THE DETERMINATION OF THE CONTAMINATION LEVEL BY ORGANOCHLORINE PESTICIDES OF GREENN FODDER

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Abstract

The present paper presents the results of the qualitative and quantitative determination of organochlorine pesticides under sanitary veterinary surveillance in green fodder. The purified extract was analyzed by gas chromatography. The results confirmed the presence of the most persistent OCPs compounds, their concentration being under of the MRL value.

Keywords: green fodder, organochlorine pesticide contamination, gas chromatography

INTRODUCTION

As known, the contamination of animal origin food by chemical contaminants is due mainly to water and food-stuff ingested by animals. So it is very important to monitor the level of contaminants in this environments in order to prevent further sanitary-veterinary problems *(*Nag and Raikwar, 2011, Waliszewski and al., 2004, Gill and al., 2001, Singh and al, 1997). This aspect is most important with toxics which are bioaccumulable such as the organochlorine pesticides (OCP in this paper). Because of their persistence in air, water and soil and their traceability, this kind of contaminant is under surveillance in environmental factors as well as in food-stuff and human food in all European Union countries as well as around the world (Katagi, 2010, Sarkar and al., 2008, Bakore et al, 2004 and 2002).The contamination sources of green fodder are water and soil from the cultivation areas, this is whi these environment factors make the object of the studies regarding the OCP contamination in Romania (Neamtu and al., 2009) and other European countries such as the Check Republic (Koci and al, 2007). While in EU the use of OCP for crops protection or silo treatments has been banned more than 20 years ago, regarding all the compounds, in Asia, South America or South Africa some of them are still in use, especially for the control of malaria (Sarkar and al., 2008). Due to their distinct persistence in the environment maintained by the continuous use in other areas, the EFSA specialists are drawing up and coordinating monitoring programs about the presence of OCPs in fodders and food (EFSA a, b, 2005, a, b, 2006). But do to the fact that pollution has no boundary, the incriminated substances are found in areas where they are not

in use such as Mount Everest (Wang et al, 2007). That can be a problem for Romania which borders with non EU countries having a less restrictive legislation, even if they are monitoring the level of OCPs in vegetals like Serbia (Škrbič and Predojevič, 2008). The surveillance of such contaminants as OCPs is needed because of their important impact on human health. The main OCPs, ranked as POPs and which are under sanitary-veterinary surveillance have medium to high toxicity, the increasing order of toxicity being: HCH, Clordan, DDT, Lindan, Toxafen, Heptaclor, Dieldrin, Aldrin. The presented order refers to acute toxicity, which does not fully reflect the real toxicological risk that the long-term experiments reflect. For example, the γHCH isomer has an acute toxicity higher than the βHCH isomer, but on a long term administration it is less toxic. (Alexa, 2003).

MATERIALS AND METHODS

Materials

For the study that makes the object of the present paper, three series of green fodder samples were tested. Since this paper is a research study, not the result of a control activity, the name of the village from where the samples have been taken, was not revealed. They were coded by letters and numbers (Tables 1 and 2). From geographical point of view it is the area near the municipality of Oradea

Methods

The OCP are extracted from the matrix by liquid/liquid technique using a mixture of acetonitril/water (65:35 V/V), followed by liquid/liquid partition with light petroleum. The extract is purified on an activated Florisil column. The OCP are eluted with mix of ethylic ether/light petroleum in variable proportions. (SR EN 12393/2/2004).

We have used the gas chromatography method (Zhao and al., 2011, Tadeo, Ed., 2008, Hura, 2006, Yan and al., 2005), as set forth by current legislation for the calculation of OCP residues in vegetal products.We have used a GC 2010 Shimadzu gas chromatograph, capillary column type RTX - CL- pesticides, detector with electrons capture (ECD), .

For the qualitative and quantitative calculation of the contaminants possibly present in the tested products, we used a standard produced by the RESTEK company No 32292, Lot nr A021837, type “Organochlorine pesticide Mix AB ≠2” having a concentration of 200 ppb. The standard was used at 50 ppb dilution.The purified extract, retaken in petroleum ether underwent chromatography under the same conditions as the standard test, as well as the blanks-test of the used reagents, according to the separation/purification method.

RESULTS AND DISCUSSIONS

The results are written in table 1 for the qualitative determination, separated on the three elutions performed. Only the positively identified compounds are mentioned.

Table 1

Qualitative calculation of the organochlorine pesticide residues in green fodder, (n=6)

A	B	C	D - FV1			D - FV2			D – FV3		
			E_A	E_B	E_C	E_A	E_B	E_C			
1	α HCH	7.194	7.179			7.183			7,188		
2	γ HCH	8.426	8.409	8.413		8.410	8.415		8,418	8.422	
3	β HCH	8.886			8.791						8.765
11	α endosulfan	16.753	16.73			16.744			16.723		
13	Endrin	18.878	18.831			18.848			18.840		
14	4,4' DDD	19.853	19.809			19.814			19.901		
16	4,4' DDT	21.305	21.273		21.464	21.288		21.378	21.277		21.389
19	Sulfat endosulfan	24.693	24.798						24.803		

Legend: A – Eluation order; B – Organochlorine compound from the sample; Retention time in the standard; D - FV1, FV2 – retention time in green fodder 1, respectively 2; E_A, E_B, E_C – Eluation solvents used: A, B, C

The results of the quantum determinations are presented in table 2 for the three series of samples tested. The concentration written in the table represents the amount of the values from the three elutions applied, where it was necessary. The expression of the concentration as isomer amount for α and β HCH, endosulfan and DDT complies with the European norms (EFSA a, b 2005 and EFSA a, b, 2006) and the national ones, respectively Order 12/2006, 118/2007, 160/2007 referring to the contamination of fodders with OCPs (Legis).

Table 2

Qualitative calculation of the organochlorine residues in samples of green fodders (n=6)

Nr. (*)	Organochlorine compound found in the sample	x MRL ppm	Concentration in the sample, ppm		
			FV1	FV2	FV3
1 3	HCH (Sum of isomers α and β)	0,01	0.0007+ 0,0004= 0.0011	0,0005	0,0009+ 0,0004= 0,0013
2	γ HCH	0,01	0,0009	0,0012	0,0034
11 15 19	Endosulfan (Sum of α and β and endosulfan expressed in endosulfan)	0,05	0,0018+ 0,0003= 0,0021	0,0021	0,0032+ 0,0006= 0,0038
13	Endrin	0,01	0,0008	0,0013	0,0016
10 14 16	DDT (Sum of DDT, DDE and DDD isomers expressed in DDT)	0,05	0,0001+ 0,0006= 0,0007	0,0002	0,0008+ 0,0005= 0,0013

Legend :(*) – se it refers to the eluation order of the compounds in the samples
MRL – maximum residues level; FV1, FV2 – green fodder 1, respectively 2

Referring to the type of OCP under sanitary-veterinary surveillance that appears in the three series of samples of tested green fodders one can make the following considerations:

- pesticides that can be found in all the tested samples are: α şi γHCH, αEndosulfan, Endrin and 4,4'DDT;

It is noteworthy that there are two categories of compounds, that is OCPs used until recently such γHCH and αEndosulfan and OCP with high persistency and accumulation in the environment, from where they can be stored by fodders, respectively Endrin and 4,4'DDT;

- the pesticides βHCH and endosulfan sulfate appear in 66,6% of the tested samples;
- the compounds found in all the samples appear in the same type of eluent.

The α and β isomers of HCH are components of the same technical products, but the time elapsed since they have been discontinued leads to the different apparition in the tested samples. The metabolites of the pesticides with high incidence, such are endosulfan sulphate, appear randomly.

- the great majority of the compounds are found in eluent A;

Referring to value of the concentration for the OCPs positively identified:

- OCPs identified positively in green fodders samples have residue values under the MRL value, the difference being in the range order.

The situation is due to the short period of life of the green mass and, implicitly the reduced period of contact with soil and water through which they can be impurified. These values have the same range order10^{-2} with the ones found in a study on the vegetation of the Asian mountains. So, Wang et al., 2006, have found in the grass at altitude between 4700 – 5620 m, concentrations for HCH isomers between 0,0003 – 0,0078 ppm and for Endosulfan values between 0,0001 – 0031. For DDT the values found were between 0,0011–0,0069 ppm which means a range order superior to those from the grass tested in the present work and it reflects the continuous use of DD in this area of the world, especially for the control of some tropical diseases. This way, the effect of the transport through air way of the pesticides, especially powdery ones, is once again proved.

CONCLUSIONS

The tested green fodder shows a more reduced impurification that the complex fodder samples previously tasted (Chis, 2010). However, their are between those found in milk and sour cream samples collected in the same area (Chis et al, 2008 a and b) which shows once again the persistence in the environment of this POPs (Thomas and al., 2008) and it registers in the world research in the field. (Salem and al., 2009, Nag, 2008). The lowest

concentration values found in green fodder, strengthens the opinion that in complex fodder the cereals could be the major source of contamination.

For green fodder, the most probable source of contamination are the soil and the water. For this reason, the future studies will be made in this direction, as suggested by the studies in other countries. (Nag and Raikwar, 2010.

In the limit of the fact that in the studies performed at European level by the EFSA specialists the types of fodders tested are not entirely mentioned, the comparison with the concentration values found in the tested samples, leads to the observation that the values found for the HCH, Endosulfan, Endrin isomers and for DDT (isomer amount) are comparable as range order with the European ones, registered after the year 2000 (EFSA a, b, 2005, a, b 2006).

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