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Organochlorinated Pesticides and PCB In Some Medicinal Plants from South-East Albania

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Abstract: In this paper are presented concentrations of organochlorinated pesticides and polychlorinated biphenyls (PCB) in some medicinal plants from South-East Albania. Many medicinal plants grow in Albania due to appropriate Mediterranean climate. Twelve different species of medicinal plants were taken in May 2017 in Pogradeci-Korca-Kolonja-Permeti region (South-East Albania).
Ultrasonic extraction used for extracting organochlorinated pesticides, their residues and PCBs from medicinal plant samples. Clean-up procedure was performed using firstly silicagel with sulfuric acid and a second clean-up procedure in an "open" florisil column. Qualitative and quantitative analysis was realized in HP 6890 Series II, gas chromatograph equipped with μECD detector. For separation of organochlorinated pesticides and PCB markers was used Rtx-5 capillary column (30m x 0.32mm x 0.25μm).
The highest level of organochlorine pollutants was found to the samples of Mentha longifoglia L. because these plans were grow near the agricultural areas. The main origin of organochlorine pesticides could be as result of their previous uses for agricultural purposes. Profile PCB marker were as following: PCB 28 > PCB 138 > PCB 153. This fact confirms atmospheric origin of these compounds in the wild ecosystem of medicinal plants.
Keywords: Organoclorined pesticides; PCBs; Medicinal plants; GC/ECD

INTRODUCTION

Albania is a country reach in medicinal plants due to appropriate Mediterranean climate. Around 3,200 various medicinal herbs, of which 350 species are exported ensuring that Albania develops its position as an important exporting country. In this study, twelve of most known samples from South-East Albania were taken to analyze. The export of medicinal herbs occupies the main place in the Albanian economy. It's the largest exporter of Salvia officinalis L. and many other herbs mostly in Germany, USA, France, etc. After 90' the medicinal herbs industry is shrinking. Before 90' Albania earned about 3-4 times more than recent years. The green export success could help to ease the precarious economic situation, especially in rural areas, and stop further decline. Migration is rife in Albania's less developed mountainous regions, especially amongst young people. The remaining inhabitants have few ways of making a living. Apart from growing agricultural products like potatoes, maize and fruit or rearing livestock, commercial picking is one of the few ways of improving the family's income. If the plants were cultivated instead of being picked wild as they have been so far, the harvest could be increased 2-10 times. Trade in medicinal herbs could be turned into an engine for development in many regions of the country. Local wild medicinal herbs have been seen as a means of overcoming a short-term emergency rather than as a stable economic sector. Other problems include environmental damage, diminishing quality due to over-picking and the decline of certain species of medicinal herb. The Albanian export trade companies are relatively new and small. Their goal is to cultivate the medicinal herbs and prepare them before export. Despite all the problems, there is considerable potential for developing the medicinal herbs industry. Collection areas and types of medicinal herbs [1-5] according to their value should be clearly defined by the authorities and also keep statistics on volume, prices and trading companies. So far, the authorities have no control over the quality and sustainability of these export products [6].

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MATERIAL AND METHOD

Plant collection

Plant samples were choose as: fruits (Juniperus communs L., Juniperus Oxcycedrus L.), flowers, leaves and branches (Salvia officinalis L., Laurus nobilis L., Thymus vulgaris L., Oregano vulgare L., Sideritis raiser L., Tilia tomentosa L., Achillea millefolie L. and Hypericum perforatum L.). Samples were selected from areas of South-East Albania (Pogradec-Korca-Kolonja-Permeti). These plants are usually grown in these areas. The samples were taken in altitude 600 to 1300 m. All the collected species were dried in a Thermostat MEMERT, with air circulation in temperature 400 C, along 5 days.

Preparation of medicinal plants for OCP and PCB analysis

10 g of each medicinal plant samples was blended and homogenized with anhydrous sodium sulphate (1:3) in a mortar. Samples were taken in to an Erlenmeyer (100 ml). 50 ml of solvent mixture Hexane/Dichloromethane (3:1) were added into the sample and sonicated for 60 minutes, in 30oC using an ultrasonic bath (UM4-Unitra). Internal standard (PCB-29) was added previously to each sample (10μl) prior extraction procedure. Extracts were transferred into glass flasks by careful decantation. The residue was subsequently washed three times with 10 ml of pure dichloromethane and these volumes were combined with the extract. The final extract was concentrated to 5 ml. The concentrated extracts were then subject of the clean-up procedure. Firstly, silica gel treated with sulphuric acid (45% in mass) was added for each extract. The extract was passed throw into a Florisil open glass column for a second clean-up step. Organochlorine pesticides and PCBs were eluted simultaneously using a 10 ml mixture of Hexane/Dichloromethane (4:1). The extracts were concentrated to 2 ml before injection in gas chromatograph for qualitative and quantitative analyze [7].

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 Rtx-5 (30m x 0.33mm x 0.25 um) capillary column. The split/splitless injector and detector temperatures were set at 2800C and 3000C, respectively. Carrier gas at 1 ml/min and make-up gas at 25 ml/min was nitrogen. The initial oven temperature was kept at 600C for 4min, which was increased, to 2000C at 200C/min, held for 7 min, and then increased to 2800C at 40C/min for 20min. The temperature was finally increased to 3000C, at 100C/min, held for 7min. Injection volume was 2μl, when splitless injections were made. Analyses of chlorinated pesticides and PCB markers were done simultaneously [8]. The relative response factors of the different individual of chlorinated pesticides and PCB congeners were determined by injecting the standard solutions of PCBs (prepared by making appropriate dilutions of a stock solution provided by IAEA/MEL, Monaco, France) spiked with the same quantity of the solution of internal standard PCB-29 used for spiking the samples. Organochlorinated pesticides and PCB quantification was performed by internal standard method [9-12]. The following organchlorinated pesticides: Hexachlorobenzene (HCB), Dieldrin, Endrine, alfa-, beta-, delta- and gama-isomer (Lindane) of Hexachlorocyclohexane, Heptachlor, Heptachlor epoxide, DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), Methoxychlor,Endosulfanes and Mirex were detected. Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180).

RESULTS AND DISCUSIONS

Organochlorinated pesticides, their metabolites and PCBs marker were analyzed in medicinal plant samples from Pogradec, Korca, Kolonja and Permeti. For this study were determined organochlorine pesticides and PCB in fruits (*Juniperus communs L., Juniperus Oxcycedrus L.*), flowers, leaves and branches (*Salvia officinalis L., Laurus nobilis L., Thymus vulgaris L., Oregano vulgare L., Sideritis raiser L., Tilia tomentosa L., Achillea millefolie L.* and *Hypericum perforatum L.*) from South-East Albania. These data were reported in ng/g (dry weight) level. They were shown for the total, distribution and profile of chlorinated pesticides and PCBs in below graphs. Total of organochlorine pesticides in medicinal plants of South-East Albania was shown in Figure 1. Sample of *Mentha longifolia* was observed to have the maximum level of 102.5 ng/g d.w. The average of OCPs in all analyzed samples was 25.9 ng/g d.w. *Mentha longifoglia* samples were most polluted because these plans usually grow near the agricultural areas. The main origin of organochlorine pesticides could be as result of their previous uses for agricultural purposes. Distribution of pesticides was shown in Figure 2. Most of investigated chlorinated pesticides were not detected in the plant samples, or were in very low concentrations (Aldrine, Lidane, Metoxichlor, DDT and Mirex). Thehighest concentrations of OCPs were detected for HCHs, mostly for α- and β- isomers. This fact is connected with HCHs volatility and previous use of Lindane in tree fruits that grow in altitude of more than 800 m. Lindane and delta isomer were found in very low concentrations. The highest concentration of OCPs was found for degradation products of pesticides such are Heptachlorepoxide, Dieldrin, Endrine and DDE. Presence of pesticides in wild medicinal plants could be mostly because of their previous use, their physical properties and because of their degradation processes. Atmospheric factors (wind, rainfall and snow) could affect their levels and distribution. Profile of individual pesticides was shown in Figure 3 and profile of pesticide classes was shown in Figure 4. Individual profile of pesticides was: alfa-HCH > beta-HCH > Dieldrin > Aldrin > Heptachlorepoxid > Endosulfan sulfate. Total of cyclopentadiene pesticides (Heptachlor, Heptachlorepoxide, Aldrin, Dieldrin, Endrin, Endrin keton) were higher (11.5 ng/g d.w.) than other pesticides. This fact is connected with higher concentration of Heptachlor and Heptachlorepoxide in *Mentha longifolia* samples. Heptachlor could be in use near areas of stations for *Mentha* samples. Note that some banned pesticides could be in use under false trade name in Albania and other countries [13]. ordinary pesticides found for all samples were HCHs. Their average was 9.4 ng/g d.w. Endosulfanes (3.1 ng/g d.w.) were found higher than DDTs (2.9 ng/g d.w.). Found levels could be considered lower than reported levels for environmental samples by respective areas [7,13].

Total of PCB markers was shown in Figure 5. *Laurus nobilis* (27.6 ng/g d.w.), *Chamaemelum nobile* (25.3 ng/g d.w.) and *Tilia tomentosa* (24.1 ng/g d.w.) were most polluted samples. These samples were taken near populated areas (near cities and villages of SE Albania) where anthropogenic impact is higher. Most of PCB markers were not detected in the analyzed native plants from South-East Albania. PCB marker distribution (Figure 6) confirms this fact. The most often PCB markers found for all samples were PCB 28 and PCB 52. For 75% of samples were detected PCB 153 and PCB 153. This was also the profile of PCB (Figure 7) in medicinal plants from South-East Albania. Their profile was PCB 28 > PCB 52 > PCB 138 > PCB 153. The most chlorinated polychlorinated biphenyls (PCB 180 and PCB 209) weren't found in analyzed samples. The high concentrations of less chlorinated PCB 28 and PCB 52 can be a result of atmospheric deposition origin of PCBs in this area. PCB 153 and PCB 138 can bioaccumulate easy in biota samples. Atmospheric factors and PCB properties are the main reasons for levels and distribution of PCBs in analyzed medicinal samples from South-East Albania.

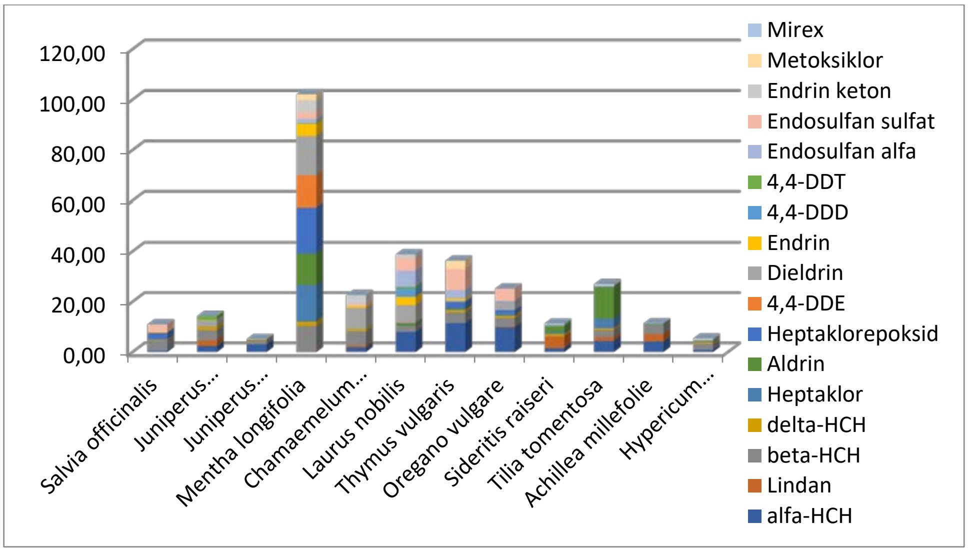

Figure 1. Total of organochlorine pesticides (ng/g) in medicinal plants of South-East Albania

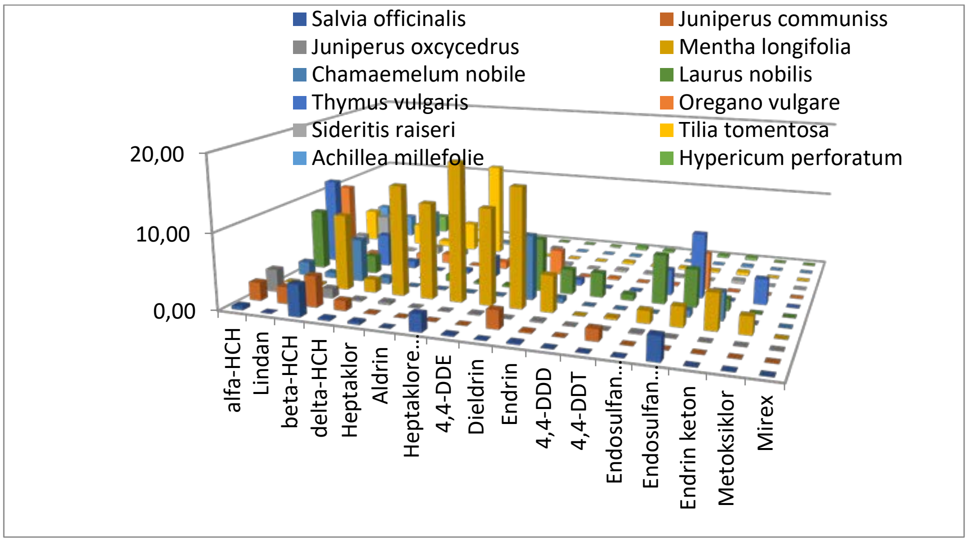

Figure 2. Distribution of OCPs (ng/g) in medicinal plants of South-East Albania

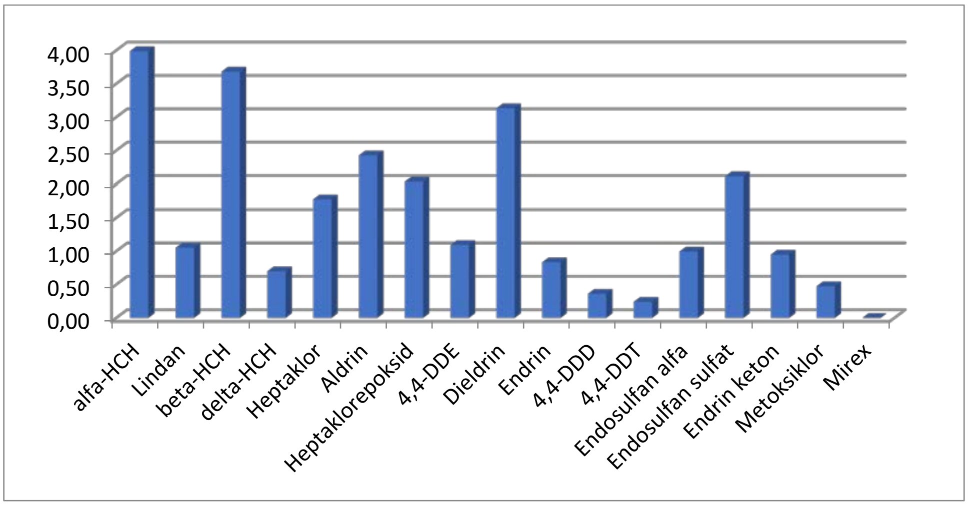

Figure 3. Profile of organochlorine pesticides (ng/g) in medicinal plants

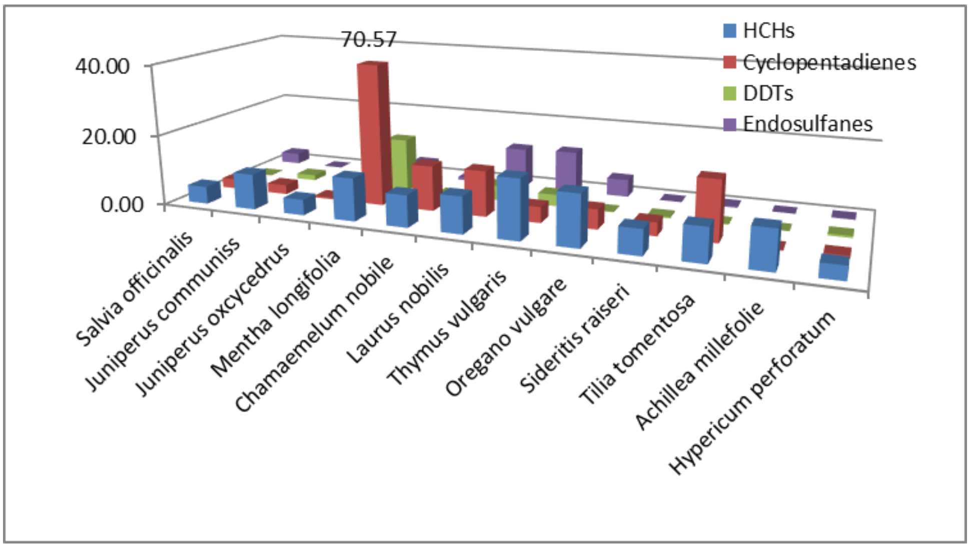

Figure 4. Classes of organochlorine pesticides (ng/g) in medicinal plants

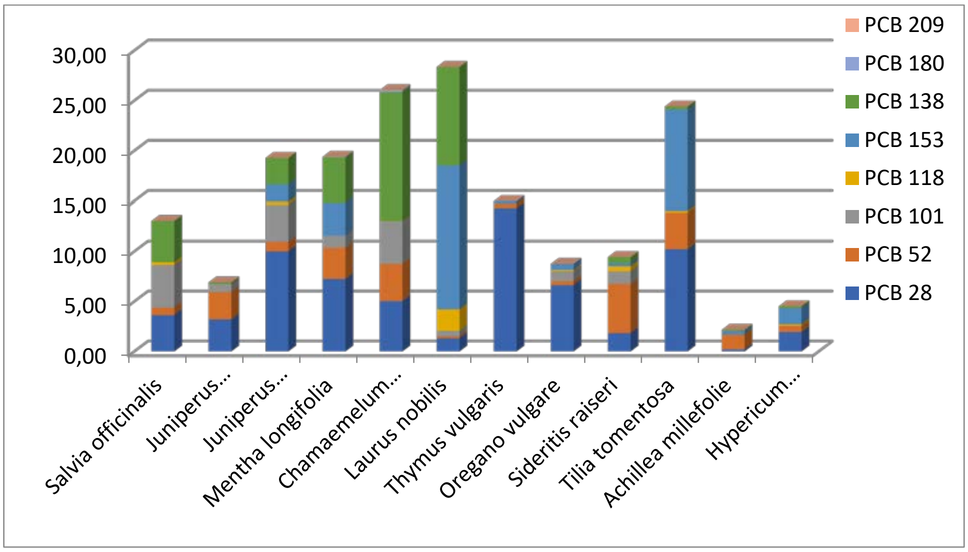

Figure 5. Total of PCB (ng/g) in medicinal plants of South-East Albania

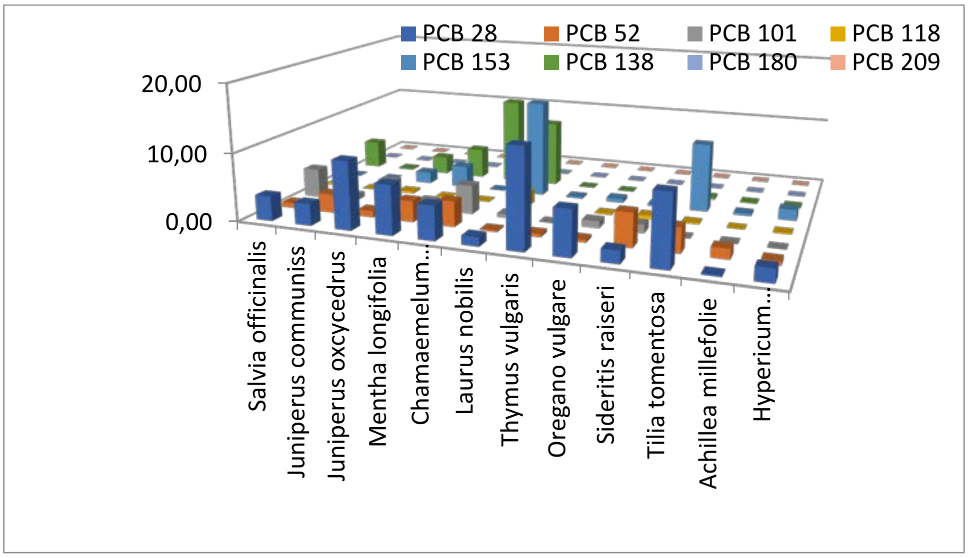

Figure 6. Distribution of PCB (ng/g) in medicinal plants of South-East Albania

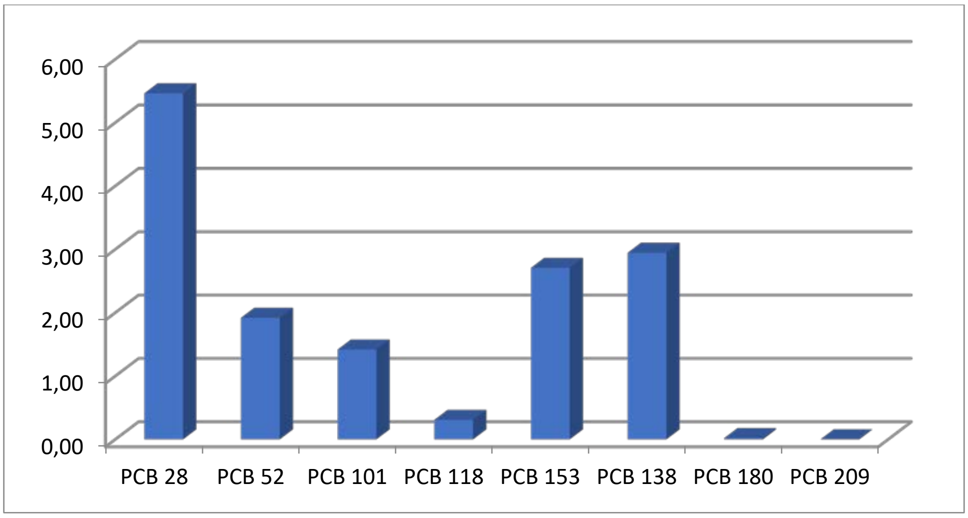

Figure 7. Profile of PCB (ng/g) in medicinal plants of South-East Albania

CONCLUSIONS

Based on our study, Albanian medicinal plants collected in wild, results free of chlorinated pesticides (Aldrine, DDT, Lindane, Metoxichlor and Mirex). Also, most of PCB markers were not detected in the analysed Albanian native plants. Mentha longifoglia samples were most polluted sample with organochlorine pesticides because these plans grow near the agricultural areas. The main origin of organochlorine pesticides could be as result of their previous uses for agricultural purposes. The highest concentration of OCPs was found for degradation products of pesticides. Heptachlor and Heptachlorepoxide were found in higher concentrations in Mentha longifolia samples because these plants grow near agricultural areas. Alfa and beta-HCH were the most detected pesticides found for all samples. Volatile PCBs (PCB28 and PCB 52) were found in higher concentration as result of atmospheric deposition. Total of PCB markers were higher in Laurus nobilis, Chamaemelum nobile and Tilia tomentosa because these samples were taken near population areas where anthropogenic impact is higher. OCP and PCB levels were lower than reported levels for environmental samples by this region.

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