



Levels of Organchlorinated Pesticides and PCB in OliveOil of Vlora Region, Albania

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Abstract: In this study were evaluated levels of organochlorinated pesticides and polychlorinated biphenyls in extra virgin olive oil samples from Vlora region (South Albania), in January 2015. Vlora region is known for olive oil production. Organochlorinated pesticides are used wide for agricultural purposes until 90' in Albania. PCBs were used in Albania as electric transformer oil after 90' therefore these compound were reported in many areas because of their atmospheric deposition. In general these pollutants are stable compounds, lipophilic, withtoxic properties. Ultrasonic bath extraction assisted with n-Hexane as organic solvent and two clean-up steps have been used for analytical treatment of olive oil samples. The quantitative analysis of organochlorinateds pesticides and PCBs were performed by the gas chromatography method with electron capture detector. The profiles of detected pesticides were: Endosulphanes > HCHs > Aldrines Mirex > Methoxychlor > DDTs. PCB 28, the volatile PCB marker was the main congener for all analyzed samples. The levels of contaminants observed for the olive oil samples could be because of their before use for agricultural purposes, oil production proces, atmospheric deposition for Vlora region.

Keywords: *Organochlorinated pesticides, PCBs, Olive oil, Gas chromatography*

Introduction

The olive tree is native to the Mediterranean basin. Wild olives were collected by Neolithic peoples as early as the 8th millennium BC. Olives are evergreen tree, slow growing, long-lived, uniquely adapted to the climate of the Mediterranean basin and considered a defining feature of this climate. The olive tree, olive fruit and olive oil have been at the core of Mediterranean agriculture and trade since early cultivation times, to the various cultures and civilizations of the Mediterranean Basin (Smart and Simmons, 1995; Vosen et al, 2011). The olive and olive oil sector is an important segment of Albanian primary production and agro industry. The Adriatic costal region, in the western part of the country has a typical Mediterranean climate. This climate makes Albania an important producer of olives and olive oil forthe region. Large olive plantations were established to the entire coast from Saranda (South) to Shkodra (North) and inland river valleys in the districts of Peqin/ Elbasan, Berat/Skrapar, and Mallakastër/Tepelenë. Recently, according the data on country olive oil quantity has ranked Albania as 16th in world production (Kapaj, 2012).

In Albania olive oil is produced by grinding olives using large millstones (traditional and early method) or steel drums (modern method).The olive paste generally stays under the stones for 30 to 40 minutes. In steel drum mills the grinding process takes about 20 minutes. After grinding, the paste is stirred slowly for another 20 to 30 minutes in a particular container (malaxation), where the microscopic oil drops unite into bigger drops, which facilitates the mechanical extraction. The paste is then pressed by centrifugation/ the water is thereafter separated from the oil in a second centrifugation. The oil produced by only mechanical means as described above is called virgin oil. Extra virgin olive oil is virgin olive oil that satisfies specific high chemical and organoleptic criteria (low free acidity, no or very little organoleptic defects). A higher grade extra virgin olive oil is mostly dependent on favorable weather conditions; a drought during the flowering phase, for example, can result in lower quality (virgin) oil. Sometimes the produced oil will be filtered to eliminate remaining solid particles that may reduce the shelf life of the product. Unfiltered fresh olive oil is called cloudy olive oil. This form of olive oil for more ecological and less-processed is called "green" products. The remaining paste (pomace) still contains a small quantity (about 5–10%) of oil that cannot be extracted by further

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pressing, but only with chemical solvents. This is done in specialized chemical plants, not in the oil mills. The resulting oil is not "virgin" but "pomace oil" (Kiritsakis et al 1998; Harwood and Aparico, 2000).

The growth of the olive trees, different treatment for higher production of fruit and the production of olive oil may be affected by the presence of various contaminants such as pesticides, PCBs, etc. Before 90' organochlorinated pesticides were used widely in Albania for agricultural purposes. The main agricultural areas were in the western of the country (Shkodra, Durresi, Tirana, Fieri, Lushnja, Vlora). The most used organochlorinated pesticides were DDT, Lindane, HCB, Aldrin and Heptachlors. The scale of pesticides use after 90' in agriculture generally has decreased but the mismanagement of old pesticides, for some years after 90' was another source of pesticides contamination in many areas of Albania. PCBs were not used before 90' in Albania. They were used mainly as electric transformer oil after 90' (Nuro et al 2007). Commercial PCB mixtures were used in a wide variety of applications and mainly as dielectric fluids in capacitors and transformers, and as heat exchange fluids. Organochlorinated pesticides and PCB are chemically stable, lipophilic compounds (cause them to accumulate in biota), cause adverse effects because their toxicity (Safe, 1994; Erickson, 2001; Hansen, 2002).

Materials and Methods

Sampling of olive oil samples

18 Olive oil samples were collected in 6 stations in Vlora region, South Albania in March 2015. The olive oil stations were: Trevian, Aliban, Panaja, Kanine, Pus i Mezinit and Selenice. These areas are known in Vlora and Albanian for olive oil production. Extra virgin olive oil samples were selected for this study. Samples were transported and stored at +4°C before analysis.

Preparation of olive oil samples for pesticide residues and PCB analysis

The extraction method used was based on EN 1258 for determination of organochlorine pesticides in fatty matrices. About 10 ml of olive oil was put into a flask and about 20 ml of hexane was added and the samples were extracted for 30 min in ultrasonic bath. The sample was spiked with recovery standard (PCB 29) before extraction. 20 g of silicagel with 45% acid sulphuric (m/m) were added for lipids hydrolyze. For a second clean-up procedure were used a Florisil 5% water column. Extracts were concentrated under a Kuderna Danish to approximately 2 ml and analyzed using gas chromatography-ECD (Kalantzi et al 2002; Santillo et al, 2004, Nuro et al 2007; Lazaro et al 1995). The following organochlorine pesticides: hexachlorocyclohexane (HCH) isomers, dieldrin, endrin, heptachlors, endosulphanes, methoxychlor, mirex and the DDT-related chemicals (*o,p*-DDE, *p,p*-DDE, *p,p*-DDD, *p,p*-DDT) were detected. PCB markers were studied simultaneously with above pesticides in olive oil samples.

Apparatus and chromatography

Gas chromatographic analyses were performed with an HP 6890 Series II gas chromatograph equipped with a ⁶³Ni electron-capture detector and a split/splitless injector. The column used was a Rtx-5 [low/mid polarity, 5% (phenyl methyl siloxane)] (30 m x 33 mm I.D., x 25mm film). The split/splitless injector and detector temperatures were set at 280°C and 300°C, respectively. Carrier gas was He at 1 ml/min and make-up gas were nitrogen at 24ml/min. The initial oven temperature was kept at 60°C for 4 min, which was increased, to 200°C at 20°C/min, held for 7 min, and then increased to 280°C at 4°C/min for 20 min. The temperature was finally increased to 300°C, at 10°C/min, held for 7 min. Injection volume was 2 µl, when splitless injections were made. Pesticide quantification was performed by internal standard method (Santillo, 2004).

Results and Discussion

Levels of organochlorinated pesticides, their metabolites and polychlorinated biphenyls were analyzed in extra virgin olive oil samples of Vlora region, in South of Albanian. Olive oil samples were collected in January 2015. EN 1528/1/2/3/4 protocols were used for determination of chlorinated compounds in oil samples. Organochlorine pollutants were detected using capillary gas chromatography with ECD technique. Total of organochlorinated pesticides in olive oil samples were shown in Figure 1. The totals were between 4.2-48.7 µg/L. The average of pesticides in oil samples were 10.7 µg/L.

The minimum was for Trebian, Aliban and Panaja samples while the maximum for Kanina sample. The role of pesticides in respective agricultural areas could do the difference. The level of pesticides for all analyzed samples were lower than the accepted dairy intake. Distribution of organochlorinated pesticides in olive oil samples was shown in Figure 2. The distributions of pesticides were almost the same for all analyzed samples because the same origin of pollution. The profiles of detected pesticides were: Endosulphanes > HCHs > Aldrines Mirex > Methoxychlor > DDTs (Figure 3). The concentrations and profile of organochlorinated pesticides could be because of their previous use for agricultural processes, pesticide degradation rate, metabolism of pesticides in different plants, etc.

Total of PCB markers in olive oil samples was shown in Figure 4. The average of PCB in oil samples were 5.2 ug/L. The minimum was for Kanian sample with 1.6 ug/L and the maximum for Selenica sample with 15.6 µg/L. The PCB levels were lower than accepted limit for all samples. The presence of PCB in oil samples could be because of industrial process for oil production or other factors such as soil contaminations, atmospheric factors, etc. Distribution of PCB markers in olive oil samples (Figure 5) were almost the same for all oil samples. This could be connected with their same origin of pollution for oil samples with PCBs. Profile of PCB markers in olive oil samples was shown if Figure 6. PCB 28, the volatile PCB marker was the main congener for all analyzed samples. Presence of PCB 209 in oil samples could be maybe for accidental reasons. Only Selenica sample was shown higher levels of this congener. The presence of PCB, their distribution and profile in oil samples could be because of industrial process for oil production, soil contaminations, atmospheric factors, etc.

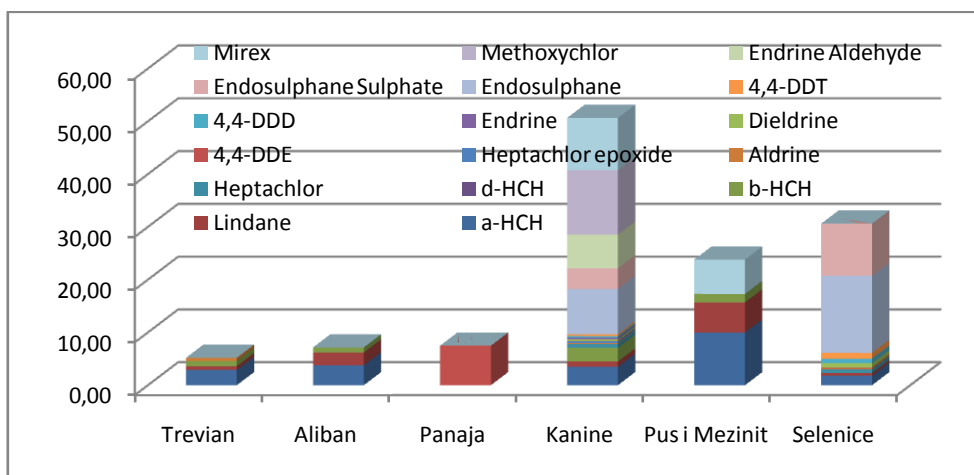


Figure 1. Total of organochlorinated pesticides (ug/L) in olive oil samples from Vlora region

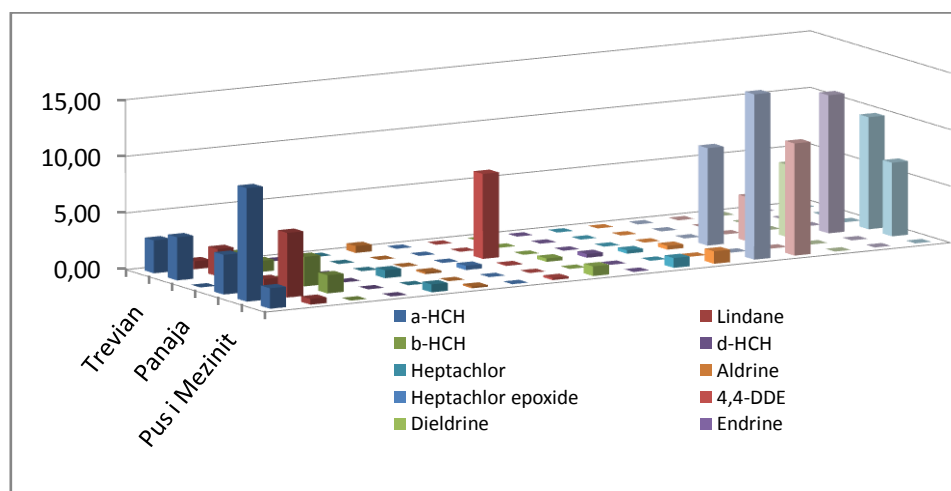


Figure 2. Distribution of organochlorinated pesticides (ug/L) in olive oil samples, January 2015

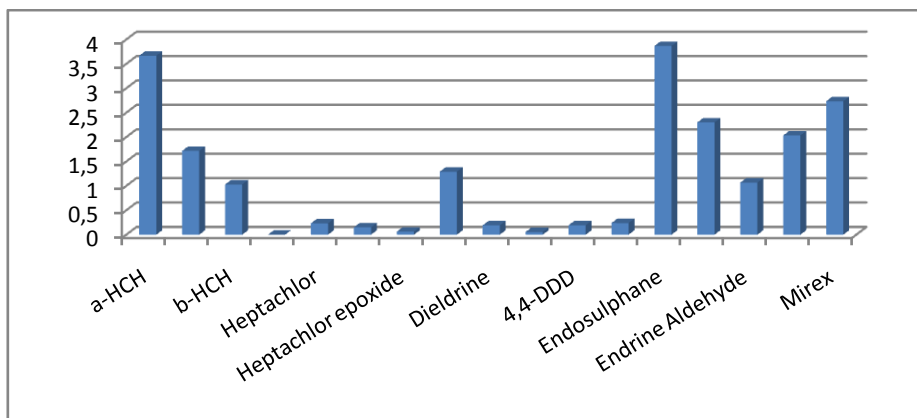


Figure 3. Profile of organochlorinated pesticides(ug/L) in olive oil samples

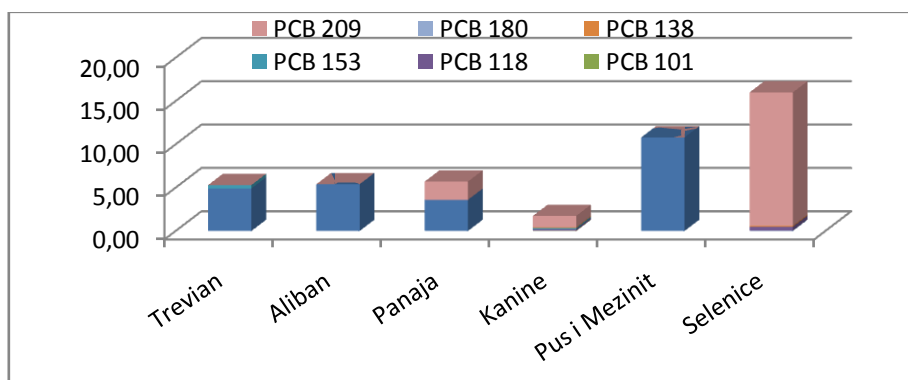


Figure 4. Total of PCB markers (ug/L) in olive oil samples, Vlora region

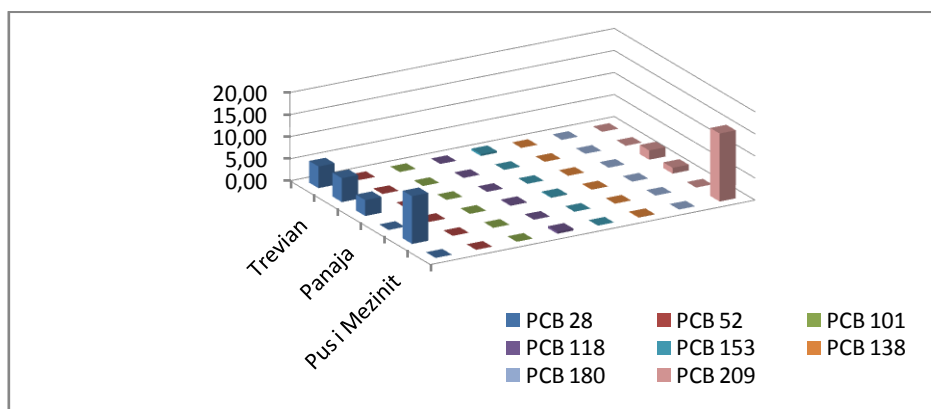


Figure 5. Distribution of PCB markers (ug/L) in olive oil samples

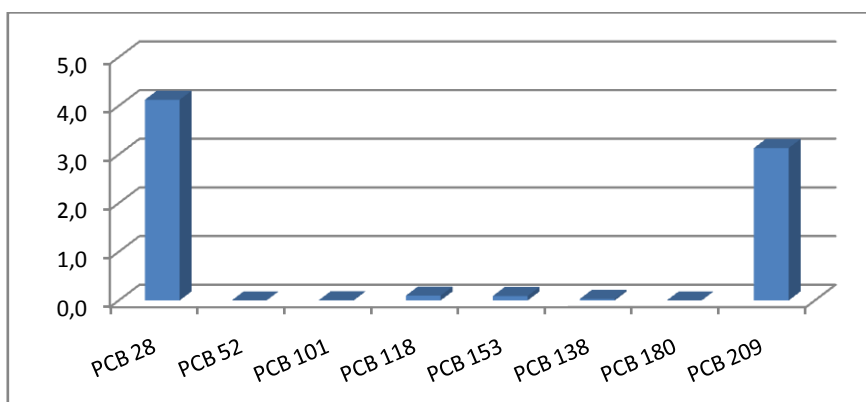


Figure 6. Profile of PCB markers (ug/L) in olive oil samples, January 2015

Conclusions

Levels of organochlorinated pesticides, their metabolites and polychlorinated biphenyls were analyzed in extra virgin olive oil samples of Vlorë region (South Albania) in January 2015. EN 1528/1/2/3/4 protocols were used for determination of chlorinated compounds in oil samples. Almost in all analyzed olive oil samples from Vlorë were found organochlorinated pollutants concentrations. The presented data about concentrations of organochlorinated pesticides and PCB are the first reported data. The distribution of pesticides depends from country or region origin and also from metabolism of pesticides in different plants. The profile of detected pesticides were Endosulphanes > HCHs > Aldrin > Mirex > Methoxychlor > DDTs. The concentrations and profile of organochlorinated pesticides could be because of their previous use for agricultural processes, pesticide degradation rate, metabolism of pesticides in different plants, etc. The PCB 28, the volatile PCB marker was the main congener for all analyzed samples. Presence of PCB 209 in oil samples could be maybe for accidental reasons. Only Selenica sample was shown higher levels of this congener. The presence of PCB, their distribution and profile in oil samples could be because of industrial process for oil production, soil contaminations, atmospheric factors, etc. Levels of organochlorine pesticides and PCBs found in olive oil samples from Vlorë region are lower than the rate allowed in food products.

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