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Influence of pH in concentration of Persistent Organic Pesticides residues in agricultural soils

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Abstract

Over the past century, there has been a wide use of pesticides in agricultural products. However, only 10 % of pesticides reach the target, and the other part is spreaded in the air, soil and water. Although, pesticides save farmers' time and money, they are known for having negative effects on human health and environment, while the soil contamination with Persistent Organic Pollutants (POPs) pesticides is very alarming. It is evident, that due to its large retention capacity for hydrophobic compounds, soil is used as an effective sink for POPs pesticides and it plays an important role in the global distribution and fate of these chemicals. The soil properties, like pH and temperature, influence the degradation rates of pesticides. The most favourable soil pH for the best degradation of pesticides is around 7.

The goal of this paper is to study the correlation between soil pH and the concentration of POPs pesticides. In this study we have included some farms of agricultural areas in Albania. A total of 72 samples were collected in the period of June - December 2015. We have determined the pH of soil with pH meter and POPs pesticide residues with Gas chromatography techniques. The values of pH ranged from 5.7 to 8.34, and the values of dichlorodiphenyltrichloroethane(DDT) residues ranged from 0.1 to 220.69 µg/kg. From this study resulted that in general, in soils with pH < 7, the concentration of DDT was lower than the concentration of DDT in soils with pH > 7.

Keywords: POPs pesticides; pH - meter; Gas chromatography.

1.Introduction

Pesticides have been widely used for agriculture purposesandamajor concern regarding their use is the diffuse pollution. However, the actual distribution of pesticides in the soil is poorly understood, due to the wide variety of pesticide residues in the soil on a regional scale[7]. Only 10 % of applied pesticides reach the target organism, so a high percentage is deposited on non-target areas (soil, water, sediments) impacting this way the wild life, beside affecting the public health. Due to the extensive pesticides use, currently there are many polluted sites with these compounds (mainly soils) [8].

Persistent organic pollutants (POPs) are toxic chemicals that persist in the environment and bio magnify in the food chain. Their accumulation takes place preferentially in the upper soil horizons rich in organic matter[4].Their persistence in the environment still makes them to be detected in different environmental matrices, such as soil and sediments, despite the fact that their use has been banned[6].In some areas, these residues concentration were found in soil, exceededing the level set by the national soil quality standards[10]. Once a persistent pesticide has entered in the food chain, it can undergo "bio-magnification", i.e., accumulation in the body tissues of organisms, where it may reach concentrations many times higher than in the surrounding environment[1].The DDTs are some representatives of the POPs family[5].

Soil plays an important role in the distribution of POPs, like an effective sink for these chemicals, due to its large retention capacity for hydrophobic

compounds [2].The fate of organic compounds in soils depends on chemical-specific parameters, environmental factors and on soil parameters such as temperature, soil type, pH, water content and organic matter.The soil system physical and chemical characteristics, such as moisture content, organic matter and clay type, nutrients, temperature, salinity and pH, influence the sorption, desorption, degradation and biodegradation of pesticides. The pH-value can affect the concentrations of OCP in soil by influencing the microbiological activity in the soil[9].Soil pH may affect pesticide adsorption, abiotic and biotic degradation processes. It influences the sorptive behavior of pesticide molecule on clay and organic surfaces and thus, the chemical speciation, mobility and bioavailability. However, the effect of pH will depend on the compound being degraded and the organisms responsible for the degradation. Studies have shown a more rapid degradation in soils with higher pH[8]. Once residues bind through sorption soil, microbial activity can be limited when pH reachs the value of 8-8.5[7]. Studies suggest that the most competent soil pH, for the best grade of degradation is around pH 7 (neutral pH) and below this range the breakdown is slowed down[3].

In this study we have taken in consideration some organic and conventional greenhouses and farms in Shkodra, Lezha, Fushe - Kruja, Tirana, Durresi, Lushnjaareas and an olive groves in Dhermi.The aim of this paper is to study the correlation between the soil pH and the concentration of POPs pesticides residues.

2. Material and Methods

2.1 Site Description and sample collection

In this study there are included organic and conventional greenhouses and farms from Shkodra (Velipoje, ShtojiVjeter, Stajke, Kosmaç, Mjede), Lezha (Zejmen, Piraj, Grykezeze), Fushe -Kruja (Tapize),Tirana (Marikaj), Durresi (Hamalle, GjiriiLalzit, Rade), Lushnja(Divjake) and an olive groves inVlora (Dhermi).

A total of 72 samples were collected from organic and convencionalgreenhouses and farms of these areas,using a soil auger in a depth of 0-25 cm. Sampling was done in the period June - December 2015, and in compliance with Standard ISO10381-1, 2: 2002. Each soil sample was the result of 10 -15 subsamples, using a random sampling method. These subsamples were collected in a bucket and after being homogenized thoroughly were put in a bag of polyethylene. The samples were labeled with a code number and were stored at 4 ^{o}C.

In the figure 1, there is presented the map of Albania with the sampling locations.

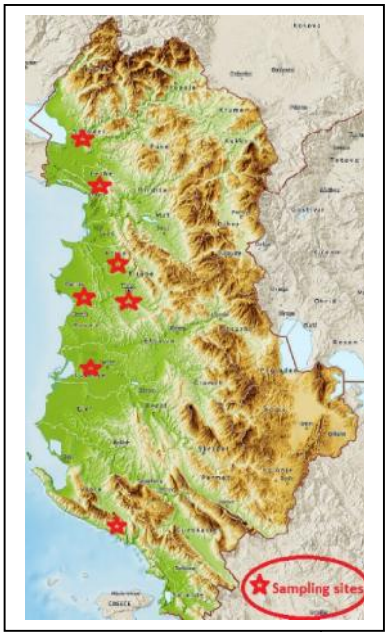

Figure 1: **Map of the Albania and sampling sites**

Analysis of soil pH wereperformed in Albanian Customs Laboratory (Customs General Directorate). Extraction and analysis of soil samples for POPs pesticides were performed at the Institute of Soil Science and Soil Conservation Justus Liebig University, Giessen, Laboratory of Faculty of Agriculture, Novi Sad University, and Institute of Public Health, Belgrade,Serbiaaccording to the Standard DIN ISO 10382:2002 and ISO 10382:2002.

2.2Soil pH analysis

Analyses of soil pH were performed according to the ASTM D 4972-2013 protocol,using the pH-Meter “inoLab_ids Multi 9420”.

The samples were dried in natural conditionsin the laboratory, and have been sieved through a no. 10 sieve (2 mm holes) to remove the coarser soil fraction. Approximately 10 g soil samples wereprepared as above, then were placed in aerlenmajer and treated with 10mL of distilled water. The content was shacked thoroughly for about one hour, and then was measured with pH-meter. Calibration of the pH-meter was done before the measurements, using the buffer solutions with pH 4, 7 and 9.

2.3 POPs pesticides residues analysis

2.3.1 Analysis in Laboratory of Justus Liebig University, Giessen

Analysis of the samples of Tirana, Durres and Lushnja were based onStandard DIN ISO 10382: 2002. Soil samples were extracted twice. The soil sample (1 g) was weighted in a clear SPME vial. Than 5 mL of acetone and 5 mL petroleum etherwere added in the vial, then it was shaken for 15 min and centrifuged. After that, the supernatant was transferred in the amber SPME vial. Extraction was repeated with 5 mL petroleum ether. The second supernatant was transferred to the supernatant obtained previously. The supernatant was shaken in the Vortex. From the amber vial, an aliquot(12 mL) was taken and was evaporated under a gentle flow of N_2. It was added IS TCN (1 ppb; 2 µL 5 ppm Standard), 100 µL methanol, 10 mL saline (735,10 mg $CaCl_2$ and 50g NaCl in 500 mL MQ water), 1 ppb ^{13}C HCB (2 µL at 5 ppm), 1 ppb ^{13}C 2,4´-DDT (2 µL at 5 ppm). Then it was shaken briefly in the Vortex. The extracted samples were analyzed in GC-MS, full scan mode, in order to qualitatively check a broad range of chlorinated pesticides. Only DDT and DDT transformation products pesticide residues were detected.

Quantitative analysis were performed in the SIM mode, based on the use of one target and two qualifier ions.

2.3.2 Analysis in Laboratory of University of Novi Sad, and Institute of Public Health, Belgrade, Serbia

Analysis of the samples of Shkodra, Lezha, Fushe -Kruja and Dhermi were based onStandard ISO 10382: 2002.For each soil sample 20 g of soil samples were weighted in an erlenmeyer. 50 mL of acetone was added and was shaken for 15 minutes. Then 50 mL of petroleum etherwas added and was shaken again for 15 minutes. The extraction was repeated again with 50 mL of petroleum ether. The extracts were collected into a separator funnel of 2 liters capacity and acetone was removed by shaking it twice with 500 mL of water. After that, the extract was dried over sodium sulfate and was transferred in the evaporator to reduce the volume of extract to 10 mL. The concentrated extract was transferred in a calibrated tube and was concentrated to 1 mL, in a gentle stream of nitrogen. 2 mL of TBA reagents sulfite was added in 1 mL of the concentrated extract, and was shaken for 1 minute. 10 mL of water was added and was shaken again for about 1 minute. The organic layer was separated from the aqueous layer with a Pasteur pipette, than a few crystals of anhydrous sodium sulfatewere added to remove residual traces of water. The entire concentrated extract was separated by column chromatography on silica gel in two fractions to separate the nonpolar pesticides from the polar pesticides. Into each of the two fractions, 10 µL of the standard solution injectionwas added to each extracted soil samples. Identification and quantitative analyses of DDT residues were performed by using Gas Chromatography Mass Spectrometry (GC/MS) in multiple reactions monitoring (MRM). From analysis only DDT, DDT transformation products pesticide residues and Endosulfan II (beta isomer) residues were detected. Endosulfan II (beta isomer)was present onlyin three of the total soil samples analysed.

POPspesticides were identified according to their retention times, target and qualifier ions. The quantitation was based on the peak area ratio of the targets to that of internal standards.The concentration of pesticide residues in soil samples was determined by interpolation of the relative peak areas for each

pesticide to IS peak area in the sample on the calibration curve.

3. Results and Discussion

The results taken for soil pH and ΣDDT residues are presented in the table 1. ΣDDT represents DDT (Dichlorodiphenyltrichloroethane**)** and its transformed products DDE (Dichlorodiphenyldichloroethylene)and DDD (Dichlorodiphenyldichloroethane). Taken in consideration the results of the moisture of soil samples, the values of ΣDDT residues are calculated in µg/kg (dry matter).

From the table 1, as we can see, the values of pH ranged from 5.7 to 8.34, which belonged to an organic farm (sample M3DV) and to an organic greenhouse (S3M3K) respectively.

In the figure 2, there are presented the frequency of occurrence of pH values within a data samples distribution, and with ranges of grouped values.

Table 1.The Results of pH and DDT residues for the analyzed soil samples.

Sample Code	pH	ΣDDT µg/kg	Sample Code	pH	ΣDDT µg/kg	Sample Code	pH	ΣDDT µg/kg	Sample Code	pH	ΣDDT µg/kg
S1M1K	8.12	84.86	M4DV	6.17	n.d.	M12	7.80	n.d.	M30	7.38	n.d.
S2M2K	8.28	145.98	M5DV	6.48	n.d.	M13	7.91	10.89	M31	6.60	6.57
S3M3K	8.34	161.5	M6DV	6.05	0.1	M14	7.99	9.09	M32	7.50	5.42
S4M4K	8.15	220.69	M7DU	6.45	0.13	M15	6.96	n.d.	M33	6.26	n.d.
M1HK	6.42	0.64	M1DM	6.78	8.25	M16	7.86	n.d.	M34	6.20	7.97
M2HK	7.76	2.62	M2DD	7.26	56.41	M17	6.55	n.d.	M35	6.51	n.d.
M3HK	6.67	0.46	M3DIV	7.84	152.71	M18	7.09	n.d.	M36	6.36	n.d.
M4HK	6.11	n.d.	M1	7.64	8.79	M19	7.04	8.81	M37	6.56	n.d.
M5HK	6.87	0.26	M2	7.93	n.d.	M20	7.58	6.97	M38	6.68	n.d.
M1GJ	7.25	13.33	M3	7.28	10.82	M21	6.71	n.d.	M39	6.80	8.12
M2GJ	7.04	3.45	M4	7.42	11.83	M22	6.44	n.d.	M40	6.49	13.59
M3GJ	7.20	9.34	M5	7.41	n.d.	M23	6.88	11.53	M41	6.83	12.97
M4GJ	7.19	10.81	M6	7.42	7.28	M24	6.80	n.d.	M42	7.07	11.3
M5GJ	7.34	10.48	M7	6.52	n.d.	M25	6.50	n.d.	M43	7.07	13.54
M6GJ	7.37	10.5	M8	6.99	n.d.	M26	6.86	6.53	M44	7.40	13.19
M1DV	7.32	0.25	M9	7.09	6.39	M27	6.89	n.d.	M45	6.75	11.38
M2DV	7.02	0.16	M10	6.83	n.d.	M28	6.43	n.d.	M46	6.91	8.93
M3DV	5.70	n.d.	M11	7.04	10.8	M29	6.54	n.d.	M47	6.40	n.d.

n.d. - not detected; ΣDDT - DDT and its transformed products DDE and DDD.

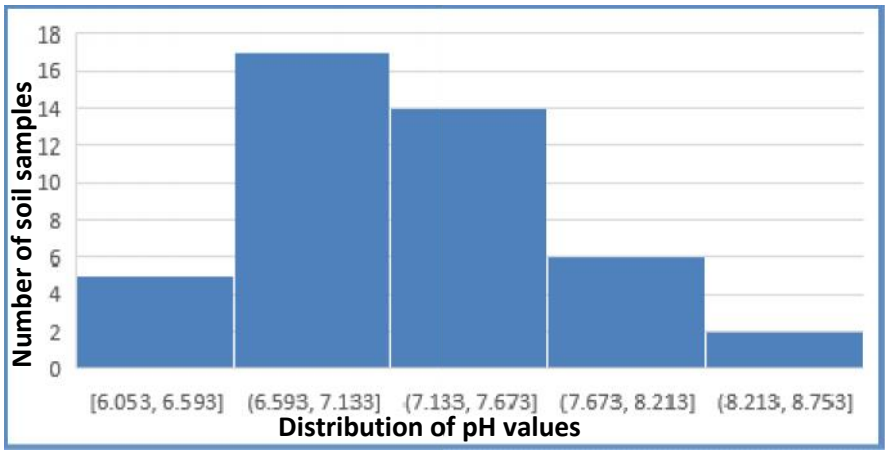

Figure 2. The frequency of pH values occurrence within a data samples distribution

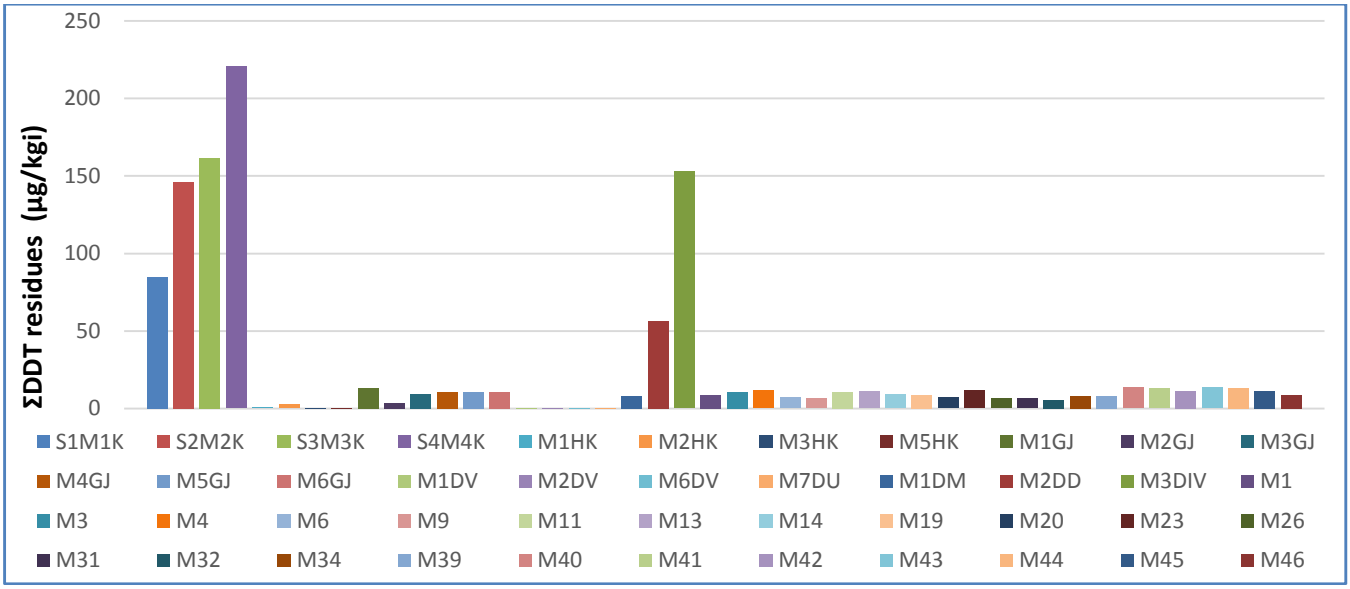

Figure 3. Soil samples that have resulted positive with ΣDDT residues in µg/kg.

Fromthe figure 2, it is evident that mostly soils under the study are almost neutral, they have resulted with pH from 6.57 to 7.61, and only a small part of them resulted acid soils and basic soils.

In the figure 3, there are presentedsoil samples with the values of the ΣDDT residues, whichhave resulted positive, calculated in µg/kg.

Samples S1M1K, S2M2K, S3M3K. S4M4K, M2DD andM3DIV have resulted with the highest values ofΣDDTs residues, 84.86, 145.98, 161.5, 220.69, 56.41, 152.71 µg/kgrespectvely. The pH values of these samples were 7.99,7.98, 8.34, 8.15, 7.26 and 7.84 respectvely. According to the previous study, microbial activity can be limited when pH reachs the value of 8-8.5, and propably this values of soil pH is one of the factors that had influenced the high concentrations of ΣDDTs residues of these samples. Also, the studies have suggested that pH around 7 (neutral pH) is the most favourable for degradation of the pesticides, so we would espect the lowest values of the POPs pesticides residues. In our study for the values of soil pH from 6.75 to 7.25 theresultedvaluesof ΣDDTs residues were from 6.39 to 56.41 µg/kg. However, we should take into consideration that the pH value is just one of themany factors which influence the POPs pesticides residues degradation.

Based on the data taken from the analysis that have resulted positive with ΣDDTs residues, presented in the table 1, we have calculated(IBM SPSS Statistics) the coefficient of linear correlation (r) between values of soil pH (the independent variable x) and concentration ofΣDDTs residues (the dependent variable y). The value ofcoefficient of linear correlation (r) resulted 0.63.

4.Conclusions

In general, soils with pH <7,have the concentration of ΣDDTs residues lower than soils with pH > 7. This shows a positive correlation between soil pH and ΣDDTs residues concentration.

Acid soils with pH lower than 6.5 have not resulted with ΣDDTs residues or have resulted with the low level of them. Basic soilswith pH higher than 7.98have resulted with the highest values of ΣDDTs residues.

Value 0.63 of correlation linear coefficient shows that between the soil pH and concentration of ΣDDTs residues resulted a moderately positive correlation.

5.Acknowledgements

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6.References

1. Ghabbour SI, Zidan Z, Sobhy HM, Mikhai WZ, Selim M:**Monitoring of Pesticid Residues in Strawberry and Soil from Different Farming Systems in Egypt.**American-Eurasian J. Agric. & Environ. Sci., 2012, **12** (2):, 177-187.
2. Gomes HI: **Coupling electrokinetics and iron nanoparticles for the remediation of contaminated soils.**PhD Dissertation.Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Lisbon, Portugal, 2014.
3. Hellebrandt A:**The potential of biodegradation on 1, 1, 1-trichloro-2, 2-bis (p-chlorophenyl) ethane, based upon co-metabolism of indigenous bacteria.**Graduation thesis, Mälardalen University, School of Sustainable Development of Society and Technology (HST) Vesprem, Hungary, 2010.
4. Mukaj M, Mai S, Cara M:**Relationship between Soil Organic Matter and Pesticides Residues in Agricultural Soils.**Proceedings of the 4th Global Virtual Conference 2016 (pp. 288-291): EDIS - Publishing Institution of the University of Zilina, Zilina.
5. Ninga E, Shahu E, Ciko K, Beli E, Boci, I:**Presence of DDTs AND PCBs in fish harvested in Fierza Lake, Albania**. Proceedings of the the 4th Global Virtual Conference 2016 (pp. 292-294): EDIS - Publishing Institution of the University of Zilina,Zilina.
6. Okoya AA, Torto N, Ogundowokan AO, Asubiojo OI:**Organochlorine (OC) pesticide residues in soils of major cocoa plantations in Ondo State, Southwestern Nigeria**. African Journal of Agricultural Research, Vol. 2013, **8:** (28), 3842-3848.
7. Pyne E:**Occurrence and Distribution of Pesticide Residues in Soil as a Result of Long-Term Application.**M.Sc. Sustainable Development Thesis. Utrecht University, Faculty of Geosciences, Environmental Sciences Departement, Utrecht, Netherland, 2015.
8. Shahgholi H, Ahangar AG: **Factors controlling degradation of pesticides in the soil environment:** A Review. TI Journals, Agriculture Science Developments, 2014, 3: (8) , 273-278.
9. Wang F, Jiang X, Bian Y, Yao F, Gao H, Yu G, Minch JC, Scroll R:**Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China.**Journal of Environmental Sciences, 2007, 19 , 584-590.
10. Zhao YC, Yi XY, Zhang M, Liu L, Ma W J:**Fundamental study of degradation of dichlorodiphenyltrichloroethane in soil by laccase from white rot fungi.**Int. J. Environ. Sci. Tech., 2010 7:(2) , 359-366.