Int.J.Curr.Microbiol.App.Sci (2016) *5*(4): 55-63

International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 5 Number 4(2016) pp. 55-63**
Journal homepage: http://www.ijcmas.com

Original Research Article http://dx.doi.org/10.20546/ijcmas.2016.504.009

Determination of Some Chlorinated Organic Pollutants in Plants and Soil Samples from Kosovo

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Keywords

Organochlorinated pesticides, PCB, Soil samples, Plant samples, Fruit samples, Gas chromatography.

Article Info

Accepted:
08 March 2016
Available Online:
10 April 2016

A B S T R A C T

The present study presents the data obtained for organochlorinated pesticides and PCB in the 4 stations near Peja, Kosovo in July 2015. In the selected agricultural areas (stations) soil samples, the upper side of plants and tomato fruit samples were taken for analyze for an area of $1m^2$. Usage of heavy farm equipment, application of agrochemicals, emissions of industries, etc, all generate a number of pollutants, which after deposition in soil may influence crop quality. Thus, input of these contaminants into the agricultural areas should be carefully monitored. In the analytical method were combined ultrasonic bath extractions assisted by organic solvents, acid hydrolysis and a Florisil column for samples clean-up for soil and biota samples. The qualitative and quantitative analysis of the organochlorinated pesticides and PCB in all samples was performed by gas chromatography technique using electron capture detector (GC/ECD). Optima-5 (60m x 0.33mm x 0.25µm) capillary column was used for isolation and determination of organochlorinated pesticides dhe PCB. In all studied samples were found organochlorinated pesticides and PCB. These facts reflect the presence of pesticides because their previous use, bioaccumulation processes, geographical position, slope, soil geology, crop type, irrigation water used, atmospheric depositionin agricultural areas in Kosovo.

Introduction

Human exposure to chlorinated organic pollutants primarily occurs through food contamination. Fish, meat, fruit, vegetables and other dairy products are the most important dietary sources of pesticides and their metabolites for humans. It is widely accepted that these pollutants will be present in food for many years to come (Lazaro *et al.*, 1996). Great concern was caused by chlorinated compounds, which proved to be extremely persistent in the environment and accumulative in the food chain (Penttila & Siivinen, 1996; WHO & FAO 1983; Wilhelm *et al.*, 2002). The application of DDT and many other chlorinated pesticides has been banned in most countries since the

1970s (Rogan and Chen, 2005). The hopes that it would be possible to clear the environment of the residues of the compound have proved to be futile; despite the passage of time, the monitoring of the environment and food in many countries has confirmed the ubiquity of the compound (Skibniewska *et al.*, 2000). The fate of a pesticide applied to soil depends largely on two of its properties: persistence and adsorption. Once applied to cropland, a pesticide may be taken up by plants, adsorbed to plant surfaces, broken down by sunlight (photdegradation), or ingested by animals, insects, worms or microorganisms in the soil. It may move downward in the soil and either adhere to soil particles or dissolve in soil water. The pesticide may vaporize and enter the atmosphere (volatilization) or break down via microbial and chemical pathways into less toxic compounds. Pesticides may be leached out of the root zone by rain or irrigation water or wash off the surface of the land. Properly applied pesticides can reach surface and underground waters in two ways: in runoff and by leaching. Runoff is the physical transport of pollutants (chemicals or soil) over the ground surface by rainwater, snowmelt or irrigation water that does not penetrate the soil. In the leaching process, pollutants are carried through the soil by rain or irrigation water as it moves downward. The fate of a pesticide applied to soil depends largely on two of its properties: persistence and adsorption.

Most pesticides in the soil break down or "degrade" over time as a result of several chemical and microbiological reactions. However, some pesticides will continue to degrade by chemical reactions after they have left the root zone. Factors controlling pesticide adsorption include pesticide charge; soil pH, temperature and water content; the presence of previously adsorbed chemicals that have a stronger bond to soil particles; and the amount and type of organic matter present. In general, pesticide adsorption relates inversely to pesticide solubility in water. Highly soluble pesticides are weakly adsorbed and pose a greater threat of groundwater contamination (Penttila and Siivinen, 1996).

Materials and Methods

Sampling of Tomato Plants, Tomato Fruits and Soil Samples

Four stations near Peja, Kosovowere choosing for this study in July 2015. Tomato plant, tomato fruit and soil samples were taken in the selected agricultural areas (stations).The upper side of plants, fruits and soil samples were taken for analyze for an area of $1m^2$. Selected sampling stations were: Qyshke (station 1), Leshan (station 2), Raushiq (station 3) and Peje (station 4). Tomato plants and tomato fruits were transported in plastic bags in $+4^oC$. Soil samples were taken until 30 cm depth.

Sample Preparation for Tomato Plants and Tomato Fruits

The plant and fruit samples were homogenized with anhydrous sodium sulphate and were extracted by ultrasonic bath assisted extraction (10g fresh weight of biota with 50 ml hexane/dichloromethane 3/1, (v/v). The extract was purified by shaking with 15g silica gel, impregnated previously with 45% sulfuric acid. A further clean-up of this extract was performed in an open glass column packed with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane/dichloromethane 4/1(v/v). The extract was concentrated to 1 ml and analyzed by GC-ECD (Nuro *et al.*, 2007).

Soil Sample Treatment for GC Analyze

A fresh sub-sample from 20 g of soil samples were extracted by ultrasonic bath assisted extraction with 50 ml hexane/dichloromethane 3/1, (v/v). The extract was purified by shaking with 2 gr sodium sulphate and 2g silica gel, impregnated previously with 45% sulfuric acid. A further clean-up of this extract was performed in a open glass column packed with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane/dichloromethane 4/1(v/v). The extract was concentrated to 1 ml in nitrogen concentrator and after that analyzed by GC-ECD (Nuro *et al.,* 2007).

Gas Chromatography Analyze

Gas chromatographic analyses of organochlorinate pesticides and PCBs were performed with a DANI 1000 gas chromatograph equipped with a ^{63}Ni Electron Capture Detector and a split/splitless injector. The column used was an Optima-5 (low/mid polarity, 5% phenyl methyl siloxane 60 m x 0.33 mm x 0.25µm film). The split/splitless injector and detector temperatures were set at 300^{0}C and 320^{0}C, respectively.

Carrier gas was helium at 2 ml/min and make-up gas was nitrogen at 25 ml/min flow. The initial oven temperature was kept at 60^{0}C for 4 minutes, than increased to 200^{0}C at 20^{0}C/min, and then increased to 280^{0}C at 40C/min. The temperature was finally increased to 300^{0}C, at 10^{0}C/min, than held for 7 minutes.

Injection volume was 1µl and injections were done in splitless mode. Organochlorine pesticide quantification was performed by external standard method based in Top Mix 40 standard (Nuro *et al.,* 2007).

Results and Discussion

The upper side of plants, fruits and soil samples were taken for analyze for an area of 1m^2. Selected sampling stations were agricultural areas near Peja, Kosovo. Analyze of chlorinated pesticides were performed using GC/ECD technique. Table 1 show organochlorinated pesticides data for soil, plant and fruit samples from agricultural areas near Peje, Kosovo. Figure 1 shown total concentration of organochlorinated pesticides in plant, tomato fruit and soil samples. The higher levels were found for F1, F2 and P3. It was shown that higher levels were for Fruits > Plant > Soil. This could be because of metabolism process from soil to plant and after that to fruit. Higher levels in fruit samples could be also because of pesticide treatments from agricultural purposes. These pesticides could be chlorinated pesticides. Figure 2 shown distributions of organochlorinated pesticides in all analyzed samples. There was noted the same distribution in all samples. The highest levels were for HCHs, Endrines, Endosulphanes and DDT metabolites. Figure 3 shown dendrogram of Cluster Analyze for organochlorinated pesticides in samples analyzed. It was shown the higher similarities for 1-16 (Teknazen cis-Chlordane) with 91.3%; 19-20 (Dieldrin-DDE) with 89.6%; 8-26 (e-HCH-Chlordekon) with 87.4%; 9-25 (Heptachlor-DDT) with 83.3% and 11-30 (Isodrin-Methoxychlor) with 82.1%. It is evident that highersimilarities were for the organochlorinated pesticides used in the past for these areas. Station 1 was the most polluted while station 4 less polluted for third type of samples. This could be conected to their geographical position, slope, soil geology, type of crops, water used for irrigation, etc. Figure 4 shown dendrogram of Cluster Analyze for stations

for concentrations found organochlorianted pesticides. It seems that the levels found in tomato plants P2-P4 with 98.6% and then 84.3% P1 were with higher similarities. This may be indicative of bioaccumulation processes to the tomato plant belong to the concentration of pesticides in the soil sample.

Table.1 Organochlorinated Pesticides Data for Soil, Plant and Fruit Samples

		S1	P1	F1	S2	P2	F2	S3	P3	F3	S4	P4	F4
1	**Teknazen**	2.80	0.40	3.50	1.10	0.90	2.90	2.80	2.60	0.80	0.00	0.00	1.70
2	**HCB**	0.50	2.00	1.10	7.10	0.20	1.00	0.00	1.50	0.20	0.10	0.10	3.40
3	**Kvintozen**	0.00	1.50	1.00	4.30	2.00	9.80	0.50	9.80	2.00	0.00	0.20	1.60
4	**a-HCH**	1.10	1.10	7.30	1.10	1.50	6.30	2.70	6.30	5.40	0.10	0.10	1.40
5	**b-HCH**	2.70	1.30	0.60	0.50	2.60	2.10	7.10	1.10	2.60	0.00	0.10	0.70
6	**Lindane**	7.10	1.50	0.20	0.00	1.10	6.00	2.80	1.00	1.70	0.10	0.00	1.90
7	**d-HCH**	1.10	1.10	0.50	0.00	7.60	0.70	0.50	1.50	7.60	0.10	0.00	5.40
8	**e-HCH**	0.00	0.40	28.70	0.00	1.10	1.20	0.00	1.50	1.40	0.00	0.00	1.20
9	**Heptachlor**	0.00	0.40	0.40	0.50	0.40	1.20	1.10	0.40	3.20	0.20	0.00	0.50
10	**Aldrin**	0.00	9.80	0.50	2.70	1.50	1.50	2.80	1.50	1.90	0.00	0.00	1.70
11	**Isodrine**	0.50	6.30	1.10	1.10	1.30	2.30	0.00	0.40	1.90	0.10	0.10	1.60
12	**Heptachlor epoxide cis**	0.50	1.10	0.30	4.30	1.50	1.50	0.50	1.50	1.10	0.00	0.10	0.80
13	**Heptachlor epoxide trans**	7.10	1.30	2.60	4.30	1.10	1.70	7.10	1.30	1.70	0.00	0.00	1.80
14	**Oxychordane**	0.50	1.50	2.10	2.80	1.50	1.80	7.10	0.40	1.80	0.10	0.40	2.10
15	**Chlordane trans**	1.10	1.10	1.50	0.50	1.30	2.10	10.80	9.80	1.20	0.10	0.10	2.10
16	**Chlordan cis**	0.00	1.30	1.70	0.00	1.10	1.80	2.10	6.30	2.10	0.00	0.00	1.80
17	**2,4'-DDE**	0.50	1.10	1.60	1.10	1.50	2.10	2.80	1.10	1.70	0.00	0.00	1.70
18	**Endosulphan alfa**	7.10	0.40	0.90	2.80	1.30	1.80	0.50	1.30	2.10	0.00	0.10	1.80
19	**Dieldrin**	4.30	1.50	1.80	0.00	0.40	2.10	0.00	1.50	1.80	0.00	0.00	2.10
20	**4.4'-DDE**	4.30	0.40	0.00	0.50	1.10	1.80	1.10	1.10	2.10	0.10	0.00	1.80
21	**2.4-DDD**	0.00	6.40	0.00	6.20	1.50	1.10	2.80	1.50	1.70	0.10	0.10	0.00
22	**Endrin**	0.00	0.40	1.70	7.10	0.40	30.30	2.10	30.30	1.20	0.00	0.00	1.20
23	**Endosulphan beta**	2.80	1.30	1.10	2.10	0.00	1.50	0.50	1.10	0.00	0.00	0.10	1.10
24	**4.4-DDD**	0.50	0.00	0.00	6.20	0.00	0.00	2.10	0.00	0.00	0.00	0.00	1.70
25	**2.4-DDT**	0.00	0.40	1.20	0.00	1.30	1.70	2.80	0.40	1.20	0.20	0.00	0.00
26	**Chlordekon**	1.10	1.30	23.70	0.00	1.30	1.20	0.50	1.10	1.50	0.00	0.00	1.70
27	**Endosulphansulphat**	2.80	0.40	31.70	7.10	0.40	1.70	0.00	0.40	1.10	0.50	0.00	1.20
28	**4,4'-DDT**	2.10	0.00	1.70	0.50	0.00	0.00	1.10	0.00	0.00	0.10	0.00	1.50
29	**Dicofol**	0.50	3.00	1.10	0.00	1.00	1.70	2.80	4.00	1.10	0.00	0.10	0.00
30	**Methoxychlor**	0.00	6.00	1.20	0.50	3.50	1.10	0.00	9.90	1.10	0.10	0.00	1.70
31	**Mirex**	0.70	13.20	1.10	2.10	32.20	16.90	0.00	16.90	1.20	0.00	5.30	1.70
	Total	51.70	67.90	121.90	66.50	72.60	108.90	67.00	117.50	54.40	2.00	6.90	48.90

Table.2 PCB Data in Soil, Plant and Tomato Fruit Samples

		S1	P1	F1	S2	P2	F2	S3	P3	F3	S4	P4	F4
1	**PCB 28**	0.00	0.00	0.00	0.20	0.20	0.10	0.30	0.00	0.10	0.10	0.10	0.00
2	**PCB 52**	0.00	0.00	0.40	0.00	0.00	0.20	0.20	0.20	0.40	0.00	0.00	0.00
3	**PCB 101**	0.40	0.30	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	**PCB 118**	0.10	0.00	0.00	0.40	0.10	0.10	0.00	0.00	0.00	0.10	0.30	0.10
5	**PCB 153**	0.30	0.30	0.10	0.00	0.00	0.00	0.30	0.10	0.10	0.00	0.00	0.00
6	**PCB 138**	0.00	0.00	0.00	0.20	0.20	0.10	0.00	0.00	0.00	0.00	0.30	0.10
7	**PCB 180**	0.40	0.00	0.40	1.20	0.00	0.00	0.30	0.30	0.10	0.00	0.00	0.00
	Total	**1.20**	**0.60**	**1.20**	**2.00**	**0.50**	**0.50**	**1.10**	**0.60**	**0.70**	**0.20**	**0.70**	**0.20**

Figure.1 Total of Organochlorianted Pesticides in Soil, Plant and Tomato Fruit Samples

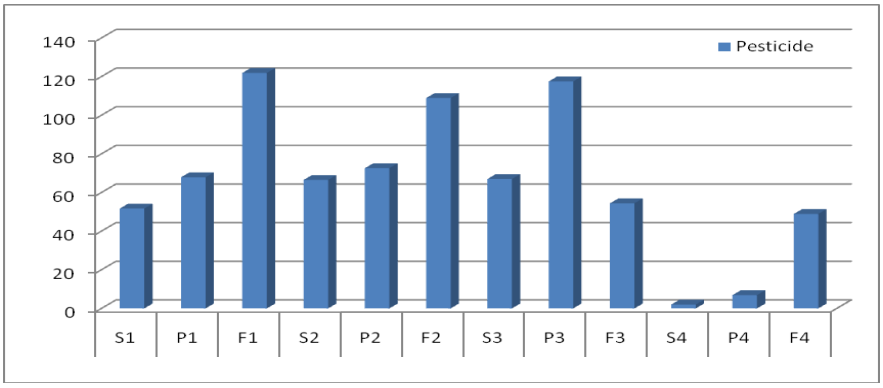


Figure.2 Distribution of Organochlorianted Pesticides in Soil, Plant and Tomato Fruit Samples

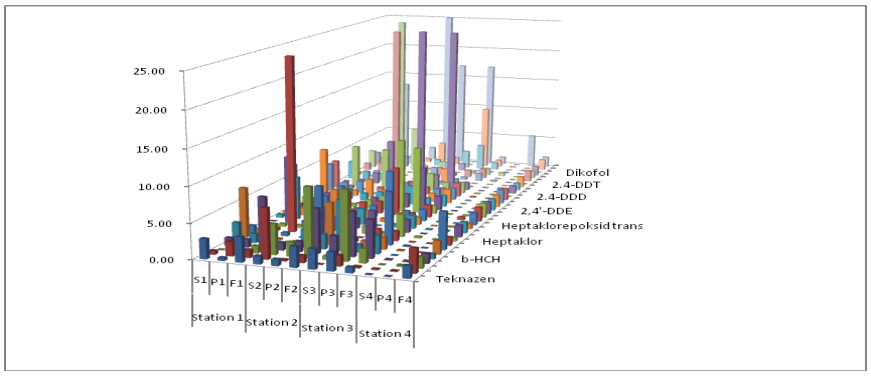


Figure.3 Dendrogram of Cluster Analyze for Organochlorianted Pesticides in Analyzed Samples

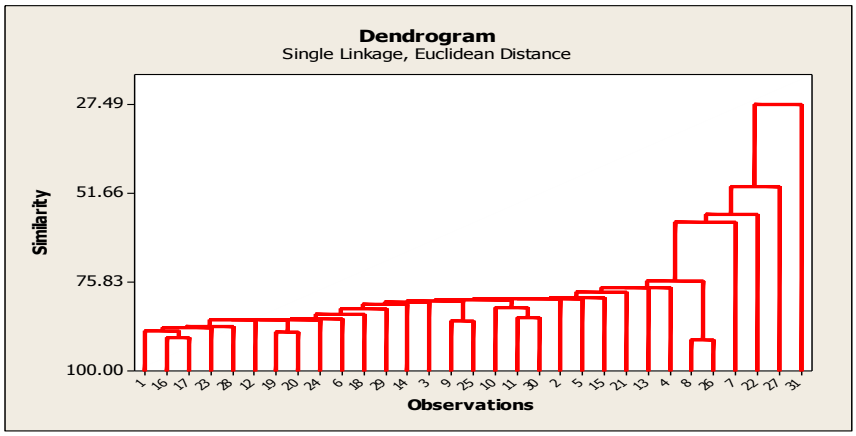


Figure.4 Dendrogram of Cluster Analyze for Stations for Found Organochlorianted Pesticides in Analyzed Samples

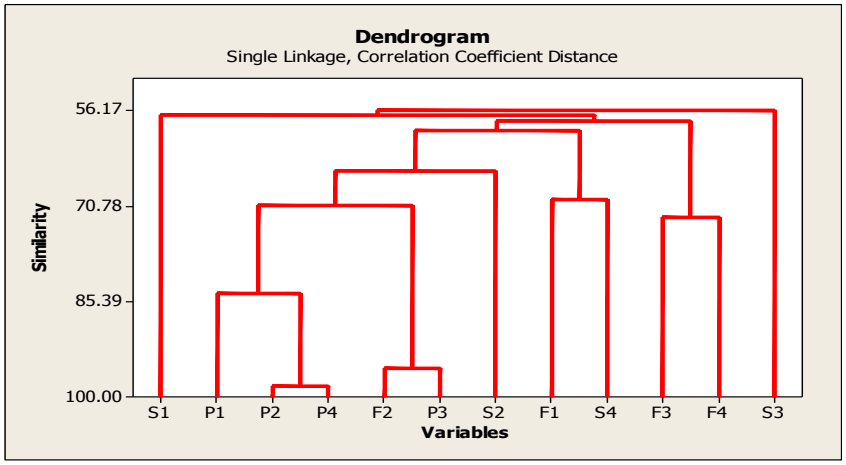


Figure.5 Total of PCB in Analyzed in Soil, Plant and Tomato Fruit Samples

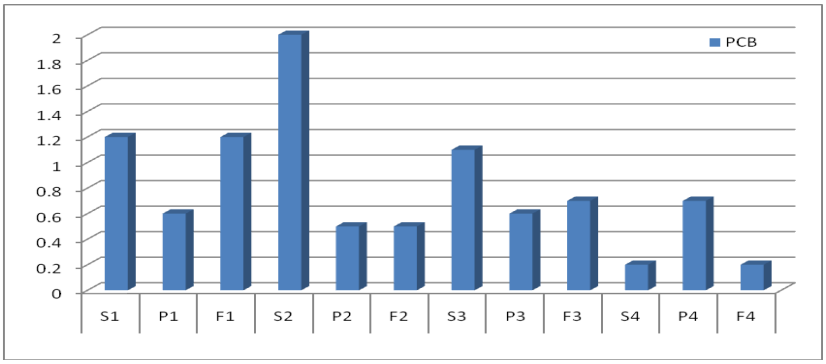


Figure.6 Distribution of PCB in Analyzed in Soil, Plant and Tomato Fruit Samples

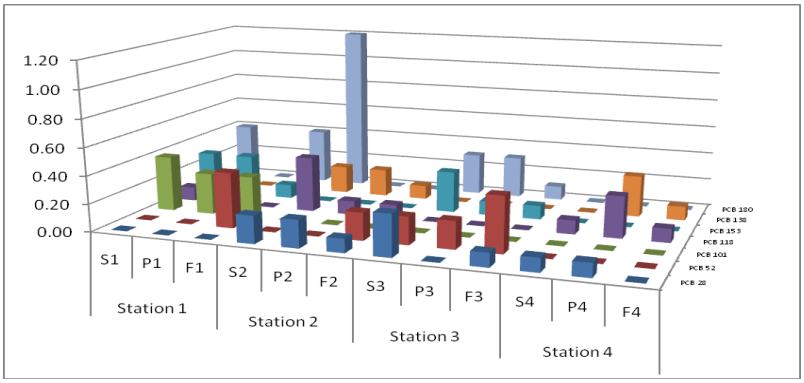


Figure.7 Dendrogram of Cluster Analyze for PCBs in Analyzed samples

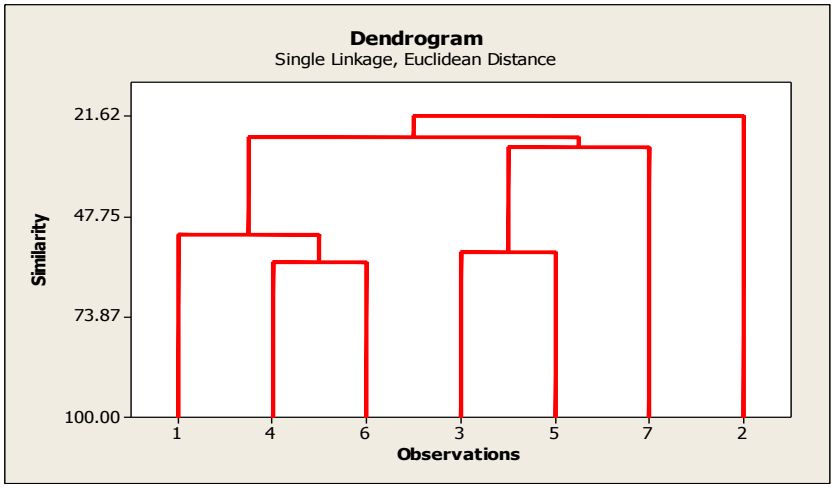
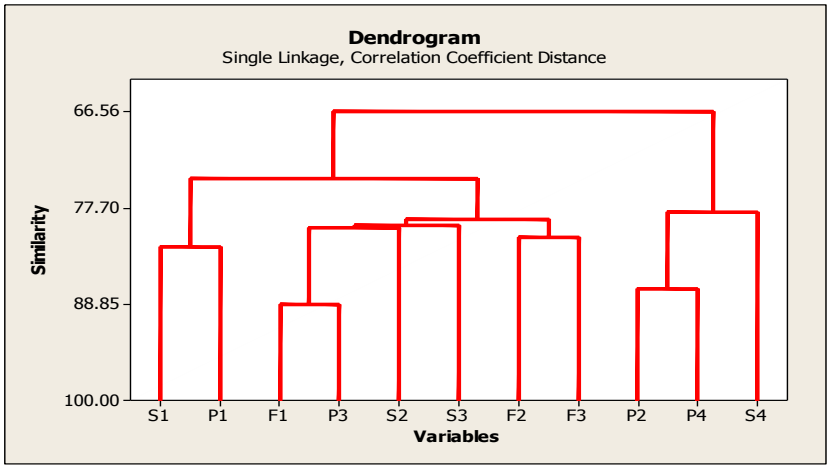


Figure.8 Dendogram of Cluster Analyze for Stations for PCB Analyze



After that fruit samples shown higher similarities. Soil samples have shown the smaller similarity and the higher difference concern to found data about the pesticides. This is associated with the amount of exposure of these lands by organochlorine pesticides. Other factors are also geographical position, slope, soil geology, crop type, irrigation water used, etc.

Table 2 show PCB markers data for soil, plant and fruit samples from agricultural areas near Peje, Kosovo. Figure 5 shown total concentrations of PCBs in plant, tomato fruit and soil samples. The higher levels were found for S2, S1 and S3. It was shown that higher levels were for soil samples. This could be because of pollution origin with PCB in these areas. Station 1 was the most polluted while station 4 less polluted for third type of samples. Figure 6 shown distributions of PCB in all analyzed samples. There was noted the same distribution in all samples. Volatile PCBs were detected and also non-volatile one. Figure 7 shown dendrogram ofCluster Analyze forPCB markers data in analyzed samples. It was shown the higher similarities for 4-6 (PCB 118 – PCB 138) with 66.4% after that PCB 28 with 54.3% similarity and 3-5 (PCB 101-PCB 153) with 64.1%. This could be connected to their geographical position, slope, soil geology, water used for irrigation, etc.

Figure 8 shown dendrogram of Cluster Analyze for stations for concentrations found PCB markers. It seems that the levels found in soilS1-P1 (station 1), S2-S3 (soil samples), F2-F3 (tomato fruit samples), P2-P4 (tomato plant) were with higher similarities. This may be indicative the same origin of pollution, bioaccumulation processes, geographical position, slope, soil geology, crop type, irrigation water used, PCB atmospheric deposition, etc.,

In conclusion, Determinations of organochlorinated pesticides and PCBs in soil, plant and tomato fruit samples were realized in Institute of Agricultural, Peja, Kosovo. Organochlorinated pesticides and PCBs were determining based in EU protocols in soil and non-fatty food samples. The higher levels of organochlorinated pesticides and PCB markers were for Station 1 samples located in Qyshke. Peja samples (Station 4) were the "clean" samples. It was shown that higher levels were for Fruits > Plant > Soil. This could be because of metabolism process from soil to plant and after that to fruit. Higher levels in fruit samples could be also because of pesticide treatments from agricultural purposes. Distribution of organochlorinated pesticides were the same for all samples. The highest levels were for HCHs, Endrines, Endosulphanes and DDT metabolites. This could be connected to their geographical position, slope, soil geology, type of crops, water used for irrigation, etc.Organochlorinated pesticide levels were lower than acceptable concentration in soil and samples. PCBs were detected for all samples. The higher levels were found for soil samples. This could be because of pollution origin with PCB in these areas. Volatile PCBs were detected and also non-volatile one. This could be connected to their geographical position, slope, soil geology, water used for irrigation, PCB atmospheric deposition, etc.

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How to cite this article:

Vlora Gashi, Ardian Maçi, Aurel Nuro and Orinda Gashi. 2016. Determination of Some Chlorinated Organic Pollutants in Plants and Soil Samples from Kosovo. *Int.J.Curr.Microbiol.App.Sci.* 5(4): 55-63. doi: http://dx.doi.org/10.20546/ijcmas.2016.504.009