

## ORGANOCHLORINE PESTICIDES IMPACT ON VEGETABLES

Kovacs Melinda Haydee<sup>1),2)</sup>, Mirela Miclean<sup>1)</sup>, Dalma Eموke Kovacs<sup>1)</sup>, Oana Cadar<sup>1)</sup>, M. Roman<sup>1)</sup>, Lacrimioara Senila<sup>1)</sup>, Dorina Simedru<sup>1)</sup>, Anca Naghiu<sup>1)</sup>

<sup>1)</sup>INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, 400293-Cluj-Napoca, melinda.kovacs@icia.ro

<sup>2)</sup>Babes-Bolyai University, Mihail Kogalniceanu nr. 1, 400084 Cluj-Napoca, Romania

**Abstract.** Fruits and vegetables may contain besides nutrients also contaminants as a consequence of polluted environmental media (water, soil, air). Through this work organochlorine pesticides (OCPs) presence was monitored in soil and potato samples collected from Cluj – Bistrita-Nasaud region. In higher amount were detected p,p'-DDE and  $\gamma$ -HCH. Good correlation was observed between OCPs amount in soil samples and those in potato samples.

**Keywords:** organochlorine pesticides, gas chromatography, vegetables, contamination

### INTRODUCTION

The European Union (EU), as well as national and regional governments support the organic agriculture and food sector. The health benefits of a diet rich in vegetables and fruits have been recognized for some time. Epidemiological studies have indicated that high fruit and vegetable consumption can be associated with a decreased mortality from several chronic diseases, such as cardiovascular diseases, certain cancers and obesity [1, 2, 3].

Unfortunately, fruits and vegetables may contain besides nutrients also contaminants as a consequence of polluted environmental media (water, soil, air). In the first instance environment contamination is a consequence of our lifestyle and of activities which help to improve our commodity from every day. Therefore, the presence of organic and inorganic contaminants from our surrounding media become more imminent with the time passing.

Hopelessly, a wide range of environmental contaminants pose an accumulation tendency mainly in soil (and partially in water) that finally result in their uptake by vegetation (including fruits and vegetables) and bioaccumulation by other living things, fact that have serious effects on us. Those, food safety remain a major concern worldwide and food consumption has been identified as the major pathway for human exposure to certain environmental contaminants, accounting for > 90 % of intake compared to inhalation or dermal routes of exposure [4].

The environmental analysis helps to protect the natural environment and human health through testing contaminants (organic, inorganic) and other hazardous toxins and pollutants in soil, water, air and food (e.g. vegetables, fruits). Food safety testing includes the analysis of agricultural products and foods, with a focus on regulatory compliance and enforcement. This rapidly growing issue is being driven by the liberalization of global trade, an increasingly stringent regulatory environment and heightened public awareness of food safety issues [5]. Concerns is supported by that about 30 % of human cancers are caused by low exposure to initiating carcinogenic contaminants in the diet [6].

Fruit and vegetables contamination monitoring programs at worldwide level have been carried out over several years by many investigators. In Romania, most of monitoring programs were directed to environmental media and less to vegetables and fruits [7, 8, 9].

Also to the best of our knowledge, correlation between contaminants level of surrounding environmental media and monitored vegetables or fruits was not taking into consideration. Importance of such investigation that fulfill this lack of data are given by that it could contribute to improving food safety, warn of actual and potential food scares, and facilitate evaluation of possible health hazards by providing information on levels of contaminants in commodities produced in different agriculture environment (land, garden).

Though this work, relationship between environmental media contaminants – considering organochlorine pesticides – and potato (*Solanum tuberosum L.*) was studied.

## MATERIAL AND METHODS

A total of 18 kg of potato samples were collected corresponding to 31 different agricultural and garden sampling sites in Cluj – Bistrita-Nasaud region. Each sample unit were washed and the remained debris removed, after that was chopped into small pieces, mixed, minimized by quartering to 50 g. All samples were homogenized with 100 mL portions of acetonitrile for 2 min in a warring blender at high speed and then filtered. The aqueous filtrate was shaken vigorously with 50 mL petroleum ether for approximately 5 min in a separatory funnel. Saturated NaCl and 200 distilled water were added to the same separatory funnel and shaken again for 1 min. The organic layer was collected and about 10 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> was added to the organic solvent layer and shaken vigorously. This layer was subjected to a clean-up process (according with method described by Mansour et al., 2009 [5]) in a column containing 15 g activated Florisil and 2 g anhydrous Na<sub>2</sub>SO<sub>4</sub> on the upper Florisil layer. Finally, the extracts were concentrated under vacuum to 1 mL. The detection and quantification of pesticide residues in the samples were performed on a Thermo Electron Ultra Trace GC equipped with <sup>63</sup>Ni electron capture detector (ECD) and a flame ionization detector (FID). A TR-V1 Trace GC capillary column with cyanopropylphenyl polysiloxane phase type with 0.53 mm I.D. x 3.0 μm film thickness x 30 m length was used. The chromatograph oven temperature was set at 60 °C and held for 5 min after that was raised to 120 °C (kept for 5 min) at 7 °C·min<sup>-1</sup>, than to 280 °C at rate of 15 °C·min<sup>-1</sup>, and hold for 10 min. The detector and the injector temperature was set at 300 and 250 °C, respectively. Soil samples preparation and analysis were done according with method described elsewhere [10].

## RESULTS AND DISCUSSIONS

The monitored organochlorine pesticides were α-, β-, γ-, δ-HCH, o,p'-DDT, o,p'-DDD, o,p'-DDE, p,p'-DDT, p,p'-DDD, p,p'-DDE, α-endosulfan, β-endosulfan, endosulfan sulfate, cis-chlordane (CT) and trans-chlordane (TC). The detected range as well mean value for soil and potato samples, considering all sampling sites, are presented in Table 1.

Considering the HCH group in soil samples, γ-HCH was detected in higher amount (n = 28, no of samples in that was detected) while δ-HCH was detected in only 9 samples. In potato samples γ-HCH was detected in 19 samples while δ-HCH was detected only in 2 samples in lower level than in the soil samples.

Among DDT group p,p'-DDE was detected in the highest concentration followed by p,p'-DDT. DDT and its isomers were detected in all soil as well potato samples, even if in some sample cases (soil, potato) in very low amount. OCPs as  $\alpha$ -endosulfan, CT and TC were determined in fewer samples as well in lower amount (see Table 1).

Table 1  
Organochlorine pesticides (OCPs) detected in soil and potato samples

Organochlorine pesticides (OCPs)	Soil samples		Potato samples	
	Mean (ng·kg <sup>-1</sup> )	Range (ng·kg <sup>-1</sup> )	Mean (ng·kg <sup>-1</sup> )	Range (ng·kg <sup>-1</sup> )
$\alpha$ -HCH	8.51	0.64 – 13.24	5.91	1.05 – 8.11
$\beta$ -HCH	10.15	1.28 – 17.11	4.15	0.56 – 9.33
$\gamma$ -HCH	15.66	0.85 – 21.25	8.66	0.44 – 13.14
$\delta$ -HCH	4.28	0.55 – 9.32	2.15	0.62 – 8.89
o,p'-DDT	13.11	2.05 – 24.15	7.88	0.55 – 11.27
o,p'-DDD	5.17	0.84 – 12.38	3.05	0.41 – 16.32
o,p'-DDE	9.15	2.48 – 16.28	4.58	0.38 – 7.29
p,p'-DDT	14.05	0.92 – 26.31	7.18	0.55 – 9.77
p,p'-DDD	12.15	1.57 – 30.27	7.09	1.15 – 13.27
p,p'-DDE	28.12	3.55 – 42.82	12.86	2.08 – 17.25
$\alpha$ -endosulfan	2.95	0.90 – 6.01	1.86	0.92 – 8.85
$\beta$ -endosulfan	7.14	1.15 – 10.22	4.59	1.15 – 7.05
endosulfan sulfate	6.88	0.86 – 14.06	3.46	0.56 – 5.29
CT	2.77	0.46 – 7.79	1.65	0.77 – 4.25
TC	3.16	0.59 – 9.01	1.92	1.22 – 5.01

A good correlation between potato and soil can indicate that potato accumulate OCPs from the soil. Thus, the linear regression of OCPs concentration between potato and soil was used to identify possible pathways for OCPs to enter in potato through soil (accumulation). The significant regression results are shown in Table 2. These results suggest that OCPs in potato are mainly from soil.

Table 2  
Simple linear regression of the concentration of organochlorine pesticides (OCPs) between soil and potato samples

OCPs	Equation	R	p
$\gamma$ -HCH	$y = -0.66 + 1.07x$	0.73	0.002
o,p'-DDT	$y = -0.89 + 1.53x$	0.80	0.0006
p,p'-DDT	$y = -0.91 + 1.28x$	0.87	<0.0001
p,p'-DDE	$y = -0.99 + 2.08x$	0.77	0.0007
$\beta$ -endosulfan	$y = -1.03 + 1.34x$	0.76	0.001

## CONCLUSIONS

OCPs were analysed from 31 soil and corresponding potato samples, but there was no soil or potato samples in that at least one of the monitored OCPs has not been detected. Lower amount of OCPs were detected in potato samples than in soil samples. OCPs belonging to HCH and DDT (with their isomers) group were detected in higher amount both in soil as well potato samples. The linear regression of OCPs concentration between potato and soil, suggested that OCPs in potato are mainly from soil.

## REFERENCES

1. Hoefkens, C., Sioen, I., Baert, K., Meulenaer, B. D., Henauw, D. S., Vandekinderen, I., Devlieghere, F., Opsomer, A., Verbeke, W., Camp, J.V. (2010). Consuming organic versus conventional vegetables: The effect on nutrient and contaminant intakes, *Food and Chemical Toxicology*, 48(11): 3058 – 3066.
2. Hoefkens, C., Sioen, I., Henauw, D. S., Vandekinderen, I., Baert, K., Meulenaer, B. D., Devlieghere, F., Camp, J.V. (2009). Development of vegetable composition databases based on available data for probabilistic nutrient and contaminant intake assessments, *Food Chemistry*, 113(3): 799 – 803.
3. Bes-Rastrollo, M., Martinez-Gonzalez, M. A., Sanchez-Villegas, A., de la Fuente Arrillaga, C., Martinez, J. A. (2006). Association of fibre intake and fruit/vegetable consumption with weight gain in a Mediterranean population, *Nutrition*, 22(5): 504 – 511.
4. Mansour, A. S., Belal, H. M., Abour-Arab, A. K. A., Gad, F. M. (2009). Monitoring of pesticides and heavy metals in cucumber fruits produced from different farming systems, *Chemosphere*, 75(5): 601 – 609.
5. Mansour, A. S., Gad, F. M. (2010). Risk assessment of pesticides and heavy metals contaminants in vegetables: A novel bioassay method using *Daphnia magna* Straus, *Food and Chemical Toxicology*, 48(1): 377 – 389.
6. Tricker, A. R., Preussmann, R. (1990). Chemical food contaminants in the initiation of cancer, *Proceedings of Nutritional Society*, 49: 133 – 144.
7. Ene, A., Bogdevich, O., Sion, A. (2012). Levels and distribution of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in topsoils from SE Romania, *Science of The Total Environment*, 439: 76 – 86.
8. Tarcau, D., Cucu-Man, S., Boruvkova, J., Klanova, J., Covaci, A. (2013). Organochlorine pesticides in soil, moss and tree-bark from North-Eastern Romania, *Science of The Total Environment*, 457: 317 – 324.
9. Dobrină, S., Birghila, S., Coatu, V. (2008). Assessment of polycyclic aromatic hydrocarbons in honey and propolis produced from various flowering trees and plants in Romania, *Journal of Food Composition and Analysis*, 21: 71 – 77.
10. Kovacs, M. H., Ristoiu, D. (2012). Survey of human exposure to organic pollutants coming from home produced vegetables and animals, *Environmental Engineering and Management Journal*, 11(3): 589 – 595.