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Organochlorine pesticides residues in commercial milk: a systematic review

Residuos de pesticidas organoclorados en leche commercial: una revisión sistemática

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Abstract

Milk is a very important food for human consumption, mainly due to its content of fat, protein, vitamins and minerals. However, the use of organochlorine pesticides (OCP) for decades has contaminated the soil, water and air, and thus has also contaminated the milk. In this sense, in the present work a review of scientific articles was carried out, between the years 2000 and 2018, related to the evaluation of the degree of contamination of different types of milk by OCPs in different regions of the world. As a result, it was observed that although OCPs have been banned for use in agriculture since the 1980s, these compounds or their metabolites have still been detected in many samples, and in some cases the levels were above the maximum allowed by the World Health Organization. In addition, most of the samples presented contamination, which makes them a great risk to human health due to their bioaccumulation.

Keywords: DDT metabolites; persistent organic pollutants; hexachlorobenzene; cyclodienes; chlorinated hydrocarbons.

Resumen

La leche es un alimento importante en la dieta de la población humana, principalmente por su contenido en grasas, proteínas, vitaminas y minerales. No obstante, el uso de pesticidas organoclorados (PCO) durante décadas ha contaminado el suelo, el agua y el aire y, por tanto, también ha contaminado la leche. En este sentido, en el presente trabajo se realizó una revisión de los artículos científicos, entre 2000 y 2018, relacionados con la evaluación del grado de contaminación de diferentes tipos de leche por PCO en varias regiones del mundo. Como resultado, se observó que, aunque el uso de los PCO ha sido prohibido en la agricultura desde la década de 1980, estos compuestos o sus metabolitos aún se han detectado en muchas muestras, y en algunos casos los niveles se encontraban por encima del máximo permitido por la Organización Mundial de la Salud. Además, la mayoría de las muestras presentaron contaminación, lo que las convierte en un gran riesgo para la salud humana debido a su bioacumulación.

Palabras clave: metabolitos del DDT; contaminantes orgánicos persistentes; hexaclorobenceno; ciclodienos; hidrocarburos clorados.

Introduction

Milk is a fundamental food for a healthy and balanced diet, since its composition is rich in minerals (e.g. Ca, Na), fat acids, proteins and vitamins (Haug et al. 2007). In addition, studies have shown that milk consumption is related to the prevention of chronic diseases (e.g. cardiovascular diseases, cancer, obesity and diabetes), as well as, it has a great importance in the formation of bones (Pereira, 2014). However, high-fat animal foods are potential sources of contaminants, mainly by persistent organic pollutants (POPs): organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs).

Persistent organic pollutants are very resistant to chemical transformations and due of their low polarity; they are usually bio-accumulated in higher fat tissues (Darko and Acquaah, 2008). Organochlorine pesticides stand out among these persistent compounds, since they were used on a large scale in the control of agricultural pests, mainly, between 1940 and 1990, as well as in the control of tropical diseases (e.g. malaria, chagas disease) transmitted by insects (Santos et al., 2015).

OCPs include chlorinated derivatives of diphenyl ethane (including DDT and its metabolites DDE and DDD and methoxychlor); hexachlorobenzene (BHC); the group of hexachlorocyclohexanes (α-HCH, β-HCH, γ-HCH and Δ-HCH or lindane); the group of cyclodienes (aldrin, dieldrin, endrin, chlordane, nonachlor, heptachlor and heptachloro-epoxide), and chlorinated hydrocarbons (dodecachlor, toxaphene, and chlordecone) (Klassen 1985). The DDT was one of the most commonly used organochloride pesticides due to its ability to kill a wide spectrum of insects, to have a low production cost and to have no odor (Lallas, 2001). In the 1940s, DDT was widely applied with great efficiency in the control and insects in agriculture and of diseases whose vectors were insects, being considered one of the great triumphs of that period (D'Amato et al., 2002).

Based on the denunciations made in the book 'Silent Spring' of 1962 the writer Rachel Carson, a large number of studies on the ecological impacts of these products were carried out. These studies pointed to the harmful effects of organochlorine pesticides, which led several European countries to ban the use of DDT and other OCPs in agriculture (D'Amato et al., 2002).

However, despite the banishment of these pesticides for use in agriculture, their use is still permitted in the control of vectors of tropical diseases (e.g. malaria, leishmaniasis, chagas disease) (D'Amato et al., 2002; Santos et al. 2015). In addition, it is important to note that because these compounds are highly resistant to biotransformation, they can be bio cumulated in foods such as meat and milk, which makes them a risk to human health (Ronchi et al., 2006; Kampire et al., 2011; Deti et al., 2014).

In this context, several studies found the presence of DDT and its metabolites, as well as other OCPs, in different matrices (eg soil, water, milk), pointing out the risks to public health (Lemes et al., 2004; Rojas-Squella et al., 2013). In addition, several studies indicate that rates of reduction in organochlorine levels in the terrestrial environment are slow and that due to the low costs these pesticides are still used legally or illegally in some countries (Liess et al., 2005; Jayaraj et al., 2017). In this sense, the main route of human exposure to organochlorines is through food, especially those rich in fat such as: meat, fish and dairy products (Jayaraj et al., 2017). Among these, milk stands out, since it is a fundamental food for the development of children besides their derivatives being widely consumed in the human diet. Therefore, a continuous assessment of OCP levels is required, especially in milk, in order to minimize the risk to human health (Luzardo et al., 2012; Avancini et al., 2013).

Residues of pesticides and their metabolites can be found in milk due to contamination of water, use of pesticides in the control of ectoparasites directly in the animal, consumption of contaminated pastures and/or rations (Bajwa and Sandhu, 2014). The presence of these compounds in milk may represent a potential risk to public health, so milk is used as an indicator to measure the persistence of chemicals in agriculture and environmental pollutants.

In this context, the objective of this work was to perform a systematic review of studies aimed at analysing the levels of OCPs in milk samples marketed and consumed by the world population. In addition, to assess which pesticides were most found and which regions presented levels of these pesticides above the maximum allowed by FAO/WHO.

Methodology

This systematic review study was developed using the following articles and virtual database platforms: SciELO, PubMed, Science Direct, Lilacs, Medline, Elsevier. A total of 100 items were found using the following keywords: organochlorines, residues, pesticides, milk for consumption. Of these, 29 articles were selected, covering the years 2000 to 2018 (Table 1). The articles were separated according to the regions where the studies were conducted in: European, Asian, South American, North American and African countries.

Table 1. Summary of selected articles.

Author	Region	Sample type	Organochlorine pesticides detected
Luzardo et al. (2012)	Spain (Canary Islands)	Fresh and organic bovine milk	p,p'-DDE, aldrin, cis-chlordane, trans-chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), endosulfan (α and β)
Cerkvenik et al. (2000)	Slovenia	Fresh bovine milk	α-HCH, lindane, heptachlor, DDT.
Ronchi et al. (2006)	Italy	Fresh bovine milk	β-HCH
Tsakiris et al. (2015)	Greece	Pasteurized bovine milk	DDT, DDE, DDD
Witczak et al. (2016)	Poland	Goat milk	HCH (α, γ) and p,p'-DDD
Zhong et al. (2003)	China	Conventional bovine milk	HCH, DDT and aldrin
John et al. (2000)	India (Rajasthan)	Bovine and buffalo milk	DDT, DDE and p,p'-DDD, isomers of hexachlorocyclohexane (HCH, α, β and γ), heptachlor epoxide and aldrin.
Nag and Raikwar (2008)	India (Bundelkhand)	Bovine milk	HCH (α, β, γ and Δ), endosulfan (α, β and sulfate), DDD, DDE and DDT
Pandit and Sahu (2002)	India (Mumbai)	Bovine milk	HCH (α, β, γ and Δ), DDD, DDE and DDT
Pandit et al. (2002)	India (Maharashtra)	Bovine milk	DDT and HCH
Kaushik et al. (2014)	India (Haryana)	Fresh bovine milk	HCH (α, β and γ), DDT and endosulfan
Salem et al. (2009)	Jordan	Bovine milk	HCH (α, β and γ) and p,p'-DDE
Sajid et al. (2016)	Pakistan (Faisalabad)	Fresh bovine and buffalo milk	Cyhalothrin, deltamethrin, endosulfan (α and β), bifenthrin, permethrin, cypermethrin, chlorpyrifos, perfinophos
Singh et al. (2013)	Bengal (Nadia District)	Bovine milk	Lindane, endosulfan (α and β)
Bulut et al. (2011)	Turkey (Afyonkarashisar)	Bovine, buffalo and ovine milk	HCH (α, β, γ and Δ), vinclozolin, heptachlor, aldrin, tetraconazole, trans-chordan-γ, heptachlor epoxide, α-endosulfan, cis-chlordane-α, dieldrin, endrin, β-ndosulfan, endosulfan sulfate and methoxychlor.
Avancini et al. (2013)	Brazil (Mato Grosso do Sul)	Bovine milk	Aldrin, DDT, mirex, endosulfan, chlordane, dicofol, heptachlor and dieldrin
Heck et al. (2007)	Brazil (Rio Grande do Sul)	Fresh and pasteurized bovine milk	α-HCH, lindane, aldrin, HCB, pp'-DDE, op'-DDD, pp'-DDD and op'-DDT) and PCBs (congeners 10, 28, 52, 138 and 180)
Díaz-Pongutá et al. (2012)	Colombia (Córdoba)	Fresh bovine milk	p,p'-DDT, α-HCH, β-HCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide and chlordane
Lemes et al. (2004)	Brazil (São Paulo)	Bovine milk	No pesticides was detected
Hernández et al. (2010)	Colombia (São Pedro)	Fresh bovine milk	p-DDT, endrin, endosulfan, γ-chlordane, heptachloroxide, γ-BHC, endosulfan; heptachlor, heptachlor epoxide; γ -CLD: γ -clendal
Lans-Ceballos et al. (2018)	Colombia (Monteria)	Pasteurized bovine milk	Σα-HCH/βHCH, γ-HCH, δ-HCH, ΣAldrin/Dieldrin, ΣHeptachlor/Heptachlor epoxide, Endrin, α-chlordane, γ-chlordane and Endosulfan I
Gutiérrez et al. (2012)	Mexico (Chiapas)	Organic bovine milk	HCH (α, β and γ), heptachlor epoxide, DDT, aldrin, dieldrin and endrin
Tolentino et al. (2014)	Mexico	Milk with special formula for children	α-HCH, γ-HCH, aldrin, heptachlor and heptachlor epoxide
Guitierrez et al. (2013)	Mexico (Hidalgo)	Fresh bovine milk	α-HCH, endosulfan α, p, p›-DDT , dieldrin, endrin e heptacloro.
Schettino et al. (2013)	Mexico (Central Region)	Goat milk	HCH (α, β, γ and Δ), heptachlor, heptachlor epoxide, aldrin, dieldrin and p, p-DDT
Darko and Acquaah (2008)	Ghana (Kumasi)	Fresh bovine milk	Lindane, aldrin, dieldrin, endosulfan, dichlorodiphenyltrichloroethane (DDT)
Kampire et al. (2011)	Kampala	Fresh and pasteurized bovine milk	Aldrin, dieldrin, endosulfan, lindane, DDT, DDE, DDD
Shaker and Elsharkawy (2015)	Egypt (Assiut)	Milk bufalino	Alachlor, dieldrin, HCB, lindane and methoxychlor
Deti et al. (2014)	Ethiopia	Bovine and goat milk	Aldrin, endosulfan (α and β), p,p'-DDE, o,p'-DDT and p, p'-DDT)

Results

European countries

The population of the Canary Islands archipelago has one of the highest rates of milk intake in Spain and Europe. Luzardo et al. (2012) evaluated the organochlorine pesticide (OCP) levels in 16 conventional and 10 organic bovine milk sold in this region of Spain. In relation to DDT, only the metabolite p,p'-DDE was detected in about 80% of the samples evaluated, with average contents of 4.85 and 4.74 ng g^{-1}, respectively, for conventional and organic milk. Hexachlorobenzene (HCB), aldrin, cis/trans-chlordane, dieldrin, endrin and heptachlor were also detected in the samples. Endosulfan (α and β isomers) was also detected in 50% of conventional milk samples and only in 10% of organic milk samples. Total OCP levels were higher in conventional than in organic bovine milk. Finally, it was found that the average levels of organochlorine pesticides in milk were below the maximum residue limit (MRL) established by legislation (FAO/WHO, 2014).

Cerkvenik et al. (2000) conducted a study where they evaluated pesticide levels in 188 samples of fresh bovine milk from 19 dairy farms in Slovenia. The levels of α-HCH, lindane and heptachlor were below the detection limit (0.003 mg kg^{-1}) in 86%, 90% and 100% of the samples, respectively. The maximum α-HCH content was 0.008 mg kg^{-1} and lindane 0.023 mg kg^{-1}. However, DDT was detected in more than 93% of the samples, with levels among 0.005 and 0.020 mg kg^{-1}. OCPs residue levels in all samples were below the maximum tolerance levels.

In Central Italy in 2005 a large area contaminated with hexachlorocyclohexane was found, which presented average levels of this pesticide around 0.08 mg kg^{-1} of soil (Ronchi et al., 2006). In order to augment the presence of HCH and to understand its metabolites, dairy cows were fed fodder and supplements, obtained from the contaminated region (with HCH levels below the LOD) and after evaluating their contents in the milk, collecting samples each three weeks, for three months. The HCH levels found in the samples were higher than the permitted limit in the European Union (0.003 mg kg^{-1}), which confirms the bioaccumulation of this pesticide and the potential risk for humans.

In order to evaluate the potential health risks, especially of children, due to the consumption of milk contaminated with DDT residues and their metabolites, Tsakiris et al. (2015) evaluated 196 samples of pasteurized bovine milk marketed in Greece. DDT or one of its metabolites was detected in 97.4% of the samples, at levels higher than the maximum permitted by the European Union. Witczak et al. (2016) recently evaluated the presence of organochlorine pesticides in goat leida produced on two farms in Poland between 2009 and 2013. The results showed that the majority of the samples had levels below the maximum limit (8 ng g^{-1}). The highest levels detected were HCH (γ- and β) (4.85 ng g^{-1}) and p, p'-DDD (7.86 ng g^{-1}).

Asian countries

Zhong et al. (2003) evaluated the levels of organochlorine pesticides and their metabolic residues in 72 samples of commercial milk in China. The mean total HCH and DDT contents were, respectively, 0.038 and 0.046 mg kg^{-1}. In addition, the aldrin pesticide was detected in nine samples, with mean contents of 0.035 mg kg^{-1}. Heptachlor and its metabolites were not found in any sample analyzed. Finally, only three samples showed levels of DDT and HCH above the level of tolerance accepted by the FAO/WHO (FAO, 2014).

In 2000 John et al. (2000) evaluated bovine and buffalo milk samples in the city of Jaipur in India to assess the degree of local contamination by organochlorine pesticide residues. In this study, all samples analyzed were contaminated by DDT, DDE and DDD, HCH (α, β and γ isomers), heptachlor epoxide and aldrin. In addition, all samples showed seasonal variations in pesticide contents, which may be associated with the pesticide application periods in agriculture, among other factors. Samples collected during the winter season contained higher levels of residue compared to the other seasons. Regarding the maximum tolerance limit, aldrin, HCH (α, β and γ) and heptachlor were found to be above the recommended maximum limit, whereas DDT and its metabolites were below. Nag and Raikwar (2008) monitored organochlorine pesticide levels in 325 bovine milk samples in the Bundelkhand region of India. Of these samples, a total of 206 (63.38%) had contamination with at least one type of organochlorine pesticide or one of its metabolites. The mean concentration of HCH (α, β, γ and Δ) was 0.162 mg kg^{-1}. Endosulfan (α, β and sulfate) was detected in 89 samples with a mean concentration of 0.0492 mg kg^{-1} whereas DDT and its metabolites (DDE and DDD) were detected in 114 samples with a concentration of 0.1724 mg kg^{-1}. Finally, dicofol was detected in 17 samples. However, only five samples presented levels of α-HCH above the maximum allowed level.

Another study carried out in Mumbai, India, monitored the organochlorine pesticide content in 520 samples of bovine milk, where most of them presented contamination by some type of pesticide (α-HCH, β-HCH, γ-HCH, Δ-HCH, DDD, DDE and DDT), however only α-HCH presented high levels in some samples (Pandit and Sahu, 2002). Pandit et al. (2002) evaluated the levels of organochlorine pesticides in samples of commercial bovine milk in different cities of Maharashtra in India. In these samples, the levels of DDT and its metabolites were higher than those of HCH, which may be related to the use of this product in the antimalarial sanitary control, very common in that region. All levels of organochlorine pesticide residues in milk were below the maximum levels allowed by FAO/WHO, 2014.

In 2014 Kaushik et al. (2014) evaluated the seasonal trends of organochlorine pesticide residues in fresh bovine milk from rural areas of Haryana, India. During the post-monsoon season (alternation between the rainy season and the dry season) the highest contamination by HCH and DDT was detected in 43% and 53% of the samples, respectively, while endosulfan presented the highest levels in 36% of the samples during winter. During the study period, only 2% of the milk samples exceeded the maximum residue limit recommended by the WHO, 1% of samples for α-HCH and γ-HCH, 9% for β-HCH recommended by PFAA and 30% of DDT as prescribed by FAO/WHO, 2014

In Jordan, the levels of organochlorine pesticide residues in 233 milk samples (commercial milk, butter, cheese and yoghurts) were evaluated. HCH (α, β and γ) were only detected in 21 milk samples (Salem et al., 2009). In addition, two milk samples had pp'-DDE levels above the maximum limit allowed by FAO/WHO, 2014. The impact of seasonal variation on organochlorine pesticide residues on buffalo and bovine milk from selected farms in the Faisalabad region of Pakistan was analysed by Sajid et al. (2016). Two hundred milk samples from 20 dairy farms were randomly selected to evaluate the incidence of organochlorine pesticide residues. The results evidenced the presence of cyhalothrin, deltamethrin, endosulfan (α, β), bifenthrin, permethrin, cypermethrin, chlorpyrifos, perfinophos. The results showed that approximately 80% of bovine and buffalo samples were contaminated with some type of OCPs, mainly in winter. Samples of buffalo milk 85% (winter) and 78% (summer), and bovine 83% (winter) and 75% (summer) presented some type of contamination. Endosulfan (α, β) contaminated samples exceeded the maximum levels allowed by FAO/WHO, (2014) in both winter and summer.

Bulut et al. (2011) analyzed the levels of organochlorine pesticide residues in bovine, buffalo and sheep milk in the Afyonkarahisar region of Turkey. The results indicated that the samples were contaminated by HCH (α, β, γ and Δ), hexachlorobenzene (HCB), vinclozolin, heptachlor, aldrin, tetraconazole, trans-chlordane-γ, heptachlor epoxide, (trans-isomer) α-endosulfan, cis-chlordane-α, dieldrin, endrin, β-endosulfan, endosulfan sulfate and Methoxychlor. The dominant pesticides in all the samples examined were β-HCH with the following average concentrations: in buffalo milk 63.36 ng mL^{-1}, in bovine milk 91.32 ng mL^{-1} and in sheep milk 122.98 ng mL^{-1}. The levels of organochlorine pesticides were found to have a mean concentration of 243.81 ng mL^{-1} in sheep milk, 151.02 ng mL^{-1} in bovine milk and 133.38 ng mL^{-1} in buffalo milk. However, only heptachlor epoxide exceeded the acceptable limit in relation to European Union (EU) regulations.

South America's countries

In Brazil, Avancini et al. (2013) evaluated the presence of organochlorine compounds in 100 samples of bovine milk in the state of Mato Grosso do Sul. A total of 90% of the samples had some type of organochlorine pesticides. Among the contaminated samples (% in parenthesis) were contaminated with aldrin DDT (44), mirex (36), endosulfan (32), chlordane (17), dicofol (14), heptachlor (11) and dieldrin (11). Among these samples, 47% presented levels of chlordane above the maximum allowable limit (2.0 ng g^{-1}). Of the total samples contaminated with aldrin/dieldrin, 14% had levels above the maximum permitted limits (6.0 ng g^{-1}). Finally, among the samples contaminated with heptachlor, 30% presented levels greater than 6.0 ng g^{-1}. In the state of Rio Grande do Sul, Brazil, Heck et al. (2007) verified the presence of organochlorine pesticides in samples of fresh and pasteurized milk (UHT). In all samples analyzed, α-HCH, lindane, aldrin, HCB, pp'-DDE, op'-DDD, pp'-DDD, op'-DDT) and PCBs (congeners 10, 28, 52, 138 and 180). The mean contents (ng g^{-1}) of op'-DDD, lindane and PCB 180 were, respectively, 7.38, 6.09 and 5.31. The levels of α-HCH (4 ng g^{-1}), lindane (10 ng g^{-1}), aldrin (6 ng g^{-1}) and DDT (50 ng g^{-1}) exceeded the MRL in some samples. In the state of São Paulo, Brazil, Lemes et al. (2004) evaluated levels of pesticide residues in 73 commercial bovine milk samples and no organochlorine pesticides were detected in the analyzed samples.

Hernández et al. (2010) evaluated the presence of organochlorine pesticide residues in bovine milk samples from animals fed cotton in Colombia. All samples showed contamination by at least one pesticide of this class. Eldrin, DDT (and metabolites) and aldrin had the highest mean levels (0.62, 0.59 and 0.52 µg mL^{-1}, respectively), but no sample had higher levels than the maximum allowed. Díaz-Pongutá et al. (2012) evaluated the presence of organochlorine pesticides in samples of fresh bovine milk in the region of Córdoba, Colombia. A total of

63 samples were evaluated, with the highest pesticides being p,p'-DDT (65.1%), endrin (49.2%) and dieldrin (39.7%). The other contaminants were δ-HCH (7.9%), chlordane (4.8%) and heptachlor (1.6%). Lans-Ceballos et al. (2018) evaluated the presence of OCPs in samples of pasteurized bovine milk in Montería, Colombia. Of the 144 analyzed samples, all had OCP content above the Maximum Residual Limit established by the Codex Alimentarius (FAO/WHO, 2014). Concentrations of α-HCH/β-HCH, γ-HCH, δ-HCH, aldrin/dieldrin, heptachlor/heptachlor epoxide, eldrin, α-chlordane, γ-chlordane and endosulfan were 0.53; 0.15; 0.57; 0.40; 0.22; 0.20; 0.014; 0.002 and 0.028 mg kg^{-1}, respectively.

North America countries

In the State of Chiapas, Mexico, Gutiérrez et al. (2012) analyzed bovine milk from organic farms. The following organochloride pesticide residues, α-HCH, β-HCH, γ-HCH, heptachlor epoxide, DDT and isomers, aldrin, dieldrin and endrin were identified and quantified. The mean values (ng g^{-1} in parenthesis) were: α-HCH (3.62), β-HCH, γ-HCH (0.34), heptachlor epoxide (0.67), DDT (1.53), aldrin/dieldrin (0.77) and endrin (0.66). In general, the values found in bovine milk from organic farm were lower than the limit allowed by the Codex Alimentarius (FAO/WHO, 2014). Tolentino et al. (2014) evaluated milk with its own formulation for children, marketed in southern Mexico. All samples analyzed showed α-HCH contamination and more than 80% presented β-HCH, γ-HCH, aldrin, heptachlor and heptachlor epoxide, as mean values of 0.24; 0.13; 0.32; 0.62; 0.92 and 0.18 μg kg^{-1}, respectively, however, all samples presented levels below the allowed limits. Gutierrez et al. (2013) evaluated the levels of organochlorine pesticide residues in cattle milk from farms in Hidalgo, Mexico. The organochlorine pesticide residues found were, α-HCH, endosulfan (α), p, p›-DDT, dieldrin, endrin and heptachlor. It is worth noting that OCP levels in milk were evaluated in two periods, with the highest levels during the rainy season due to pest control in the pasture and sheds. According to the Codex Alimentarius (FAO/WHO, 2014) regulations, individually analyzed pesticides did not exceed the permitted limits. Schettino et al. (2013) evaluated the levels of organochlorine contaminants in 40 milk samples of two goat breeds (Alpinas and Saanen) in central Mexico. The organochlorine pesticide residues found in the analyzed samples were HCH (α, β, γ and Δ), heptachlor, heptachlor epoxide, aldrin, dieldrin and p, p-DDT. It is worth noting that in this region agricultural production has national economic importance. It was found that the concentrations of the majority of organochlorine pesticides in the milk samples were low, however, the levels of Δ-HCH, heptachlor and heptachlor epoxide were higher than the Codex Alimentarius (FAO/WHO, 2014) in 17.3%, 50% and 13% of the samples, respectively.

African countries

Darko and Acquaah (2008) found residues of aldrin, dieldrin, endosulfan and DDT in samples of bovine milk from Kumasi in Ghana. The mean content of dieldrin was 1.32 mg kg^{-1}. The mean levels of aldrin and dieldrin and of endosulfan in milk were well below their maximum limit of 6.00 mg kg^{-1} and 4.00 mg kg^{-1}, respectively. The mean DDT content in the samples was 12.53 mg kg^{-1}. Kampire et al. (2011) evaluated samples of fresh and pasteurized bovine milk from Kampala. Aldrin, dieldrin, endosulfan, lindane, DDT and their metabolites were detected in the samples. The average concentration of organochlorine pesticides found in fresh milk samples was 0.026 (lindane), 0.002 (endosulfan), 0.007 (dieldrin) and 0.009 (aldrin) mg kg^{-1}. The mean concentrations of p, p'-DDE, p, p'-DDT and p'-DDT were 0.009; 0.033 and 0.008 mg kg^{-1} and 0.008. 0.025 and 0.007 mg kg^{-1} in fresh and pasteurized milk, respectively. Most of the residues detected were above the residue limits established by FAO/WHO, 2014. In this context, the bioaccumulation of such waste is likely to pose a risk to the health of milk consumers. The total OCP values detected in fresh milk samples were higher than the FAO/WHO tolerance levels. While only the border showed levels above the Maximum Residue Limits (MRL) in pasteurized milk samples (FAO/WHO, 2014). Shaker and Elsharkawy (2015) evaluated the OCP levels in samples of fresh buffalo milk in Assiut in Egypt. Five OCPs were detected: alachlor, dieldrin, hexachlorobenzene, lindane and methoxychlor. However, alachlor and dieldrin residue levels were lower than the MRL as established by the European Commission (EC). The level of lindane residue exceeded MRLs in 44% of the samples and methoxychlor and HCB residue also exceeded the MRLs in 33, 66 and 88% of the samples analyzed. Deti et al. (2014) verified the presence of persistent organochlorine pesticide residues in bovine and goat milk collected in different regions of Ethiopia. The study investigated the bioaccumulation of organochlorines in these two types of milk. Aldrin, α-endosulfan, β-endosulfan, p, p'-DDE, o, p'-DDT and p, p'-DDT were detected. Aldrin was detected only in a bovine milk sample and endosulfan (α) was found in a goat›s milk sample (142.1μg kg^{-1}) and a bovine milk sample (47.8μg kg^{-1}). The levels of o, p'-DDT and p, p'-DDT were high in almost all samples. The mean total DDT (excluding DDD) in the samples was 328.5 μg kg^{-1}. All pesticides were detected in one or more samples, showing the risk that this could cause to the environment and human health. All pesticide residues found were above the MRL allowed by FAO/WHO, 2014.

Discussion

In general, residues of OCPs or their metabolites were detected in all the studies presented, indicating a degree of global contamination by these pollutants. The pesticides detected in the countries studied in the European continent were: DDT, DDE, DDD, aldrin, cis and trans-chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB); endosulfan (α and β), lindane; heptachlor and HCH isomers (α, β γ). The DDT and its metabolites were the most frequent in the samples studied. It is important to note that DDT and halogenated cyclodienes were banned in European countries in the 1970s, which may indicate that they remained in the soil and passed on to the vegetation planted therein and was later bioaccumulated through animal feed. Only the study performed in Greece showed values above the maximum residue limit established for (β-HCH) (Ronchi et al., 2006).

The most detected pesticides in the Indian milk samples were the hexamerlocyclohexane (HCH) and DDT isomers and their metabolites. In Rajasthan (India) the amount of pesticides found was above the maximum residue limit for aldrin, HCH (α, β and γ) and heptachlor (John et al., 2000). In China, three analyzed samples had a residue limit above what is allowed for DDT and HCH pesticides (Zhong et al., 2003). In Bundelkhand (India) five samples obtained values above what is allowed for α-HCH (Nag and Raikwar, 2008). Also in Mumbai in India, the MRL for α-HCH was higher than that allowed in the analyzed milk samples (Pandit and Sahu, 2000). In Haryana, India, only 2% of milk samples exceeded the maximum limit for α-HCH and γ-HCH and β-HCH and DDT (Kaushik et al., 2014). In Jordan the pp'-DDE MRL in two milk samples was above the recommended value (Salem et al., 2009). In Faisalabad, Pakistan, samples of milk contaminated with endosulfan (α and β) were above the MRL (Sajid et al., 2016). In the Nadia district in Bengal the endosulfan α and β found in the milk samples were above the MRL (Singh et al., 2013). In Afyonkarahisar in Turkey the MRL was above for heptachlor epoxide in buffalo and sheep milk samples (Bulut et al., 2011). These results are associated with the different agricultural activities in each region, as well as the different types of insects that were considered as agricultural pests or even as vectors of tropical diseases.

In the selected studies in South American countries, only one residue of OCPs (Lemes et al., 2004) was found in a study carried out on samples in the state of São Paulo, Brazil. In the other samples, aldrin, dieldrin, mirex, endosulfan, chlordane, dicofol, heptachlor, heptachlor epoxide, α-HCH, lindane, HCB, pp'-DDE, op'-DDD, pp'-DDD, DDT, DDT, op'-DDT, PCB (congeners 10, 28, 52, 138 and 180), endrin, endosulfan, γ-chlordane, heptachloroxide, γ-BHC, γ-CLD and γ-clendal (Avancini et al., 2013; Hernández et al., 2010). Among these, DDT and its metabolites were detected in a larger number of samples, followed by aldrin. In the state of Mato Grosso do Sul, Brazil, the levels of chlordane, aldrin, dieldrin and heptachlor were above the maximum limit stipulated by FAO/WHO (Avancini et al., 2013). In the State of Rio Grande do Sul, also in Brazil, samples of raw, pasteurized and UHT bovine milk analyzed presented levels of α-HCH, lindane, aldrin and DDT, also above the MRL (Heck et al., 2007). It is worth mentioning that these two Brazilian states are major producers of grains, mainly soybeans and corn, and that for a long period the producers used OCPs to control agricultural pests. However, the OCPs levels in samples of fresh bovine milk in Colombia were below what is allowed (Hernández et al., 2010).

Lans-Ceballos et al. (2018) evaluated the presence of OCPs in samples of pasteurized bovine milk in Montería, Colombia. Of the 144 analyzed samples, all had OCP content above the Maximum Residual Limit established by the Codex Alimentarius (FAO/WHO, 2014). Concentrations of α-HCH/β-HCH, γ-HCH, δ-HCH, aldrin/dieldrin, heptachlor/heptachlor epoxide, eldrin, α-chlordane, γ-chlordane and endosulfan were 0.53; 0.15; 0.57; 0.40; 0.22; 0.20; 0.014; 0.002 and 0.028 mg kg^{-1}, respectively. Díaz-Pongutá et al. (2012) evaluated the presence of organochlorine pesticides in samples of fresh bovine milk in the region of Córdoba, Colombia. A total of 63 samples were evaluated, with the highest pesticides being p,p'-DDT (65.1%), endrin (49.2%) and dieldrin (39.7%). The other contaminants were δ-HCH (7.9%), chlordane (4.8%) and heptachlor (1.6%).

Among the North American countries, the four studies on the presence of organochlorine pesticide residues in commercial milk samples belong to Mexico. The organochlorine pesticides identified in the milk samples of the analyzed studies were: α-HCH, β-HCH, γ-HCH, ΔHCH, β-HCH, heptachlor, heptachlor epoxide, DDT and isomers, aldrin, dieldrin, endrin and endosulfan I. The most frequent residues found in milk samples from the four studies analyzed were HCH and heptachlor isomers, followed by Aldrin present in milk samples from three studies. The results show that the amount of organochlorine residues in the milk samples is below the recommended maximum limit (Gutierrez et al., 2012; Gutierrez et al., 2013; Tolentino et al., 2014). Only the study performed in the central region of Mexico found values above the MRL for Δ-HCH, heptachlor, and heptachlor epoxide (Schettino et al. 2013) in goat milk samples.

The organochlorine pesticides detected in the milk samples from selected African countries were: aldrin, dieldrin, lindane, alachlor, hexachlorobenzene (HCB), methoxychlor, endosulfan (α and β) and DDT and their metabolites. Among these pesticides the most frequent were lindane and aldrin. In Kampala the pesticides DDT, lindane, aldrin and dieldrin were above the MRL in both fresh bovine and pasteurized milk (Kampire et al., 2011). The levels of aldrin, endosulfan (α and β), p, p›-DDE, o, p›-DDT ep, and p›-DDT were also higher than MRLs in the bovine and goat milk samples from Ethiopia and Egypt (Deti et al., 2014). These high levels may be related to the intense use of OCPs in the control of tropical insect diseases, which are very common in poorer countries. Finally, samples of buffalo milk from Egypt showed high levels of lindane, methoxychlor and HCB (Shaker and Elsharkawy, 2015).

Conclusions

Despite the ban on the use of OCPs for agricultural purposes since the 1980s, work shows that these compounds and their metabolites are still available in the environment. Although OCP content in most samples has been below the maximum allowable limits, these residues can accumulate at higher levels in humans, posing a health risk.

The pesticide content varied greatly from region to region, which is related to several factors, such as the use of the soil for agriculture, as well as public policies related to the use of these pesticides.

Tropical regions, known as malaria epidemics and other insect-borne diseases, were the most contaminated by DDT due to their use in controlling the vectors of these diseases.

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