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Organochlorine Pesticides Residues in Bottled Drinking Water from Mexico City

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Abstract This work describes concentrations of organochlorine pesticides in bottled drinking water (BDW) in Mexico City. The results of 36 samples (1.5 and 19 L presentations, 18 samples, respectively) showed the presence of seven pesticides (HCH isomers, heptachlor, aldrin, and p,p'-DDE) in bottled water compared with the drinking water standards set by NOM-127-SSA1-1994, EPA, and World Health Organization. The concentrations of the majority of organochlorine pesticides were within drinking water standards (0.01 ng/mL) except for β-HCH of BW 3, 5, and 6 samples with values of 0.121, 0.136, and 0.192 ng/mL, respectively. It is important monitoring drinking bottled water for protecting human health.

Keywords Organochlorine pesticides · Bottled drinking water

The widespread occurrence of organic chemicals in the environment is a matter of public health concern. Pesticides are extensively used to increase agricultural production by preventing losses due to pests. However, some are among the highly persistent, toxic, and bioaccumulative contaminants in the environment generally referred to as persistent organic pollutants (POPs) (WHO (World Health Organization) 2009). These toxicants get into the human body through the food chain, and can cause serious health problems (Albert and Rendon 1988). Studies have been carried out on pesticide contamination of foodstuffs from different parts of the world. Growing urbanization, changing food habits, exploding population are just some of the contributing factors responsible for increase in demand for food commodities leading to the use of more pesticides and fertilizers (Thacker et al. 2008). Surface water is vulnerable to contamination by pesticides because it may receive run-off directly from agricultural fields, urban areas and often from areas that typically receive pesticide applications. In order to adequately assess exposure levels of the general population to pesticides, it is necessary to obtain information on pesticide concentrations in drinking water (WHO 2009; Maloschik et al. 2007).

Some pesticides are known to resist biodegradation and therefore, they can be recycled through food chains and produce a significant bioaccumulation at the higher end of the chain (Shukla et al. 2006). For this reason, pesticide residue analysis in environmental samples has received increasing attention in the last few decades, resulting in numerous environmental monitoring programs in various countries for a broad range of pesticides. A common consequence of such persistent pollution is the contamination of surface waters with pesticide residues. This calls for urgenting attention in two areas: a) re-evaluation of environmental persistence and risks of currently registered and applied pesticides, and b) thorough monitoring of potentially water-contaminating pesticides in surface waters and in natural bodies (Mukherjeez and Gopal 2002; Maloschik et al. 2007; Donald et al. 2007).

Bottled water consumption has been steadily growing up the last three decades worldwide. The main reasons for this rapid consumption increase are the lack of safe and accessible drinking water and the taste of chemicals, particularly chlorine, used to purifying tap water. Furthermore, the efficient marketing and advertising strategies followed

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by the bottled water producers have enhanced this consumption. It is a fact that consumers who live in developed countries buy bottled water as a healthy alternative to other beverages, to improve their diet and health (Leivadara et al. 2008). Mexico is in second place globally in terms of consumption of bottled drinking water after Italy (Howard 2007). This behavior is supported by the poor quality of the water supply due to lack of maintenance and insufficient reservoir capacity; the population have the idea that it is healthiest to drink bottled water. This paper presents results of a study aimed at evaluating the presence of organochlorine pesticides in drinking bottled water in Mexico City, considering those with a high consumption amongst the population.

Materials and Methods

Bottled drinking water (BDW1–BDW6) samples (six for each brand) were bought in supermarkets in Mexico City, and preserved at room temperature. The samples were in bottles of 1.5 L (BDW1–BDW3) and 19 L (BDW4–BDW6). This research took place from November 2007 to March 2008 with the intention of monitoring some persistent organic contaminants such as organochlorine pesticides.

A 500 mL aliquot of each bottled water sample was transferred to a separating funnel, then extracted by shaking with 75 mL of ether–hexane (25%, V/V). Separately another 500 mL aliquot was extracted with 75 mL of hexane and the two extracts combined so that 1 L of sample was extracted in total. The organic phase was passed through anhydrous sodium sulfate to remove remnants of water then the samples evaporated in a rotary evaporator to 5 mL. Meanwhile, a chromatographic column was prepared with florisil deactivated with deionized water (1.25%) then topped with anhydrous sodium sulfate. The sample was applied to the column and the organochlorine pesticides were eluted with a mixture of hexane–ether (9:1 and 8:2). The organic extract was concentrated in a rotary evaporator to 3 mL and transferred to a vial for GC analysis (USEPA (United States Environmental Protection Agency) 1981).

The method was optimized for the analysis of 16 organochlorine pesticides by a GC (HP 6890 Series) with an EC detector (^{63}Ni). Analysis was carried out using a HP-5MS capillary column (crosslinked 5% PH ME Siloxane, 30 m long and 2 mm ID). The oven temperature was programmed from 90°C (2 min) at 30°C min^{-1}, to 180°C (0 min) at 1°C min^{-1}, to 200°C (0 min) at 10°C min^{-1}, and to 300°C (6 min). The injection port and detector temperature were kept at 320°C and the injection technique was split/splitless (2 μL). The helium (carrier gas) and nitrogen were maintained at a flow of 6 and 60 mL min^{-1}, respectively.

The insecticides analyzed were α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, endosulfan I, *p,p′*-DDE, dieldrin, endrin, endosulfan II, *p,p′*-DDD, endrin aldehyde, endosulfan sulfate, and *p,p′*-DDT (Chem Service Inc.).

The standard solutions were made from ultra-pure solvent and standards organochlorine pesticides injected in iso-octane. The concentration calculations were made by the external standard method.

The analytical quality control scheme included periodic analysis of reactive blanks, electronic blanks and duplicate samples. The accuracy of determination was routinely checked by injection of the middle point of the calibration curve.

Results and Discussion

In Table 1 average concentrations of the pesticides in the bottled drinking water. In general, the concentrations are shown. In general, the concentrations were quite similar in the different samples. Of the pesticides analyzed compounds only endosulfan II and dieldrin did not appear in the samples while *p,p′*-DDD, endosulfan I and endosulfan sulfate appear in some analyzed samples. The presence of these organic compounds demonstrates their persistence and the potential for a daily exposure.

In Table 2 individual compounds are grouped into classes of organochlorine pesticides, where alicyclics are dominant (average 60% of total present), followed by ten cyclodienics (average 24%) and finally aromatics compounds (average 16%) in the water samples. The total concentrations among bottled drinking water do not represent significant differences.

In Fig. 1 the individual organochlorine pesticides in bottled water samples are show, and highlight the presence of HCH isomers (α and β HCH, mainly) often *p,p′*-DDE and heptachlor. Similar to difference references about permissible levels, we compared the data with guidelines for drinking water quality from EPA, WHO and NOM-127-SSA1-1994. DDT and its metabolites did not exceed the guideline value of 1.0 ng/mL, while heptachlor and heptachlor epoxide did not exceed the value of 0.03 ng/mL and individual isomers of HCH did not exceed the value of 0.2 ng/mL.

According to the Mexican regulations, application of some pesticides such as *p,p′*-DDT, endosulfan, aldrin, and heptachlor are forbidden, and they are classified by IARC and EPA as probable carcinogens. It can be assumed that

Table 1 Organochlorine pesticides (ng/mL, with standard deviation) in commercial bottled drinking water from Mexico City

Compound	BDW1	BDW2	BDW3	BDW4	BDW5	BDW6
α-HCH	0.045 (±0.073)	0.042 (±0.059)	0.098 (±0.097)	0.053 (±0.049)	0.052 (±0.063)	0.068 (±0.090)
β-HCH	0.065 (±0.068)	0.048 (±0.060)	0.121 (±0.143)	0.049 (±0.053)	0.104 (±0.136)	0.152 (±0.192)
γ-HCH	0.019 (±0.020)	0.031 (±0.035)	0.027 (±0.030)	0.026 (±0.025)	0.020 (±0.025)	0.033 (±0.043)
δ-HCH	0.040 (±0.088)	0.033 (±0.072)	0.046 (±0.096)	0.022 (±0.030)	0.012 (±0.030)	0.012 (±0.043)
Heptachlor	0.042 (±0.077)	0.036 (±0.060)	0.057 (±0.083)	0.033 (±0.035)	0.021 (±0.026)	0.042 (±0.048)
Aldrin	0.025 (±0.037)	0.020 (±0.034)	0.026 (±0.036)	0.014 (±0.015)	0.012 (±0.017)	0.027 (±0.028)
Heptachlor epoxide	0.004 (±0.010)	0.003 (±0.008)	0.007 (±0.011)	0.003 (±0.007)	0.003 (±0.008)	0.009 (±0.010)
Endosulfan I	ND	ND	0.005 (±0.008)	0.001 (±0.046)	ND	0.002 (±0.005)
p,p′-DDE	0.057 (±0.093)	0.057 (±0.092)	0.060 (±0.087)	0.029 (±0.033)	0.042 (±0.049)	0.050 (±0.064)
Dieldrin	ND	ND	ND	ND	ND	ND
Endrin	0.001 (±0.002)	0.005 (±0.013)	0.005 (±0.012)	0.005 (±0.012)	ND	0.008 (±0.020)
Endosulfan II	ND	ND	ND	ND	ND	ND
p,p′-DDD	ND	0.001 (±0.003)	0.002 (±0.005)	ND	ND	ND
Endrin aldehyde	0.004 (±0.009)	0.007 (±0.009)	0.004 (±0.009)	0.002 (±0.003)	0.001 (±0.003)	0.003 (±0.007)
Endosulfan sulfate	ND	ND	ND	ND	0.033 (±0.081)	0.015 (±0.037)
p,p′-DDT	0.004 (±0.010)	0.003 (±0.007)	0.004 (±0.010)	0.003 (±0.008)	0.003 (±0.006)	0.009 (±0.014)

HCH, Hexachlorocyclohexane; *p,p′-DDE*, 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene; *p,p′-DDD*, 1,1-dichloro-2,2-bis (4-chlorophenyl) ethane; *p,p′-DDT*, 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane; *ND*, not detected; the numbers in parentheses represent standard deviations from six samples for each brand of water

Table 2 Compound types (ng/mL) of organochlorine pesticides in drinking bottled water of Mexico City

Compound type	DBW1	DBW2	DBW3	DBW4	DBW5	DBW6
Alicyclics (α to δ HCH)	0.169 (55.2)	0.154 (53.9)	0.292 (63.6)	0.150 (62.5)	0.188 (62.0)	0.265 (61.6)
Aromatics (*p,p′*-DDE to *p,p′*-DDT)	0.061 (19.9)	0.061 (21.3)	0.063 (13.7)	0.032 (13.3)	0.045 (14.9)	0.059 (13.7)
Cyclodienics (heptachlor, aldrin, heptachlor epoxide, endosulfan I, dieldrin, endrin, endosulfan II, endrin aldehyde and endosulfan sulfate)	0.076 (24.9)	0.071 (24.8)	0.104 (22.7)	0.058 (24.2)	0.070 (23.1)	0.106 (24.7)
Total concentration	0.306	0.286	0.459	0.240	0.303	0.430

Numbers in parentheses represent percent of total concentration (n = 6 for each water brand)

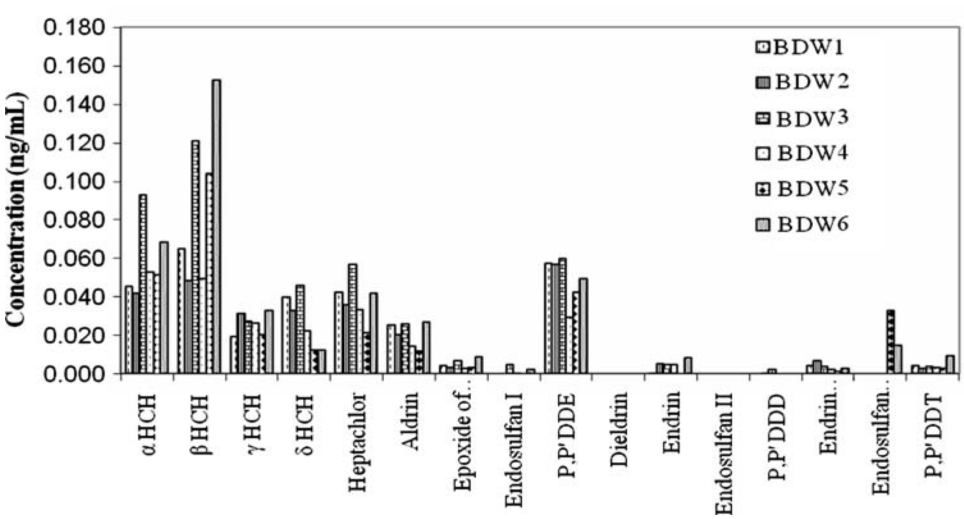

Fig. 1 Concentrations of organochlorine pesticides in bottled drinking water in samples from Mexico City

some organochlorine pesticides are used to control pests in food industries, and come to be in bottled water; further some others such as endosulfan are used in agriculture, the result is that water reservoirs for the population and industry are contaminated.

The organochlorine pesticides which were detected, showed lower concentrations than the target set by NOM-127-SSA1-1994, WHO and EPA. Harrison et al. (2000) mentioned that insecticides are more toxic that herbicides and consequently they have higher tolerable daily intakes, therefore it is important to monitor the bottled water process and to guarantying a product with low levels of these organic compounds.

The presence of pesticide residues in bottled drinking water may have both important commercial and health implications because the bottled water quality may be affected by the source, treatment type, container type and length of storage (Alabdula'Aly and Khan 1999). Good practice in the process of preparation of the bottled water is necessary to avoid contamination. The major toxicological concern regarding pesticides as contaminants of drinking water is the potential exposure of large populations to low concentrations over long periods of time. Of particular concern are substances that may be carcinogenic and those that have a tendency to bioaccumulate in the organs (Harrison et al. 2000; Ramesh and Vijayalakshmi 2002).

It is important that Mexicans Official Regulations will be more specific with reference to organic contaminant contents such as organochlorine pesticides over permissible maximum levels. The reality is that no food is free of contaminants.

We recommendation follow statements:

Monitoring studies need to be carried out periodically of bottled drinking water to guarantee the quality of a product that is of high consumption among the population. This will also help to determine general levels of environmental pollution and the persistence pattern of pesticides.

It is important to establish if the toxicity of a mixture of pesticides residues is different from the sum of the toxicities of the single compounds, or if two or more pesticides simultaneously present in drinking water have synergistic effects.

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