Study of Organochlorinated Pesticide Residues and Polychlorinated Biphenyls in Soil Samples

Vlora Gashi, Aurel Nuro, Basri Pulaj

Abstract

This paper presents and discusses the data obtained for organochlorinated pesticides and their residues in the soil samples of agricultural areas. Soil contamination is one of most important factors influencing the quality of agricultural products. Usage of heavy farm equipment, the land drainage, an exces¬sive application of agrochemicals, emissions originating from mining, metallurgical, and chemical and coal power plants and transport, all generate a number of undesired substances (nitric and sulphur oxides, PAHs, heavy metals, pesticides), which after deposition in soil may influence crop quality. Thus, input of these contaminants into the environment should be carefully monitored. Levels of organochlorinated pesticides contamination were evaluated in agriculture areas that are in use. 10 soil samples were taken in agricultural areas Plane of Dugagjini , Kosovo. Representa¬tive soil samples were collected from 0-30 cm top layer of the soil.

In the analytical method we combined ultrasonic bath extraction and a Florisil column for samples clean-up. The analysis of the organochlorinated pesticides in soil samples was performed by gas chromatography technique using electron capture detector (GC/ECD). Optima-5 (low/mid polarity, 5% phenyl methyl siloxane 60 m x 0.33 mm x 0.25µm film) capillary column was used for isolation and determination of organochlorinated pesticides. Low concentrations of organochlorinated pesticide and their metabolites were found in the studied samples. The presence of organochlorinated pesticides and their residues is probably resulting of their previous uses for agricultural purposes.

Key words: Organochlorinated pesticides, PCB marker, Soil samples, Gas chromatography

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1. Introduction

Soil contamination is one of most important factors influencing the quality of agricultural products. Usage of heavy farm equipment, the land drainage, an exces¬sive application of agrochemicals, emissions originating from mining, metallurgical, chemical and coal power plants and transport, all generate a number of undesired substances (nitric and sulphur oxides, PAHs, heavy metals, pesticides), which after deposition in soil may influence crop quality. Thus, input of these contaminants into the environment should be carefully monitored. Levels of organochlorinated pesticides contamination were evaluated in agriculture areas that are in use (Nuro & Marku, 2011). This study could be a first step for monitoring of organic pollutants in agricultural areas of Kosovo.

The concentrations and toxicity of organic compounds present in such complicated mixtures range very widely and depend also on possible interactions (synergies) among chemicals. The development of instrumental analysis techniques and the lowering of the detection limit have made it possible to identify new organic compounds that are present in the soil in very low concentrations. The list of the most commonly studied soil pollutants has been expanded to include polychlorinated biphenyls (PCBs), aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs) and polychlorinated naphtalenes (PCNs). The continuous introduction of these persistent compounds into the environment has resulted in their accumulation. Runoff is the movement of pesticides in water over a sloping surface.

The amount of pesticide runoff depends on: the slope, the texture of the soil, the soil moisture content, rainfall, and the type of pesticide used. Leaching occurs downward, upward, or sideways. Many chromatographic methods were developed last years for detecting all possible and known organic pollutants in soil samples (Di Muccio, 1996; Erikson, 2001). Determination of halogenated pollutants is based mainly in capillary GC/ECD and GC/MS methods. LOD for chlorinated pesticides and PCBs in soil samples is in ppb levels. EPA and EN norms suggested these methods as routine and confirmatory analysis for responsible laboratory.

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2. Materials and Methods

2.1 Preparing of adsorbents for determination of organochlorinated pesticides and PCBs in soil samples

Silicagel, Florisil and sodium sulphate anhydrous were activated for 12 hours on 250oC on oven. After that Silica gel was treated with 45% concentrated sulphuric acid and Florisil with 5% distilled water.

2.2 Preparation of glassware for GC analyze

Preparation of glassware for determination of organochlorinated pesticides and polychlorinated biphenyls in nano levels is very important for getting real values. All glassware was treated with sulphuric acid in rate 1:4 in volume for 6 hours. Washing firstly with distilled water and after that with organic solvents (hexane:dichloromethane). All glassware was dried in thermostat for 6 hours at 150oC (Beltran et al, 2000; Muir & Sverko, 2006).

2.3 Sampling of soil samples and their pretreatment

Levels of organochlorinated pesticides and PCBs were evaluated in agriculture areas that are in use. 10 soil samples were taken in agricultural areas Plane of Dukagjini , Kosovo. Representa¬tive soil samples were collected from 0-30 cm top layer of the soil. Sampling stations of soil samples was shown in Table 1. Soil samples were air-dried. A representative sub-sample of each sample was taken for determination of humidity and another sub-sample for determination of organochlorinated pesticides and PCBs with gas chromatographic analyze. Sub-sample data were shown in Table 2.

Table 1: Sampling stations of soil samples analyzed in Kosovo Institute of Agriculture, Peja, Kosovo

Sample	Station	Agricultural area	Depth of soil samples
T1	Memushe	Greenhouses – cucumber	0-30 cm
T2	Peje	Orchard –apple	0-30 cm
T3	Memushe	Greenhouses – tomato	0-30 cm
T4	Peje (Qyshk)	Greenhouses	0-30 cm
T5	Suhareke(Neperbisht)	Greenhouses – cucumber	0-30 cm
T6	Suhareke(Neperbisht)	Greenhouses – tomato	0-30 cm
T7	Suhareke(Neperbisht)	Greenhouses – tomato	0-30 cm
T8	Gjakove	Orchard	0-30 cm
T9	Peje (Leshan)	Greenhouses	0-30 cm
T10	Peje (Leshan)	Greenhouses	0-30 cm

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Table 2: Sub-samples data for soil samples analyzed in Kosovo Institute of Agriculture Peja, Kosovo

Sample	Fresh weight (g)	Humidity (%)	Dry weight (g)
T1	13.7	2.9	13.3
T2	14.55	6.53	13.65
T3	16.64	6.98	15.48
T4	17.08	13.15	15.1
T5	13.78	4.05	13.22
T6	16.07	8.32	14.73
T7	19.64	10.7	17.54
T8	13.87	12	12.2
T9	22.39	24.85	16.81
T10	17.13	18.2	14.5

2.4 Soil sample treatment for GC analyze

A fresh sub-sample from 10-20 g of soil samples were extracted by ultrasonic bath assisted extraction with 50 ml hexane/dichloromethane 3/1, (v/v) (Fluka, Germany, pesticide grade). The extract was purified by shaking with 2gr 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 (particle size 0.063±0.2 µm; Merck, Darmstadt,Germany), deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane/dichloromethane 4/1(v/v) (Spectroscopy grade; Fluka, Germany). The extract was concentrated to 1 ml in nitrogen concentrator and after that analyzed by GC-ECD (Beltran et al, 2000; Muir & Sverko, 2006).

2.5 Gas chromatography analyze of soil samples

Gas chromatographic analyses were performed with a DANI 1000 Gas chromatograph equipped with a 63Ni 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 3000C and 3200C, 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 1100C for 4 minutes, than increased to 2000C at 200C/min, and then increased to 2800C at 40C/min. The temperature was finally increased to 3200C, at 100C/min, than held for 7 minutes. Injection volume was 1µl and injections were done in splitless mode. Organochlorine pesticide and PCB quantification was performed by external standard method (Nuro & Marku, 2011).

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3. Results and Discussion

10 soil samples of agricultural areas in Plane of Dukagjini, Kosovo were chosen for determination of organochlorinated pesticides and PCBs. Extraction, clean-up and concentration procedures were realized in laboratory of Agricultural Institute in Peja, conform protocols for determination of PCBs and organochlorinated pesticides for soil samples.

Total of organochlorinated pesticides was shown in Figure 1. Maximum level was found for sample T5 and T8 with 0.019 mg/kg soil sample. Minimum level was for T1 sample with 0.0055 mg/kg. Distribution and profile of organochlorinated pesticides were shown respectively in Figure 2 and Figure 3. Almost all studied samples have the same distribution of organochlorinated pesticides. The most detected pesticides were: 24'-DDT, 44'-DDD, HCB, Isodrine, Heptachlor, alfa-Klordan. Note that all samples were found in higher levels metabolites and not organochlorinated pesticides. This fact suggests that found concentrations could be because of previous use of organochlorinated pesticides in agricultural areas and their degradation. All found pesticides concentrations were lower than Maximal allowed values (MAV) in the soil samples according Administrative Project instruction in Allowing Norms of Hazardous Substances and Harmful Presence in Soil, Prishtinë, Kosovo, 2011. Total of PCBs for analyzed soil samples was show in Figure 4. Maximum level was for sample T3 with 0.0025 mg/kg soil sample. In 6 soil samples PCBs were not detected. PCB levels were lower than Maximal allowed values (MAV) in the soil samples according Administrative Project instruction in Allowing Norms of Hazardous Substances and Harmful Presence in Soil, Pristine, Kosovo, 2011. Distribution of PCBs was shown in Figure 5 and their profile in Figure 6. PCB 52 and PCB 138 were most detected biphenyls. PCB 52 presence could be because of atmospheric factors. PCB 138 presence could be because of its physic-chemic properties.

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Figure 1: Total of organochlorinated pesticides for analyzed soil samples

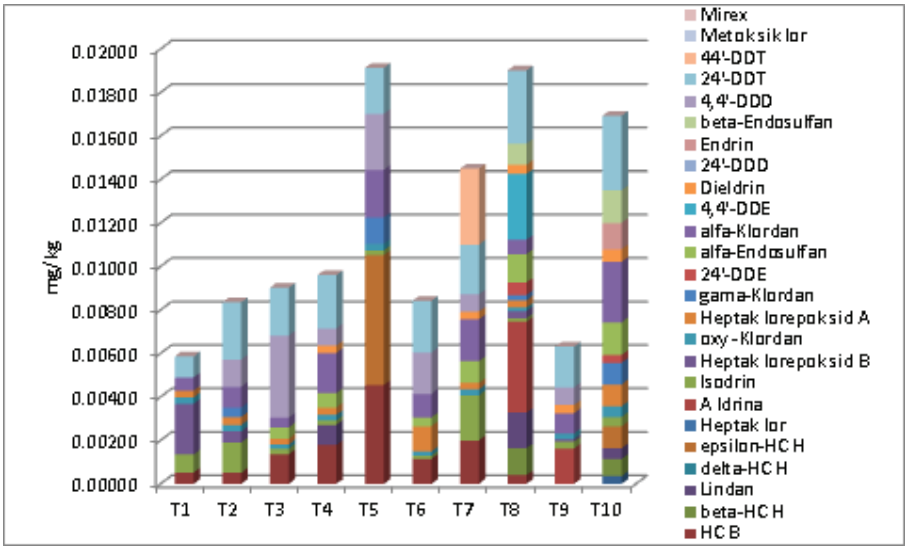

Figure 2: Distribution of organochlorinated pesticides for analyzed soil samples

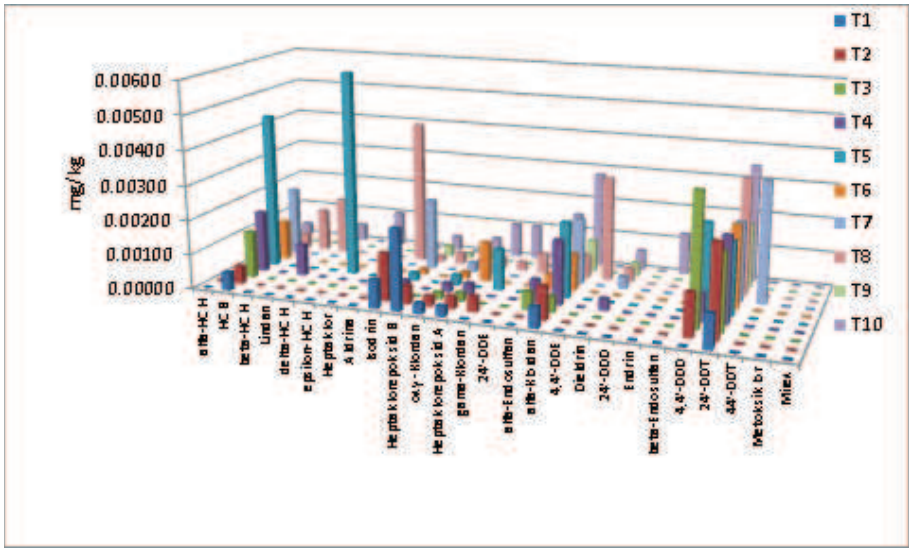

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Figure 3: Average of individual organochlorinated pesticides for analyzed soil samples

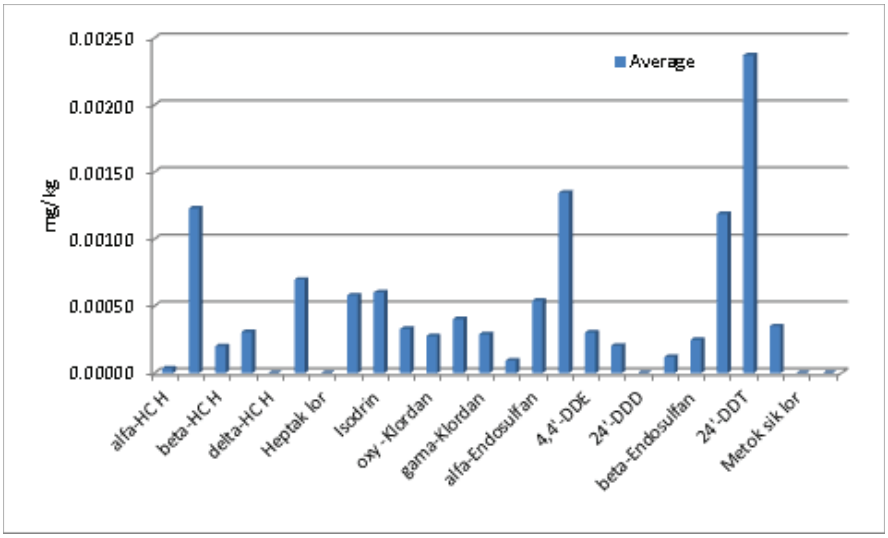

Figure 4: Total of PCBs for analyzed soil samples

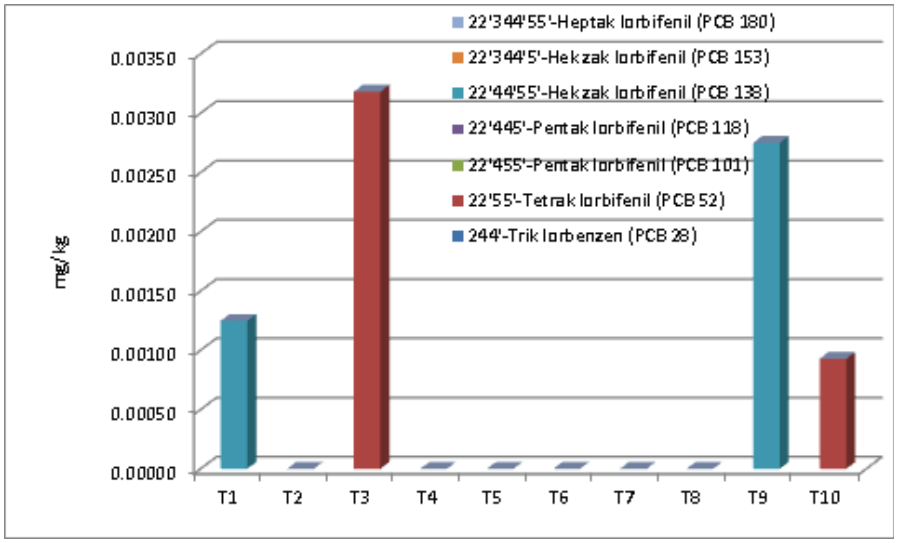

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Figure 5: Distribution of PCBs for analyzed soil samples

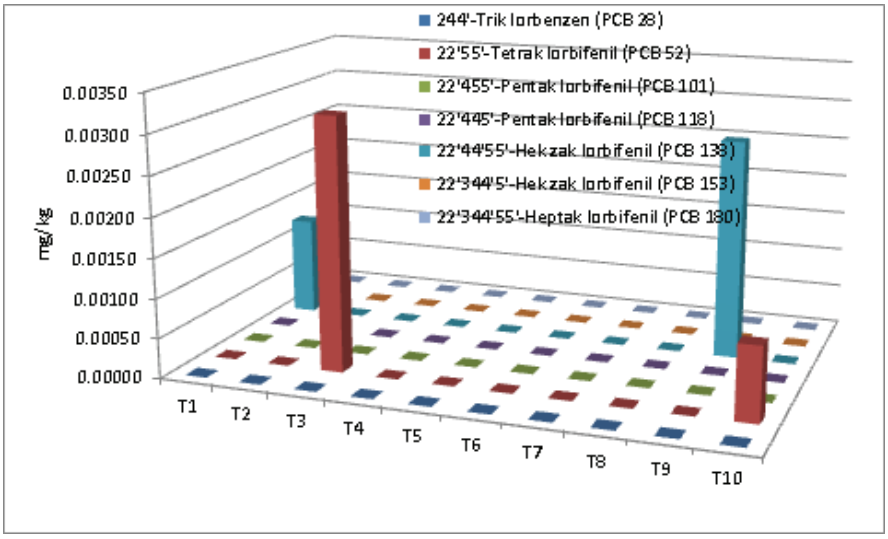
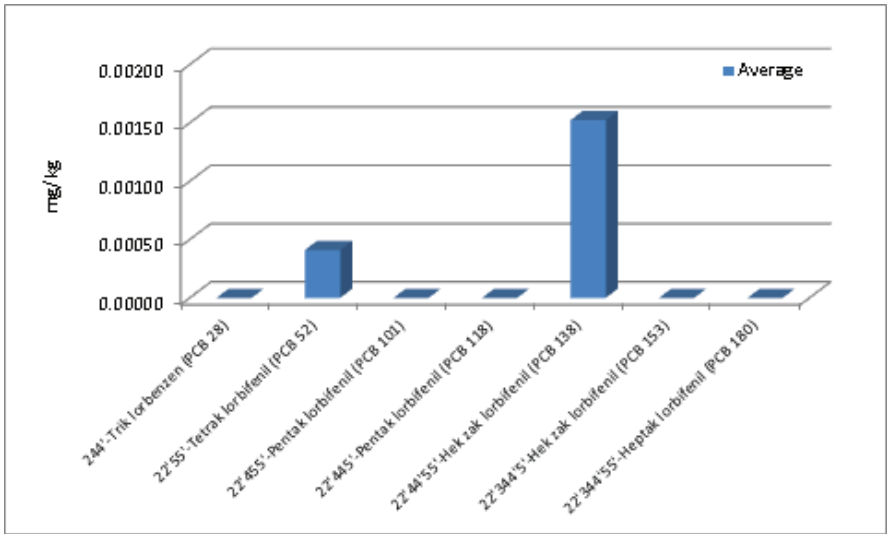


Figure 6: Average of PCBs for analyzed soil samples



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4. Conclusions

Determination of organochlorinated pesticides and PCBs in soil samples was realized based on EU protocols in laboratory of Kosovo Institute of Agriculture Institute located in Peja, Kosovo. Capillary GC/ECD were used for their qualitative and quantitative analyze.

All studied samples have the same distribution of organochlorinated pesticides. The most detected pesticides were: DDT metabolites, HCB, Isodrine, Heptachlor and alfa-Klordan. In all samples were found higher levels metabolites of organochlorinated pesticides. The previous use of organochlorinated pesticides in agricultural areas and their degradation could be main reasons. All concentrations of studied pesticides were lower than Maximal allowed values (MAV) in the soil samples.

PCBs were not detected for the main part of samples. PCB 52 and PCB 138 were most detected biphenyls. PCB 52 presence could be because of atmospheric factors. PCB 138 presence could be because of its physic-chemic properties. PCB levels were lower than Maximal allowed values (MAV) in the soil samples according Administrative Project instruction in Allowing Norms of Hazardous Substances and Harmful Presence in Soil, Prishtinë, Kosovo, 2011.

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