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Analysis of organochlorine pesticide residues in human and cow's milk in the towns of Asendabo, Serbo and Jimma in South-Western Ethiopia

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HIGHLIGHTS

- High levels of DDT were determined in human and cow milk.
- The ratio of DDT to DDE has revealed the continued use of DDT in the area.
- Transfer of the DDT from mother to child was estimated.
- Infant EDI was higher than the maximum tolerable limit.

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ABSTRACT

The level of some OCPs in human and cow milk collected from Asendabo, Serbo and Jimma in South-West Ethiopia were analyzed using GC–ECD. Results of the analysis indicated that all samples contained detectable quantities of *p,p′*-DDT and its metabolites, *p,p*-DDE and *p,p*-DDD, but none of the other OCPs analyzed. Mean levels of total DDT in the human and cow milk samples in the three areas were 12.68 and 0.389 μg g^{-1} respectively. The distributions of *p,p*-DDT, *p,p*-DDE and *p,p*-DDD in the human milk samples from the three locations followed the same trend in which the proportion of *p,p*-DDT was the highest in all the three cases, comprising 55–71% of total DDT, followed by *p,p*-DDE, 26–39%, and the least, *p,p*-DDD of 2–5%. The mean ratio of DDT/DDE concentration for the three areas was calculated to be 2.01. This value was much higher than the values reported from other countries in earlier studies and indicates the existence of a higher quantity of DDT from a fresh input in the three study areas. The mean estimated daily intake of DDT by infants from mother's milk in the three locations was found to be 62.17 μg kg^{-1} body weight, which is about three times higher than the acceptable daily intake set by WHO/FAO for total DDT, 20 μg kg^{-1} of body weight. This alarmingly high daily intake value is a cause for concern, since children are highly susceptible to effects from such environmental contaminants. The study has revealed that people in the study areas are facing exposure to DDT from recent use. The observed contamination of mother's milk and the possible transfer of the contaminant from mother to child is an obvious risk associated with breast-feeding in the study areas and possibly in other parts of the country too.

1. Introduction

Pesticides, including the organochlorines (OCPs) are chlorine-containing compounds which are found in the environment as a result of human activities. The compounds were heavily used in agriculture and to control termites and mosquitoes from the mid-1940s to mid-1980s (Brasher and Anthony, 1998). Due to their persistence, tendency to accumulate in soil, sediment, biota, and their harmful effects on wildlife, developed countries have restricted or banned many of these pesticides. The Stockholm Convention on Persistent Organic Pollutants (POPs) has also globally banned the production and use of persistent, bioaccumulative chemicals and, a number of chemicals including DDT are already listed under the Convention (IISD, 2008). Developing countries, however, maintain that they cannot afford, for reasons of cost and/or efficacy, to ban certain of these chemicals. As a result, most of these chemicals have been or continue to be used in large quantities in many developing countries, including sub-Saharan Africa (Ullah et al., 2010).

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OCPs tend to bioaccumulate in foodstuffs of animal origin, mostly in meat and tissues that contain fat, in milk and dairy products, eggs and fish due to their lipophilic nature (Waliszewski et al., 1997). The intake of contaminated feed and fodder by milch animals is the main source of entry of pesticides into the animal body which ultimately results in the contamination of milk, meat and other food consumed by human beings. Thus the human body also gets contaminated (Nag and Raikwar, 2008). OCPs have a proven detrimental impact on the human body, and children have been found to be especially susceptible (Dekoning and Karmaus, 2000). Special attention should therefore be paid to the presence of OCPs in food designed for infants. A serious phenomenon in this regard is their presence in human milk, which is the only proper food for infants. Cow milk is also a basic component of the human diet including children's diets, which contain a high proportion of milk and milk products, and diets of the elderly, for whom cow milk is considered a perfect natural food. The milk can make an important contribution to the intake of OCPs by all age groups of humans. It is an important medium of OCP accumulation and hence one of the convenient food stuffs for measuring the persistent OCPs recommended by the United Nations Environment Programme (Leslie and deBoer, 2011).

In Ethiopia, from 1950s to about 2000, DDT has been sprayed outdoors (for agricultural use) as well as indoors for malaria control by reducing the density and longevity of vector mosquitoes using IRS (ISD, 2009; Wassie et al., 2012). DDT spraying is commonly conducted during the rainy months, from June to October. Currently, however, the use of DDT is limited to indoor spraying for disease vector control. In addition to this, Ethiopia has one of the largest stockpiles of obsolete pesticides in Africa. FAO estimates that almost 3000 tons of hazardous pesticide waste has been stored at nearly 1000 sites around the country over the past 30 years threatening the health of thousands of people and polluting the environment. The most dangerous pesticides include aldrin, heptachlor, chloradane, DDT, dieldrin, endrin, malathion, pirimiphosmethyl and fenitrothion; these have been banned in most countries and are found in these dumpsites (Hussein, 2007). Most of these obsolete stockpiles in Ethiopia are removed through the support of African Stockpile Project. The level of human exposure due to the long time use of these pesticides in the country and the impact of long time presence of such huge quantities of obsolete pesticides has not been assessed at all. Therefore, the main objective of this research was to determine the levels of 18 OCP residues in human and cow milk samples collected from Jimma zone, Western Oromia, Ethiopia and assess the level of human exposure.

2. Materials and methods

2.1. Study site, and collection of human and cow milk samples

Breast milk samples were collected from mothers accessed through Jimma University Specialized Hospital in Jimma and public clinics at Asendabo and Serbo. The three towns are found in Jimma zone, Western Oromia Regional State, Ethiopia. Jimma is located 350 km south-west of the capital Addis Ababa, and the other two towns, Serbo and Asendabo, are 20 and 55 km east of Jimma respectively. The three selected areas are malarious and annual spraying of DDT for malaria control is common.

Human milk samples were collected, between March and May of 2010, from a total of 101 mothers (33 from Asendabo, 29 from Serbo and 39 from Jimma) who were either in maternity wards or attending post-natal clinics in the selected areas. Nipples of each donor mother were thoroughly cleaned with tap water and about 10 mL of milk was collected from each mother, by expressing directly into precleaned and labeled glass vials with Teflon-lined caps under supervision of a qualified nurse. A total of 30 cow milk samples (10 from each location) were also collected from randomly selected farmers' cows in the villages around Asendabo, Serbo and Jimma, following the same procedure. All milk samples were immediately transported to the laboratory in an ice-box and frozen at −20 °C in the laboratory until analysis.

2.2. Ethical clearance

Ethical approval to carry out the study was obtained from Jimma University Ethical Review Committee. Before collection of milk samples, the purpose of the study was clearly explained to each of the mothers who fulfilled the selection criteria and were requested to complete an informed consent form. A basic questionnaire was completed to collect information on mothers' age, diet, number of children, longevity in the area and occupational exposure to DDT or other pesticides.

2.3. Exclusion criteria

Those mothers who gave complicated birth or premature delivery, who were smokers or were suffering from serious disease during pregnancy, and those who were not residents of the study area were not included in the study.

2.4. Analysis of organochlorines

All sample preparation and analysis of both the human and cow milk samples was undertaken at the Quality Monitoring and Testing Laboratory of the Ministry of Agriculture. The human or cow milk samples from each of the three sampling locations were pooled and analyzed for 18 OCPs, including: HCH isomers (α-BHC, γ-BHC, β-BHC, δ-BHC), aldrine, heptachlor epoxide, heptachlor, γ-chlordane, α-chlordane, DDT and its metabolites (*p,p*-DDT, *p,p*-DDE and *p,p*-DDD), endosulfan-I, endosulfan-II, dieldrine, endrine, endosulfan sulfate, endrine ketone and methoxychlore.

Extraction and clean-up of OCP residues were performed according to the AOAC official Method 970.52 for fatty substances (AOAC, 2007). The separation, identification and quantification of OCPs were performed using Agilent Model 7890 gas chromatograph equipped with dual ^{63}Ni μ-ECD. A primary analytical column, CLP-Pestcides-2 (30 m length × 0.25 mm id, 0.25 μm film thickness) capillary column (Restek Corp, Bellefonte, PA) was used for the separation of analytes and a second CL-Pesticide column was used as a confirmatory column. The column oven temperature was set at 120 °C for 0.5 min and ramped to 180 °C at a rate of 20 °C min^{-1} and then to 280 °C at a rate of 10 °C min^{-1} with hold time of 10 min and a total acquisition time of 25.5 min. The temperatures of the detector and injector were 300 and 230 °C, respectively.

Identification of the OCP residues was carried out on the basis of retention time and confirmation using analytical column of different phase polarity. Quantification of OCPs was carried out using 1-Bromo-2-Nitrobenzene as the internal standard. The linearity of the chromatographic analysis was checked by and the use of five point external standards (all obtained from Restek Corp, USA) corresponding to each of the target OCPs.

2.5. Quality assurance

Quality control samples consisting of method blank and three spiked blanks were included in every batch of samples analyzed to check for interferences and cross-contamination. No contaminant was detected in the method blank analysis, indicating no contamination from laboratory sources. Results of the analyses of the