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# Residues of organochlorine pesticides in honeys from different geographic regions

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ABSTRACT

Organochlorine pesticides (OCPs) are of concern due to their presence in foods. Hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs), chlordane and hexachlorobenzene (HCB) in 38 honey samples from different geographic regions were analyzed with gas chromatography/ion trap mass spectrometry after accelerated solvent extraction. Mean concentrations of total HCHs (SHCHs), SDDTs, Schlordanes, and HCB in tested honeys were 2.23, 1.14, 0.45, and 0.17 ng $g^{-1}$, respectively. Concentration ranges of SHCHs, SDDTs, and Schlordanes and HCB were 0.21–8.70, 0.10–4.35, 0.02–3.75, and nd–1.16 ng $g^{-1}$, respectively, in the 38 honey samples. Honey samples from developing countries generally contained higher concentrations of ΣHCHs, ΣDDTs, Σchlordanes, and HCB than those from developed countries. A comparison of the ratios of highest and lowest concentrations of ΣHCHs, ΣDDTs, Σchlordanes, and HCB in those honeys showed relative evenness of concentrations of the OCPs in honeys from developing countries and large variation in honeys from developed countries.

## 1. Introduction

Contamination of organochlorine pesticides (OCPs) in foods has been considered a serious threat to human health because of their environmental persistence, high accumulation, and high mammalian toxicity. They are ubiquitous in the environment because of their moderate vapor pressure, low solubility, and low reactivity (Jones & de Voogt, 1999; Wang et al., 2007). OCPs production, usage and disposal into the environment have been regulated or prohibited in most countries (Hung & Thiemann, 2002). However, residues of OCPs from historical agricultural applications are still persist in many environmental media (Guzzella et al., 2005) and continue to cycle through various routes, such as atmospheric transport and runoff (Meijer, Shoeib, Jantunen, Jones, & Harner, 2003; Meijer, Shoeib, Jones, & Harner, 2003). Many studies show that OCPs bio-accumulate in plants from polluted soil (González, Miglioranza, Aizpun De Moreno, & Moreno, 2003). Bio-accumulation levels in plant tissues can reach 10 to 1000 times greater than those in ambient environmental media such as air and water (Blasco et al., 2003). OCPs can enter into food chain via not only fatty products (Qu, Suri, Bi, Sheng, & Fu, 2010), but also non-fatty products such as honey (Blasco et al., 2004; Erdoğrul, 2007).

Honey is a natural, nutritious, healthy, and popular food produced by honey bees from nectar of plants (Tewari & Irudayaraj, 2004). Honey is often consumed by children, old and ill people, particularly in developing countries, therefore, honey must be free of any chemical contamination and be safe for human consumption (Tsipi, Triantafyllou, & Hiskia, 1999). The safety and quality control of honey products have become an international issue. Contamination of foods in general by pesticides, especially OCPs, has long been a concern for consumers and industry leaders.

OCP residues in honeys from different regions have been documented. For example, Al-Rifai and Akkel (1997) detected 50 pesticides in 26 honeys from Jordan and found that the honeys were more frequently contaminated with α-, β-, and γ-isomers of hexachlorocyclohexane (HCH). Anju, Beena, Gahlawat, Sihag, and Kathpal (1997) reported detections of OCPs in all 27 honey samples that were from India. Antonescu and Mateescu (2001) analyzed OCPs in 265 honey samples collected in Romania and found that 50% and 25% were positive for HCHs and dichlorodiphenyltrichloroethanes (DDTs), respectively. Blasco et al. (2004) reported residues of hexachlorobenzene (HCB) and HCHs in 14 Valencia, honey samples from Valencia, Spain. Bogdanov, Ryll, and Roth (2003) analyzed OCPs, organophosphates and fungicides in 27 Swiss honey samples and found no significant contamination. The objectives of this study were to determine residual levels, compositions, and distributions of HCHs, DDTs, chlordanes and HCB in honey samples from different geographic regions, and to elucidate the possible sources of pollution.

## 2. Materials and methods

### 2.1. Sample collection

Thirty-eight honey samples were commercially purchased from markets or mailed from different regions worldwide. Geographical

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origin information indicated on the labels of these of honey samples was used to group them into those from economically developed countries and those from developing countries based on the current approximate economic status (Table 1). For discussion purposes, New Zealand, Hawaii and Alaska were referred to as background regions due to their geographical isolation and low human population density. All honey samples were stored at −20 °C until extraction and analysis.

### 2.2. Sample extraction, cleanup and fractionation

A mixture of surrogate standards of 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X) and decachlorobiphenyl (PCB209) was added to each 20 g of the honey samples mixed with a 3-fold amount of anhydrous sodium sulphate ($Na_2SO_4$) prior to extraction, wrapped with filter paper, and then placed in a 64-mL extraction cell. The remaining volume of the cell was filled up with clean Ottawa sand (20–30 mesh). The sample cell was loaded into an accelerated solvent extractor (ASE) 200 system (Dionex, Sunnyvale, CA, USA). The extraction was performed with a mixture of acetone and methylene chloride (1:1, v/v) at a pressure of 1500 psi and temperature of 100 °C for three static cycles, a flush volume of 60% of the cell volume and a $N_2$ purge time of 5 s. A mixture of Ottawa sand and $Na_2SO_4$ was extracted in the same manner as the sample blank. All samples were extracted in triplicate.

After the extract was further dried with 30 g of anhydrous $Na_2SO_4$, it was reduced in volume to approximately 3 mL by using a rotary evaporator, and solvent-exchanged to hexane and purified on an aluminum/silica column (20 cm × 8 mm *i.d*). The column was packed, from the bottom to top, with neutral alumina (3 cm, 3% deactivated), neutral silica gel (4 cm, 3% deactivated), 50% sulphuric acid silica (2 cm), and anhydrous sodium sulphate (2 cm). The column was eluted with 20 mL of methylene chloride/hexane (1:1) to yield the OCP fraction. The fraction was concentrated to 20 μL under a gentle stream of high purity nitrogen gas after 20 μL of dodecane were added as the trapping solvent. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard prior to gas chromatography–ion trap mass spectrometry (GC–ITMS) analysis (Wang et al., 2007).

### 2.3. Instrumental analysis

OCPs were analyzed on a Varian 3800 GC and Saturn 2000 ITMS system (Varian, Walnut Creek, CA, USA). An aliquot of 2.0 μL of sample was injected in splitless mode with an AS8400 autosampler. The purge valve was activated 2 min after the sample injection. The column flow rate was 2 mL min$^{-1}$ of carrier gas (helium). The temperatures of the injector and ion trap were 280 °C and 250 °C, respectively. A DB-5MS capillary column (30 m × 0.25 mm *i.d*., 0.25 μm film thickness) was used for separation of OCPs. The oven temperature was started at 60 °C for 1 min, increased to 290 °C at a rate of 4 °C min$^{-1}$, and then held at 290 °C for 10 min. The ITMS was operated under the conditions previously described (Xu et al., 2009).

**Table 1**
Origins of 38 honey samples from different geographic regions.

| Sample no. | Origin information | Sample no. | Origin information |
|---|---|---|---|
| Developing countries | | 19 | Ontario, Canada |
| 1 | Bee Farm, Northern Thailand | 20 | Alaska, USA |
| 2 | Bee Farm, Northern Thailand | 21 | Alaska, USA |
| 3 | Bee Farm, Northern Thailand | 22 | California, USA |
| 4 | North Eastern China | 23 | Hawaii, USA |
| 5 | Bhutan | 24 | Hawaii, USA |
| 6 | Bhutan | 25 | Hawaii, USA |
| 7 | Jakarta, Indonesia | 26 | Hawaii, USA |
| 8 | Jakarta, Indonesia | 27 | Japan |
| 9 | Vietnam | 28 | New Zealand |
| 10 | India | 29 | New Zealand |
| 11 | Brazil | 30 | Washington, USA |
| Developed countries | | 31 | Hawaii, USA |
| 12 | Hawaii, USA | 32 | Hawaii, USA |
| 13 | Maryland, USA | 33 | Hawaii, USA |
| 14 | Kent, UK | 34 | Hawaii, USA |
| 15 | Virginia, USA | 35 | Hawaii, USA |
| 16 | California, USA | 36 | Hawaii, USA |
| 17 | Wisconsin, USA | 37 | Hawaii, USA |

### 2.4. Quality assurance and quality control

HCHs, DDTs, chlordane, and HCB were not detected in the blank control. The limits of detection (LODs) were determined as signals 3 times of the background signals. Peaks that were smaller than 3 times of the signal-to-noise ratio were considered undetected. The method LODs of individual HCH, DDT, chlordane, and HCB ranged from 1 to 10 pg g$^{-1}$. The average recoveries of the surrogate standards TC*m*X and PCB209 were 60 ± 8% and 85 ± 10%, respectively. Data reported in this paper were corrected according to the recoveries of the standards.

## 3. Results and discussion

### 3.1. HCHs

The concentrations of the total HCHs (ΣHCHs sum of α-, β-, γ-, and δ-isomers) in the honey samples labelled as originating in developing and developed countries ranged from 1.16 to 8.70 (mean 4.00 ± 2.57) ng g$^{-1}$ in developing countries and from 0.21 to 4.78 (mean 1.51 ± 1.17) ng g$^{-1}$in developed countries. The concentrations were much lower than those detected in honeys produced in the central zone of Portugal and the Valencian community of Spain (Blasco et al., 2004), but were similar to those found in the honeys produced in Kahramanmaraş City, Turkey (Erdoğrul, 2007). The ratio of highest and lowest concentrations (H/L) of ΣHCHs we detected in the honeys from developed countries (22.8) was approximately 3 times larger than that (7.5) from developing countries (Table 2). This result indicated evenness of HCH contamination levels in honey samples from developing countries and large variations of HCH contamination levels in honey samples from developed countries.

Fig. 1 shows the concentrations of ΣHCHs in 38 honeys labelled as originating in developing and developed countries. Honey samples from developing countries with the highest concentrations of ΣHCHs were from Thailand (No. 2) and India (No. 10). The lowest concentration of ΣHCHs was in the honey from North Eastern China (No. 4). The ban of technical HCH production since 1983 in China may have resulted in low residues of HCHs in these honey samples. However, until recently, HCH was used heavily for pest control in Thailand and is still used in India (Sarkar et al., 2008). In the developed countries, the highest concentrations of ΣHCHs were observed in samples from California, USA (No. 22) and Ontario, Canada (No. 19) while the lowest concentrations were in honeys labelled as originating in Hawaiian Islands, USA (Nos. 12, 23–26, and 31–38) and New Zealand (No. 29), the two ‘background’ regions.

HCHs are mixtures of different isomers. Commercial HCH products mainly include technical HCHs and lindane. Technical HCHs primarily consist of α-HCH (55%–80%, w/w), β-HCH (5%–14%), γ-HCH (8%–15%), and δ-HCH (2%–16%) while lindane mainly contains γ-HCH (>98%). A high ratio of α-HCH/ γ-HCH in honey samples may indicate input of technical HCHs while a low ratio may indicate high lindane usage (Li, Zhang, Qi, Li, & Peng, 2006). The mean α-HCH/ γ-HCH ratios detected were 1.85 ± 1.30 and 2.00 ± 2.10 in honeys labelled as originating in developing and developed countries, respectively. These ratios were lower than those of technical HCHs, indicating that HCHs in the samples might derive from mixed pollution sources resulting from applications of both technical HCHs and lindane (Table 2 and Fig. 2). In addition, among the HCH isomers, β-HCH is