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Review

Extraction and clean-up methods for organochlorine pesticides determination in milk

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HIGHLIGHTS

- This review discusses extraction and clean-up methods used to monitor OCP in milk.
- Conventional extraction methods are still the most used, despite its disadvantages.
- New extraction methods have not been evaluated in detail for OCP analysis in milk.
- More research is needed to obtain the ideal method for OCPs determination in milk.

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ABSTRACT

Organochlorine pesticides (OCPs) can cause environmental damage and human health risks since they are lipophilic compounds with high resistance to degradation and long half-lives in humans. As most persistent OCPs have been banned years ago, it is expected to find these compounds at trace levels in environment. Therefore, increasingly sensitive and reliable analytical techniques are required to ensure effective monitoring of these compounds. The aim of this review is to discuss extraction and clean-up methods used to monitor OCP residues in milk, reported in the last 20 years. To carry out this review, an exhaustive bibliographic review was conducted. Despite the disadvantages of conventional extraction and clean-up methods, such as liquid–liquid, solid-phase or Soxhlet extractions, these procedures are still used due to their reliability. New extraction methods, like solid-phase microextraction, matrix solid-phase dispersion or QuEChERS, have not been thoroughly evaluated for OCP determination in milk. Almost all the methodologies analyzed in this review presented good performance characteristics according to the performance acceptability criteria set in SANCO's procedure. Comparison between limits of quantification (LOQ) and detection (LOD), for the reported methodologies, is not always possible due to the heterogeneity of the units. Thus, researchers should take into account an homogenization of LOD and LOQ units, according to the international regulations and MRLs established. Finally, more research is necessary to obtain the ideal methodology for OCPs determination in milk, which comprises the environmentally friendly characteristics of the new techniques and the reliability of the traditional methodologies.

1. Introduction

Contamination by persistent chemicals is potentially harmful to organisms at higher trophic levels in the food chain. Humans are principally exposed to these chemicals through ingestion, since diet is the most important source of chronic exposure to low doses of these substances (LeDoux, 2011). Of the 24 chemicals targeted by the Stockholm Convention, listed in the annexes of the convention text, 15 are organochlorine pesticides (OCPs): aldrin, endrin, dieldrin, chlordane, chlordecone, dichlorodiphenyltrichloroethanes (DDTs), heptachlor, mirex, toxaphene, endosulfan and isomers, hexachlorobenzene (HCB), alpha-hexachlorocycloheaxane (α-HCH), beta-hexachlorocyclohexane (β-HCH), lindane, and pentachlorobenzene (Stockholm Convention, 2009). Studies on the concentration of OCPs in the environmental showed that emission sources of these compounds (such as DDT) in the last 20 years have moved from industrialized countries to developing countries, due either to the late production ban in these countries or to the use in agriculture and control of diseases such as malaria, typhus and cholera (Choi et al., 2009). Today, OCPs have been banned for agricultural or domestic uses in Europe, North America, and many countries of South America in agreement with the Stockholm Convention. Nevertheless, some of these compounds are still applied.

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An example is the pesticide DDT which is used to control the growth of mosquitoes that spread malaria, as mentioned above, or as an antifouling agent in some developing countries. In addition, dicofol, the most frequently used acaricide, which is made of DDT and its formulated products, always contains a small amount of DDT (Chung and Chen, 2011).

OCPs can cause environmental damage and human health risks since they are lipophilic compounds with high resistance to degradation and long half-lives in humans (Chao et al., 2006; Padrón et al., 2006). The half-life of most organochlorine pesticides can range from a few years to more than 10 (Padrón et al., 2006). Several studies have reported that OCPs have endocrine-disrupting activity. It has been well established that these compounds can accumulate in human tissue and can cause chronic toxicity after long-term exposure. Many organochlorine pesticides have been found to be carcinogenic in rodent studies. In addition, they can cause non-Hodgkin's lymphoma, hepatotoxicity, immunotoxicity, developmental abnormalities, neurobehavioral effects and population declines (Qu et al., 2010).

Although most of the OCPs are no longer used, these persistent chemicals can be transferred and magnified to higher trophic levels through the food chain due to their relative stability and bioaccumulation property (Chung and Chen, 2011). These compounds have been confirmed to bioaccumulate in blood (Greizerstein et al., 1999; Jaraczewska et al., 2006), breast milk (Chao et al., 2006; Romero and Dorea, 2000; Mueller et al., 2008), and adipose tissues of humans through dietary intake (Waliszewski et al., 1995; Chao et al., 2006). The presence of these compounds in milk from other mammals has also been reported (Waliszewski et al., 1997; Real et al., 2005; Prado et al., 2007; Ashnagar et al., 2009; Kampire et al., 2011). Therefore, pesticide residue analysis in environmental samples has received increasing attention in the last few decades, resulting in many environmental monitoring programs for a broad range of pesticides (Padrón et al., 2006). Residues of OCPs (including DDT, HCB and HCH isomers) have been determined in samples from areas where these compounds were or are used (such as Africa, Asia, Latin America) (Allé et al., 2009). Nevertheless, the presence of these substances has been also detected in zones where OCPs were never used, such as the Artic. Within the circumpolar studies, several populations living in Artic and sub-Artic areas were determined to be highly exposed to persistent organic pollutants (POPs) due to their local dietary habits. Long-range atmospheric transport and deposition of POPs in the Artic have been studied through the Artic Monitoring and Assessment Program (AMAP) (Polder et al., 2003).

Among the biological matrices mentioned above, milk is a convenient sampling matrix for measuring residue concentrations of persistent OCPs. Cow's milk is considered a nearly complete food since it is a good source of protein, fat and major minerals. Additionally, it is the main constituent of the daily diet, principally for vulnerable groups such as infants, school age children and the elderly. On the other hand, milk is an ideal liquid to dissolve environmental contaminants such as pesticides because most of them are fat-soluble (Kampire et al., 2011). Due to their lipophilic properties, OCPs are primarily stored in fat-rich tissues and subsequently translocated and excreted through milk fat (Waliszewski et al., 1997). Cow's milk may contain high levels of pesticides as a result of residue accumulation in the tissues following the cattle's exposure from feeding on contaminated feedstocks or from drinking contaminated water (Kampire et al., 2011). Thus, knowledge of cow's milk contamination by OCPs provides important information about human exposure to these contaminants, through the ingestion of dairy products.

Human milk is the most complete source of nutrients (proteins, carbohydrates, fat and vitamins), immune factors and other important constituents for infants (Azeredo et al., 2008). It is a convenient matrix for monitoring POPs, such as OCPs, in humans because of the non-invasive sample collection and the suitability for determination of these lipophilic compounds due to the relatively rich lipid content (Tue et al., 2010). Additionally and not less important, the concentration of OCPs in human breast milk is a key factor for evaluating the toxic potential of contaminants in breastfeeding infants (Mihn et al., 2004), who are at the early stage of development and vulnerable to toxic contaminants (Tue et al., 2010). Infants and small children do not have fully developed detoxification mechanisms. Their immune systems are immature and their organs are in the process of rapid growth (Yu et al., 2006.). Human milk offers a unique opportunity for estimation of total chemical intake by infants during breast-feeding (Romero and Dorea, 2000).

When breast milk is employed for human biomonitoring, it is important to take into account the process of depuration, that is, the reduction of chemicals in milk during lactation (Esteban and Castaño, 2009). Since most of the organochlorine pesticides, considered POPs, have been banned years ago, it is expected that these compounds will be found at trace levels in the environment. Thus, increasingly sensitive and reliable analytical techniques are required to ensure effective monitoring of OCPs.

In order to protect health for consumers, Maximum Residue Levels (MRLs) for pesticides and different commodities have been regulated internationally. In the case of the European Union, since 1 September 2008, a new legislative framework (Regulation (EC) No. 396/2005) for pesticide residues is applicable. This regulation completes the harmonization and simplification of pesticide MRLs, while ensuring better consumer protection throughout the EU. The Codex Alimentarius Commission, established by the Food and Agriculture Organization (FAO) and World Health Organization (WHO) in 1963, develops harmonized international food standards, guidelines and codes of practice to protect the consumers' health and ensure fair trade practices in the food trade. The Commission also promotes coordination of all food standards work undertaken by international governmental and non-governmental organizations. The Codex pesticide residues in food online database contain Codex Maximum Residue Limits for Pesticides (MRLs) and Extraneous Maximum Residue Limits (EMRLs) adopted by the Codex Alimentarius Commission up to and including its 34th Session (July 2011) (Codex Alimentarius, 2012).

Table 1 summarizes the OCP MRLs established by different international regulations, the European Union (EU) and the Codex Alimentarius regulations. In the case of the EU, MRLs are established for milk and cream (not concentrated, nor containing added sugar or sweetening matter), butter and other fats derived from milk, cheese and curd (Regulation (EC) No. 396/2005). Regarding the Codex Alimentarius, MRLs are established for milks in general (Codex Alimentarius, 2012). There are no MRLs specifically established for OCPs in human milk. However, due to the similarity of the matrix and the dairy intake of both commodities, MRL values established for OCPs in milks (in general) are taken as reference for the information analysis reported in this work.

In general, food and environmental samples cannot be analyzed without some preliminary sample preparation, since contaminants are too diluted and the matrix is rather complex. Due to the low levels of detection required by regulatory bodies and the complex nature of the matrix, the efficiency of the sample preparation is very important, as well as the low level detection and identification of the target compounds (Picó et al., 2007). In the case of milk samples, one of the main difficulties related to the determination of these analytes is its high fat and protein content that can often interfere in the analytical determination. For this reason, sample extraction can be long and tedious, involving several clean-up steps to remove the co-extracted material from the matrix (Aguilera-Luiz et al., 2011).