ORGANOCHLORINE AND ORGANOPHOSPHATE PESTICIDES DETERMINATION IN PLANTS USED FOR COSMETIC PURPOSES

IOANA ADINA OANCEA[1,2], ELISABETA CHIRILA[1*] AND SIMONA DOBRINAS[1]
[1] "Ovidius" University, Chemistry and Chemical Engineering Department, 124 Mamaia Blvd. 900527 Constanta, Romania
[2] "Careless Organic Cosmetics" 42A Crinului Street, 900338, Constanta, Romania

*Correspondence Contact: echirila@yahoo.com

Abstract Recent information about the presence of pesticides in plants used for cosmetic purposes has been reported in the media and on the internet. Pesticides are toxic substances applied on plants that are going to be food or other products like cosmetics. Therefore it is not difficult to understand why people are concerned about these substances. Our goal was to determine the organochlorine and organophosphate pesticides occurrence in 5 plant materials used in the composition of value-added organic cosmetic products manufactured in Constanta county, Romania. The studied plant materials were sea buckthorn fruits, snowdrops and violets flowers, poplar buds and sea buckthorn male buds. The trace pesticides concentrations were determined using gas chromatographic technique, after the extraction and cleanup steps. There have been found 15 types of organochlorine pesticides and 8 types of organophosphate pesticides. The total organochlorine pesticides concentrations varied between 0.0173 – 0.4604 mg/kg dry plant and the total organophosphate pesticides concentrations between 0.0028 – 2.5900 mg/kg dry plant. All individual concentrations of determined pesticides ranged below the limits established by EC regulations for plants used as animal feed.

Keywords: pesticides, organic cosmetics, GC, plant materials

L.Simeonov, F. Macaev and B. Simeonova (eds.), *Environmental Security Assessment and Management of Obsolete Pesticides in Southeast Europe,*

1. Introduction

Pesticides are being used to increase production and quality in crops over the past few decades. Excessive usage of pesticides contaminates the crop itself and the environment, eventually causing disease to human beings (Ng and Zhang, 2011). Real and perceived concerns about the impact of pesticides on human health and the environment have led to strict regulation of both their application and residue levels in food and water supplies. Maximum residue limits of pesticides in food commodities and drinking water are commonly set by national regulatory authorities and international bodies, such as the Codex Alimentarius.

Cosmetic products are widely used and are directly applied to human skin. While the skin provides a protective barrier, certain ingredients may penetrate the skin and become systemically available. There is a growing interest in the pharmaceutical and cosmetic industry to use plant extracts for various fields of applications (Chirila et.al, 2008, Stanciu et al., 2010, Xu et. al., 2011).

Since 1992 in Constanta, Romania, there is a value-added brand of natural cosmetics which contain a combination between 47 plant essences obtained from fresh flowers, buds and roots grown on the company's own lands in Dobrogea County.

Recent reports in the media and on the internet show an increasing concern about the presence of toxic chemicals in cosmetics. These toxic substances may result from the intentional addition of some preservatives (Belsito et al., 2008) or from the contact of raw materials (mainly plants) with organic pollutants like pesticides from air, soil or water. They persist in various media and some can be transported over long distances to regions where they have never been used.

Suitable (reliable and cost-effective) analytical methods are needed mostly in order to enforce pesticide residue regulations, to provide toxicological risk assessment data, and to study pesticide fate in the food chains and the environment. Most analytical methods in the literature involve extraction of pesticide residues from food by organic solvents, surfactants, supercritical fluids or solid-phase extraction followed by GC, HPLC, GC-MS or ICP determination (Lambropoulou and Albanis, 2007; Cieslik et al, 2011; Pareja et al., 2011; Cajka et al., 2012; Garcia-Rodriguez et al., 2012, Gonzalez-Curbelo et al., 2012).

The aim of this study was to determinate the levels of organochlorine pesticides (OCL) and organophosphate pesticides (OP) from 5 types of plant materials used in cosmetics collected from rural sites belonging to Dobrogea county, Romania, using gas chromatography with ECD respectively termoionic detection.

2. Experimental

2.1. SAMPLING

Five types of plant materials have been investigated: snowdrop (*Galantus nivalis sp.*) and violet (*Viola odorata sp*) flowers, poplar (*Populus nigra sp.*) buds and sea buckthorn (*Hippopae rhamnoides sp.*) male buds and sea buckthorn fruits. All plants have been collected from Topraisar village, Dobrogea county. The flowers and the buds were collected in March 2012 and the sea buckthorn fruits in October 2011.

The fruits have been stored in a freezer and before analysis have been kept to room temperature for 24 hours. Other plant materials (flowers and buds) were dried in air, on special wood grid for 10 days.

2.2. SAMPLE PREPARATION

In order to obtain the extracts containing OCL and OP pesticides, 8.33 g of grinded sample have been mixed with 34 mL acetone: isooctane 1:1 (v:v) and left 24 hours at room temperature. The mixture was then centrifuged for 10 minutes at 4000 rpm.

For OCL analysis, 10 mL of extract were evaporated to dryness and after redissolved with 3 mL isooctane; to 1 mL of isooctane extract were added 50 µL OCL internal standard (mirex) solution; 1µL of the resulted solution was automatically introduced in GC.

For OP analysis, 10 mL of extract were evaporated to dryness and after redissolved with 3 mL isooctane; to 1 mL of isooctane extract were added 84 µL OP internal standard (ethion) solution; 1µL of the resulted solution was automatically introduced in GC.

2.3. REAGENTS AND EQUIPMENTS

All used reagents were supplied by Merck Darmstadt, Germany: standards of pesticides - HCH, Lindane, p,p'- DDT, p,p'- DDE, p,p'- DDD, aldrin, endrin, heptachlor, endosulfan, metoxychlor, mirex, oootriethyl phosphorothioate, thionazine, sulfotep, phorate, dimethoate, disulfoton, methyl parathion, ethyl parathion, famphur, ethion and solvents: acetone, isooctane.

A Varian 520 gas chromatograph (GC) equipped with HP–5 fused–silica capillary column (29.6m×0.32mm×0.25µm) and electron capture detector (ECD) for OCL pesticides analysis / thermoionic detector for OP pesticides analysis has been used for determinations.

Helium was used as the carrier gas with flow rate 1.5mL/min and nitrogen makes-up gas at 30 psi. The injector temperature was 250°C. The initial temperature was 170°C; the temperature increases with 10°C/min until 200°C, held 3 minutes; increases 1°C/min. until 210°C; increases 30°C/min until 260°C and then held for 3 minutes. Other chromatographic conditions were: purge time ON – 2.5 minutes; purge time OFF – 7 minutes; split/splitless inlet vent - 17.14 mL/min; septum purge vent - 4.3 mL/min.

3. Results and Discussions

Our goal was to determine the organochlorine (OCL) and organophosphate (OP) pesticides in 5 plant essences obtained from different plant materials: sea buckthorn fruits, snowdrops and violets flowers, poplar buds and sea buckthorn male buds, using gas chromatographic technique. OCL were widely used in agriculture in the past, and most of them are resistant to photochemical, biological and chemical degradation for a long period of time (Xu et al., 2011). The levels of OCL residues found in the investigated samples are given in Table 1.

TABLE 1. OCL pesticides content in plants used in cosmetics (mg/kg dry weight)

Pesticides	Retention time (min)	Plant materials				
		Flowers		Buds		Fruits
		Galantus nivalis	*Viola odorata*	*Populus nigra*	*Hippopae rhamnoides*	*Hippopae rhamnoides*
α HCH	9.137	0.0223	<QL	0.0239	0.0003	<QL
γ HCH	9.332	<QL	<QL	<QL	<QL	<QL
β HCH	9.747	0.0460	<QL	0.2866	<QL	<QL
Heptaclor	10.074	0.0063	<QL	0.0043	<QL	0.0003
λ HCH	10.585	<QL	<QL	0.0024	<QL	<QL
Aldrin	10.921	0.0236	<QL	0.0676	<QL	<QL
Heptaclor e	11.443	<QL	<QL	<QL	<QL	0.0040
Endosulfan 1	11.925	0.0120	<QL	0.0099	<QL	<QL
pp’ DDE	12.559	<QL	<QL	<QL	<QL	<QL

Endrin	13.388	0.0113	<QL	0.0079	<QL	<QL
pp' DDD	13.777	0.0157	0.0001	0.0111	0.0028	0.0059
Endosulfan 2	15.081	0.0014	0.0324	0.0072	<QL	<QL
pp' DDT	15.622	<QL	<QL	<QL	0.0012	<QL
Endrin ald.	17.104	<QL	<QL	0.0002	<QL	<QL
Endosulfan s	17.475	0.0176	0.0076	0.0161	0.0130	0.0087
Metoxychlor	18.308	0.0248	<QL	0.0232	<QL	<QL
Total		**0.1810**	**0.0401**	**0.4604**	**0.0173**	**0.0189**

QL – quantification limit

From the 16 analysed OCL pesticides, most were found in poplar buds (12), followed by snowdrop flowers (10), sea buckthorn fruits (4), sea buckthorn male buds and violet flowers (3). The highest total OCL concentration occurred in poplar buds and the smallest in sea buckthorn male buds. This could be explained by the influence of air pollution, poplar being taller than sea buckthorn tree.

OP are more toxic than OCL, but they degrade quickly by hydrolysis on exposure to sunlight, air, and soil. This is why they represent an attractive alternative to the persistent OCL. Table 2 presents the levels of OP residues in the investigated plant materials. From the 9 analysed OP individual pesticides, most in were found in snowdrop flowers (5) followed by sea buckthorn fruits and poplar buds (4), sea buckthorn male buds and violet flowers (3). The highest total OP concentration occurred in sea buckthorn fruits and the smallest in violet flowers.

TABLE 2 OP pesticides content in plants used in cosmetics (mg/kg dry weight)

Pesticides	Retention time (min)	Plant materials				
		Flowers		Buds		Fruits
		Galantus nivalis	*Viola odorata*	*Populus nigra*	*Hippopae rhamnoides*	*Hippopae rhamnoides*
ooottriethyl phosphorothioate	6.674	0.0118	0.0004	0.0131	0.0056	0.0171

Thionazin	9.461	0.0007	0.0008	0.0027	0.0008	0.0180
Sulfotep	9.878	<QL	<QL	<QL	<QL	<QL
Phorate	10.747	0.0011	<QL	<QL	<QL	<QL
Dimethoate	10.871	<QL	<QL	<QL	0.1133	<QL
Disulfoton	11.071	0.0013	0.0016	<QL	<QL	<QL
Methyl parathion	11.446	<QL	<QL	0.0324	<QL	0.0039
Ethyl parathion	11.614	0.0015	<QL	0.0006	<QL	2.5510
Famphur	11.765	<QL	<QL	<QL	<QL	<QL
Total		**0.0164**	**0.0028**	**0.0488**	**0.1197**	**2.5900**

QL – quantification limit

In the international regulations for pesticides levels in different samples there are no limits regarding pesticides in raw plant materials used for cosmetic and medical purposes. The only existing limits are in plants used for animal feed, and there are between 0.01 and 0.1 mg/kg dry weight (Official Journal of European Union, 2002).

4. Conclusions

The paper presents original studies concerning the organochlorine and organophosphate pesticides residues determination in plant materials used in cosmetics from Constanta, Romania in order to quantify the environment pollution influence on plant.

The total organochlorine pesticides content varies between 0.0173 – 0.4604 mg/kg dry weight and the total organophosphate pesticides content varies from 0.0028 mg/kg dry weight to 2.59 mg/kg dry weight.

There are no imposed limits in the international regulations for pesticides levels in raw plant materials used for cosmetic and medical purposes. Compared with the EC regulations for pesticides residues in plants for animal feed, the individual investigated pesticides concentrations do not exceed the existing limits.

References

Official Journal of European Union (2002) Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed - Council statement

Belsito D., Bickers D., Bruze M., Calow P., Greim H., Hanifin J.M., Rogers A.E., Saurat J.H., Sipes I.G., Tagami H.(2008), A toxicologic and dermatologic assessment of cyclic and non-cyclic terpene alcohols when used as fragrance ingredients, Food and Chemical Toxicology 46 S1–S71.

Cajka T., Chris Sandy C., Bachanova V., Drabova L., Kalachova K., Pulkrabova J., Hajslova J., Streamlining sample preparation and gas chromatography–tandem mass spectrometry analysis of multiple pesticide residues in tea, (in press) Anal. Chim. Acta (2012), http://dx.doi.org/10.1016/j.aca.2012.06.051.

Chirilă E., Dobrinaş S, Stanciu G., Munteanu M., Oancea I.A., Comnea I, (2008), Analytical characterization of plant materials used in cosmetics, Ovidius University Annals of Chemistry 19, 64-67.

Cieslik E., Sadowska-Rociek A, Molina Ruiz J M., Surma-Zadora M. (2011), Evaluation of QuEChERS method for the determination of organochlorine pesticide residues in selected groups of fruits Food Chemistry 125, 773–778.

García-Rodríguez D., Cela-Torrijos R., Lorenzo-Ferreira R.A., Carro-Díaz A.M. (2012), Analysis of pesticide residues in seaweeds using matrix solid-phase dispersion and gas chromatography–mass spectrometry detection Food Chemistry 135 259–267.

Gonzalez-Curbelo M.A, Herrera-Herrera A.V., Lidia M. Ravelo-Perez L.M., Hernandez-Borges J. (2012), Sample-preparation methods for pesticide-residue analysis in cereals and derivatives, Trends in Analytical Chemistry (in press) http://dx.doi.org/ 10.1016/j.trac. 2012.04.010.

Lambropoulou, D., Albanis, T., 2007. Methods of sample preparation for determination of pesticide residues in food matrices by chromatography- mass spectrometry-based techniques: a review, Anal. Bioanal. Chem., 389(6), 1663-1683.

Ng C.I., Zhang X. (2011) A quick analytical method using direct solid sample introduction and GC ECD for pesticide residues analysis in crops Talanta 85 1766– 1771.

Pareja L., Fernandez-Alba A.R., Cesio V., Heinzen H. (2011), Analytical methods for pesticide residues in rice Trends in Analytical Chemistry, 30(2), 270-291.

Stanciu G., Chirila E., Dobrinas S., Negreanu-Pirjol T., (2010) Studies regarding the determination of antioxidant properties of new plant extracts for cosmetic purposes, Revista de Chimie, 61 (1), 41-44.

Xu R., Wu J., Liu Y., Zhao R., Chen B., Yang M., Chen J. (2011), Analysis of pesticide residues using the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) pesticide multiresidue method in traditional Chinese medicine by gas chromatography with electron capture detection, Chemosphere 84, 908–912.