a total of 916 samples were analyzed, and based on QA/QC criteria the sample size for the data presented in this paper varied between 797 and 916 samples, depending on the compound. Table 1 summarizes the occurrence of target analytes in the CHDS samples. Only 8 pesticides out of 23 had a detection frequency more than 20%, with a concentration higher than their respective limits of quantitation (LOQ). Permethrin (PER) had the highest mean concentration, followed by *p,p'*-DDT and Azinphos-methyl (Figure 1). PER also had the highest detection frequency when compared with the other most detected pesticides. This can be attributed to the fact that PER is registered for use in Canada in over 230 products, and is used for a wide variety of purposes such as general insecticide products for domestic use, flea and tick control on household pets, insect control on agricultural crops, orchards, nurseries and in greenhouses[13]. PER is not produced in Canada, and there is no information available on quantities of PER being imported. Although, the mean concentration of *p,p'*-DDT was lower than PER, its detection frequency was high and was present at a somewhat high concentration in some houses (Table 1). Whether these high concentrations can be linked to close proximity of the houses to agricultural land/orchards remains to be explored. The organochlorine insecticides (DDT, dieldrin, chlordane, heptachlor) were used for agricultural purposes in Canada during the 1950s to 1970s, and even now, residues of these ''legacy'' pesticides persist, particularly in agricultural and orchard soils with high organic matter content[14]. Interestingly, these residues do not remain passively in the soil, but are capable of being remobilized to contaminate other environmental compartments[14]. It has been reported that volatilization of legacy pesticides from agricultural/orchard soils contributes to the present-day levels of chlorinated pesticides in the ambient air of North America[14]. Moreover, DDT degradation products such as DDE and DDD have very long half-lives in the soil[15]. Therefore, the observed higher detection frequency of these two DDT metabolites in house dust (Table 1) is not surprising. Diazinon is still an active product approved for many agricultural applications, although its residential uses were banned in the US and Canada in 2004. In our study, diazinon had a detection frequency of 30%>LOQ (3.2 ng/g). Azinphos-methyl (AZM) and chlorpyrifos (CPF) are broad-spectrum organophosphate insecticides used for pest control on a number of agricultural food crops (although this is no longer the case for AZM, see below). Both OP pesticides were detected at relatively high frequency (Table 1), though AZM has not been registered for use in Canada since 2006[16]. Although most of the target pesticides are legacy pesticides that have not been registered in Canada for several decades, they were still detected in house dust with a high detection frequency in Canadian house dust, and some of them at quite high concentrations (Table 1).

Table 1. Summary data of pesticide analyzed in Canadian house dust.

CAS No	Common Name / Acronym	N	LOQ (ng/g)	>LOQ (%)	Min (ng/g)	Mean (ng/g)	Median (ng/g)	95 pctl (ng/g)
298-02-2	Phorate	914	32	1	n.d.	2	0	0
13071-79-9	HCB	803	1.3	6	n.d.	6	0	9
333-41-5	Terbufos	915	12.8	3	n.d.	2	0	6
13071-79-9	**Diazinon**	**916**	3.2	**30**	n.d.	**223**	**0**	**347**
298-00-0	Methyl Parathion	916	40	0	n.d.	1	0	7
76-44-8	Heptachlor	797	1.7	6	n.d.	3	0	7
309-00-2	Aldrin	916	10.0	3	n.d.	1	0	5
121-75-5	Malathion	915	6.4	9	n.d.	6	0	16
2921-88-2	**Chlorpyrifos**	**915**	**3.2**	**36**	n.d.	**27**	**0**	**121**
56-38-2	Parathion	916	106.7	0	n.d.	1	0	0
1024-57-3	Heptachlor Epoxide	824	0.5	2	n.d.	1	0	0
3424-82-6	*o,p'*-DDE	914	0.8	7	n.d.	6	0	10
5103-71-9	*cis*-Chlordane	826	5.0	7	n.d.	37	0	**26**
39765-80-5	*trans*-Nonachlor	800	0.8	7	n.d.	818	0	**25**
60-57-1	Dieldrin	908	25.0	2	n.d.	29	0	**0**
72-55-9	***p,p'*-DDE**	**912**	**2.5**	**24**	n.d.	**403**	**0**	**88**
53-19-0	*o,p'*-DDD	913	10.0	5	n.d.	33	0	13
789-02-6	***o,p'*-DDT**	**902**	**10.0**	**30**	n.d.	**267**	**0**	**590**
72-54-8	***p,p'*-DDD**	**912**	**10.0**	**43**	n.d.	**99**	**0**	**220**
5103-73-1	*cis*-Nonachlor	814	5.0	5	n.d.	14	0	0
50-29-3	***p,p'*-DDT**	**912**	**12.5**	**40**	n.d.	**4665**	**3.8**	**649**
86-50-0	**Azinphos Methyl**	**904**	**53.3**	**29**	n.d.	**3168**	**0**	**6900**
52645-53	**Permethrin**	**914**	**10.0**	**66**	n.d.	**10052**	**167**	**15969**

n.d. = not detected; pctl = percentile

Detections of a few other pesticides were noted that have since undergone significant regulatory action (e.g., uses cancelled, including cancellation of residential use). Although the bioavailability of these chemicals from house dust is unknown, this warrants the continued collection of exposure data in future surveys in order to investigate the temporal changes in the presence of these pesticides and thus inform risk assessment or risk management decisions.

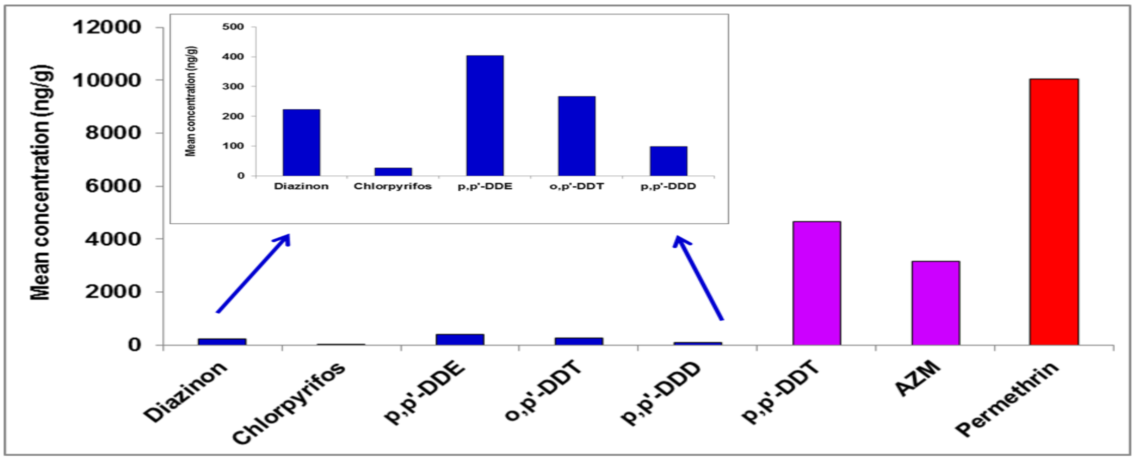

Figure 1. Mean concentration (ng/g) of commonly detected pesticides in Canadian house dust

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