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Determination of Dimethoate and Dichlorovos Pesticides Residues in Greenhouses Soils in Burj Islam, Lattakia, Syria

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Abstract The study investigated residues of the two organophosphorus pesticides Dimethoate and Dichlorvos in greenhouses' soil in Burj Islam village, Lattakia governorate, Syria. Samples were collected over a year at different time periods. Soxhlet extraction method was used for 12 hours using acetone: hexane (1:1), followed by SPE C18 cartridge for purification. The pesticides residues were determined using HPLC-DAD. Soil physicochemical properties were also determined in each location.
According to the results, the studied soil had clay texture in location 1, sandy clay loam texture in location 2 and clay loam texture in location 3. pH values of soil were moderately alkaline in all locations, as well as an adequate content of organic matter.
The results also showed that the greenhouses soil were contaminated with the residues of both pesticides, Dimethoate was detected in concentrations within (0.431-88.954ppm) in September, (0.839-2.668 ppm) in February, and (5.321-13.158 ppm) in June, while Dichlorovos concentrations ranged within (86.531-116.436 ppm) in September, (10.046-44.359 ppm) in February, and (3.252-15.806 ppm) in June, indicating extensive use of both particularly Dichlorovos, whose concentrations were higher than Dimethoate's in the studied locations. Statistically significant differences were observed of the concentrations of each pesticide among the different seasons and locations.

Keywords Organophosphorus pesticides, soil, HPLC- DAD, Syria

Introduction

Pesticides have been considered as an important component in agriculture. Global pesticide production has increased by about 11% annually, from 0.2 million tons in 1950 to over 5 million tons by 2000 [1]. However, despite significant benefits, pesticides have caused extensive damage to components of the environment, overused or misused, leading to many hazards and their concentrations in soil, water or biota has increased by years [2]. Organophosphorus pesticides (OPPs) are phosphate ester derived from phosphoric acid, some of these pesticides are chemically and biologically stable with long-term activity, used in agriculture, animal husbandry and public health [3, 4, 5]. These pesticides have been used increasingly worldwide to protect crops because of their high efficiency in pest control and low cost, and they have gradually replaced organochlorine pesticides, most of which have been banned for their long life in environment [6]. These compounds affect the nervous system of insects by inhibiting acetyl cholinesterase which is an enzyme that controls the levels of the neurotransmitter acetylcholine [4]. Dichlorovos ($C_4H_7C_{l2}O_4P$) and Dimethoate ($C_5H_{12}NO_3PS_2$) are organophosphate compounds used to control household, public health, and stored product insects. They are effective against aphids, spider mites, caterpillars, and white flies in greenhouses, outdoor fruit, and vegetable crops [7, 8].

Greenhouses crops on the Syrian coast have increased significantly, and the Syrian market is now dependent on the consumption of many vegetables from greenhouses products. Conditions in terms of temperature and humidity in greenhouses lead to insect and nematode blights which require intensive use of pesticides to control them.

Agricultural soils receive organophosphorus pesticides by applying them directly on the soil surface or while applying on crops. The soil can also be polluted with agricultural irrigation water which is contaminated with these pesticides. Soil emissions are also an important sources of air pollution. Thus, the soil is considered a major reservoir and a secondary emission source of organic pollutants, including organic phosphorous pesticides [6]. The half-life of organophosphorus pesticides in soil ranges from days, weeks to months [1]. However, the continuous and intensive use of these pesticides is cumulative.

Pesticides residues affect the soil negatively and cause vegetation toxicity and contamination of food chains [9] and this does not cause direct harm to human health, but it has a long-term risk. Studies have shown that pesticide residues cause neurobehavioral, developmental and endocrine disorders as well as congenital defects, immune impairment and cancers. They also affect soil biological properties, such as microbial diversity, soil fertility, and some invertebrates such as earthworms. In addition, they contaminate ground and surface water through filtration and runoff [7, 10, 11, 12]. Attention to the health risks associated with the pesticides residues in environment generally, and organophosphorus pesticides particularly has increased [1]. The organophosphorus residues in cereals [13], vegetables [11, 14], fruits [15], milk [16], fish [17] and groundwater [18] have been studied. However, Studies of organophosphorus residues in soil are limited. This research therefore aimed to establish a baseline for the effect of organophosphorus residues on living ecosystems and human health in the study area.

Research Objectives

- Measurement of some Physicochemical properties of the studied soil.
- Determination of the two pesticides Dimethoate and Dichlorovos residues in the greenhouses' soil samples collected from Burj Islam –Lattakia governorate– Syria.

Materials and Methods

Materials, Standards and Apparatus

The analytical grade standards of the two pesticides Dichlorvos and Dimethoate with a purity of 98.9-98.5 respectively (AccuStandard Inc,USA). HPLC-grade organic solvents (Hexane, Acetone, Acetonitrile, Methanol and Propanol). SUPCLEAN LC18 SPE Cartridges 1 ml (SUPELCO, USA). Nitrogen cylinder. Different glassware. In addition to several chemicals: Sulphuric acid (H_2SO_4) concentrated, Phosphoric acid (H_3PO_4) concentrated, Potassium Dichromate ($K_2Cr_2O_7$), Ferrous Ammonium Sulfate [$(NH_4)_2SO_4.FeSO_4.6H_2O$], Diphenylamine Indicator $(C_6H_5)_2NH$, sodium hexametaphosphate [$(NaPO_3)_{13}$], and sodium carbonate (Na_2CO_3).

High-Performance Liquid Chromatography HPLC (Shimadzu, Japan) in the higher institute for environmental research, Tishreen University, Syria. Equipped with Diod Array Detector (SPD-M20A), analytical column C18 (125x4 mm) (Wissenschaftliche Gerätebau, Germany).

Rotary evaporator (Heidolph, Germany). Soxhlet extractor. Analytical balance (Shimadzu, Japan). Ultrasonic Cleaner (Jeken, China). Hilife refrigerator with freezer down to -26ºC. Distillator based on reverse osmosis. pH meter, and electric blender.

Study area

Burj Islam village in Lattakia governorate in Syria was selected for study. This village contains approximately 3,000 greenhouses according to the agricultural unit in Burj Islam in 2018 (Figure 1). Different species of vegetables are planted, mainly cucumbers, tomatoes, peppers, beans and eggplant. These vegetables are marketed in Lattakia governorate, Syria.

Figure 1: Aerial image of the greenhouses in Burj Islam-Syria

Sampling

Three sampling locations were selected:

- Location 1: 10greenhouses to the north of the village, planting beans (*Figure 2: A*).
- Location 2: 3 greenhouses to the south of the village, planting cucumbers (*Figure 2:B*).
- Location 3: 10 greenhouses to the west of the village, planting tomatoes (*Figure 2: C*).

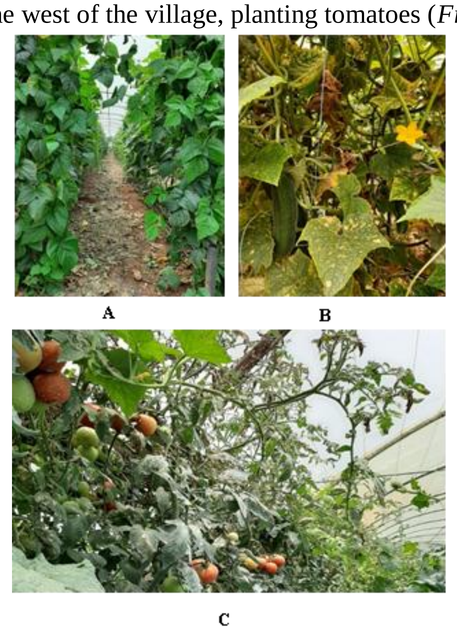

Figure 2: locations of soil samples collection

Soil samples were collected from greenhouses three times over a year as following: September 2018 by the end of the crop, February 2019: the beginning of spring season, June 2019: the beginning of the crop. A composite sample from each location was collected after dividing each location into squares (16 m^2) to collect individual samples from each square at a depth of 10-30 cm. The individual samples were collected and well mixed to comprise the composite sample. Each sample was then placed in an opaque glass bottle and transported to the laboratories of the higher institute for environmental research of Tishreen University, Syria. Soil samples were then air-dried in the shade at room temperature, and sieved through 2 mm sieve and refrigerated at about 4ºC prior to laboratory analysis.

Measurement of Some Physicochemical Parameters of Soil Samples

Soil texture was estimated using hydrometer method [19]. Soil pH is measured in a 1:5 (soil: water) suspension [20]. Soil organic matter was measured by reduction of potassium dichromate ($K_2Cr_2O_7$) by organic carbon compounds and subsequent determination of the unreduced dichromate by oxidation-reduction titration with ferrous ammonium sulfate (Walkley-Black method) [21].

Preparation of Samples for HPLC Analysis

Extraction

Three replicates of each soil sample were made for extraction of pesticides residues in soil followed by [22]. 20 g of soil sample were placed in the extraction cartridge and extracted with 200ml of acetone:hexane (1:1) for 12 hours. The extract was evaporated down to 4 ml at 40ºCin a rotary evaporator, then evaporated to dryness using a gentle stream of clean, dry nitrogen.

Purification

The residues was redissolved in 1ml of acetonitrile and loaded on SPE C18 cartridge (1ml) which was previously conditioned with 5ml acetonitrile. Then, the cartridge was washed with other 2mL of acetonitrile and 1mL of propanol**.** The resulting 4ml were concentrated to dryness using a gentle stream of clean, dry nitrogen and redissolved in 1 ml methanol**.** [23] (corresponding to the standard solutions used) to be ready for later analysis.

Instrumental analysis

The mobile phase was acetonitrile: water (75: 25, v/v) at a flow rate0.8 $mlmin^{-1}$.Thecolumn temperature was maintained at 40ºC. The injected sample volume was 20 µl. The detection wavelength for both the pesticides was selected as 195 nm for Dichlorvos and 200 nm for Dimethoate nm using PDA detector.

Statistical analysis

The results were statistically analyzed by T-test student, to compare the residues of the two pesticides between each two months of the study, differences were considered significant at $P < 0.05$**.** All statistical analyses were performed using Microsoft Excel 2010.

Results

Physicochemical Parameters of Soil Samples

Soil texture is demonstrated in **Table** 1: Location 1 soil is clay (54.50% clay), whereas location 2 soil is Sandy clay loam (55.50% sand) and location 3 soil is clay loam.

Table2: demonstrates pH values and OM% in all locations during study months.

Table 1: Soil Texture of the Study Locations

Location	%Clay	%Silt	%Sand	Soil texture
1	**54.50**	17.50	28.00	**Clay**
2	20.75	23.75	**55.50**	**Sandy clay loam**
3	39.50	21.25	39.25	**Clay loam**

Table2: pH values and %OM in all locations during study months

	Location	September	February	June

pH	1	8.18	8.10	8.05
	2	7.86	7.87	7.96
	3	7.99	7.78	7.70
OM%	1	3.99	3.34	4.14
	2	5.86	5.10	5.38
	3	6.20	6.34	6.13

Test of Dichlorvos and Dimethoate's detector linearity

Calibration curve of each pesticide was prepared with concentrations within (0.25-50) ppm for Dimethoate and (1-40) ppm for Dichlorvos. Good linearity with correlation coefficients (R^2) 0.9916, 0.9946 was found for Dimethoate and Dichlorvos, respectively. *Figure 3:* and *Figure 4:* demonstrate chromatograms of standard solutions of the two pesticides at 20 ppm. The maximum absorption wavelength (λ_{max}) was 200 - 195 nm and retention time was 5.018 – 3.4min of Dimethoate and Dichlorvos, respectively.

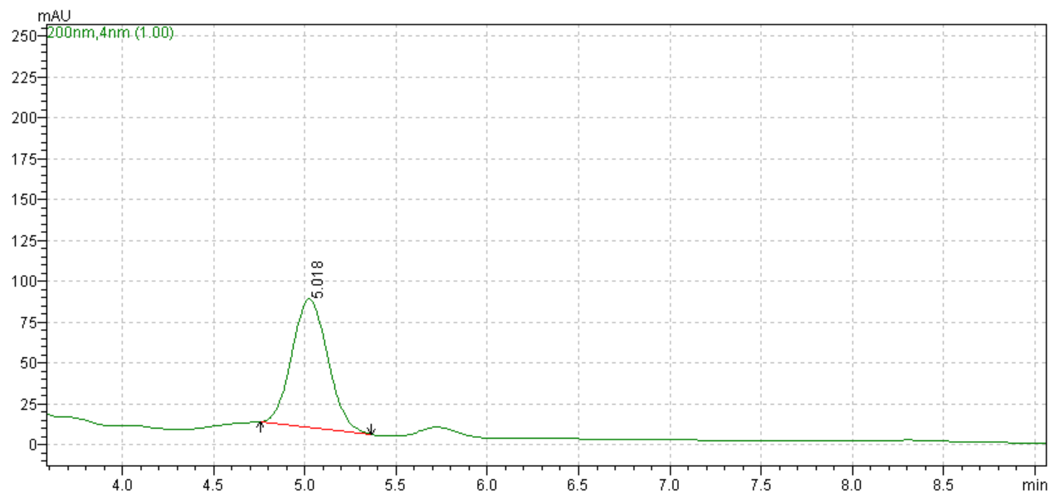

Figure 3:20 ppm Dimethoate chromatogram at 200 nm

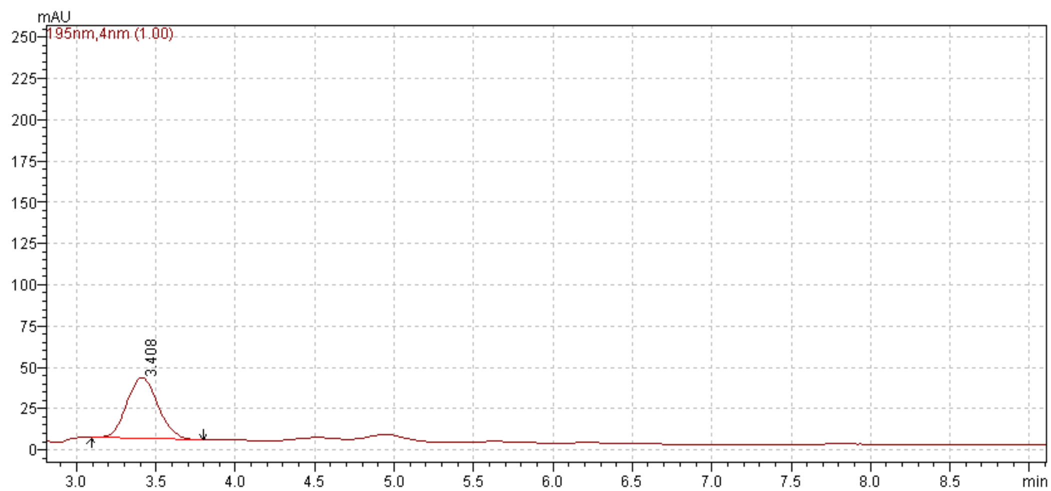

Figure 4: 20 ppm Dichlorvos chromatogram at 200 nm.

Dimethoate and Dichlorvos residues in soil samples

Residues of pesticides in soil samples during study months are demonstrated in

Table 3: The concentrations in September ranged within (0.432-88.945) ppm for Dimethoate and for Dichlorvos (86.531- 116.436), in February ranged within (0.839-2.668) ppm for Dimethoate and (10.046 -44.359) ppm for Dichlorvos, in June ranged within (5.321-13.158) ppm for Dimethoate and (3.252-15.806) for Dichlorvos.

Table 3: Dimethoate and Dichlorvos residues in soil samples during study months.

		September		February		June		average $\bar{X}$
		± SD$\bar{X}$	RSD%	± SD$\bar{X}$	RSD%	± SD$\bar{X}$	RSD%	
Dimethoate	Loc 1	2.815 ± 88.945	3.17	0.038 ± 1.285	2.99	0.460 ± 13.158	3.49	34.465
	Loc 2	0.022 ± 0.432	4.99	0.033 ± 0.839	3.97	0.113 ± 5.321	2.12	2.197
	Loc 3	0.747 ± 52.486	1.42	0.123 ±2.668	4.61	0.570 ± 12.896	4.42	22.683
Dichlorovos	Loc 1	4.412 ± 116.436	3.79	0.734 ± 33.862	2.17	0.632 ± 15.806	3.94	55.368
	Loc 2	2.474 ± 86.531	2.86	1.452 ± 44.359	3.27	0.146 ± 3.252	4.50	44.714
	Loc 3	3.253 ± 112.421	2.89	0.334 ± 10.046	3.33	0.513 ± 12.635	4.06	45.034

$\bar{X}$: Concentration mean (ppm),SD:Standard Deviation (n = 3)

Discussion

Physicochemical parameters of soil samples

pH values ranged within (7.4-8.4) at all locations during the study months indicating that soil is moderately alkaline [21], because the soil in the area is calcareous generally. The soil was rich in organic matter in all locations during the study months, the highest content of OM was in location 3 due to the repeated fertilization, against once a year in location 2 and fertilizers were not added in location 1.

Dimethoate and Dichlorvos residues in soil samples

The results indicate that there is an accumulation of pesticides in the greenhouses' soil, which may be attributed to the imbalance between pesticide spraying and its degradation. In addition to the effect of the type and intensity of the crop covering the soil, as intensive cultivation increases the persistence of the pesticide by up to threefold of the remaining in the uncultivated ground. Unsafe disposal of pesticides containers may lead to release of their residuesto the soil, as well.

Dichlorovos concentrations were higher than Dimethoate's in most locations during the study months (*Figure 5*), this may be attributed to that the Dichlorovos solubility in water is less than Dimethoate (8 g/l , 28.2 g/l respectively) [24, 25]. This is compatible with the results of a study conducted in Nigeria to determine the residues of several organophosphorus pesticides (Diazinon, Dichlorvos Chlorpyrifos, Fenitrothion) on some vegetables and agricultural soils, the mean residues concentrations of Diazinon, Chlorpyrifos, Fenitrothion were comparable, while the mean concentrations of Dichlorvos were significantly higher in all plant and soil samples [11].

The t-test demonstrates a significant difference between the two pesticides concentrations for each two months of the study. The highest concentrations of the two pesticides were in September at the three locations, this may be attributed to the intensification of pesticide spraying in summer months due to insect activity in high temperatures. In addition to the rain shortage in summer and the discontinuation of irrigation at the end of the season, thereby lack of pesticides leaching. Knowing that pesticides spraying was weekly during the period of the crop's presence, which caused the accumulation of pesticides in soil. Low concentrations of pesticides in June compared to September may be caused by pesticides leaching by irrigation water, which is daily. For February, concentrations of Dimethoate were low compared to its concentrations in other seasons, this may be attributed to the sufficient period for degradation from the beginning of December to February, in case it was not applied during this period. The high Dichlorovos concentrations may be attributed to the early use by farmers (*Figure 5*).

Average concentrations of Dimethoate and Dichlorovosin location 1 during study months were 34.465 ppm, 55.365 ppm, respectively, which is the highest among the locations (**Table** 3). This may be due to the clay soil texture in this location, which contains a high percentage of clay minerals leading to increase its ability to retain pesticides, due to the adsorption of organic substances including organic pesticides [26]. While the lowest average concentrations of Dimethoate and Dichlorovos were in location 2 (2.197 ppm, 44.714 ppm, respectively), this may be attributed to the sandy clay loam soil texture in this location (55.50% sand)which may lead to leach the two pesticides by irrigation water, particularly Dimethoate whose solubility in water is higher than Dichlorovos.

In general, there are a variety of factors influencing the behavior of pesticides in soil, such as soil texture, organic matter, pH, microorganisms activity and its effect on biodegradation, the type of crop in each location, and environmental conditions, which make it hard to consider just one factor to interpret the results in any location.

The concentrations of organophosphorus pesticides residues in greenhouses soil in this research ranged within (0.431-116.436 ppm), which are higher than organophosphorus pesticides residues concentrations detected in agricultural soilby the researchers (Vig *et al*) [27], (Fosu-Mensah *et al*) [28], (Osesua *et al*) [29], and (EL-Saeid and Alghamdi) [30] in India, Ghana, Nigeria and Saudi Arabia, Which were ranged within (1.16 - 41.97 ppm), (0.01.0.04 ppm), (0.09 - 3.79 ppm), (0.009 - 0.367 ppm) respectively, while the concentrations that were detected in this research were lower than those detected by (Akan *et al*) [11] in vegetable-planted soil in Nigeria (50-275 ppm).

It should be noted that according to the European Union, the maximum residue limit (MRL) of Dimethoate and Dichlorvos in cucumbers, tomatoes, and beans (planted vegetables in greenhouses soil in this study) is 0.01 ppm [31, 32], and according to the report of the Joint FAO/WHO meeting on pesticide residues (JMPR) in 2019 for Dimethoate and for Dichlorovos in 2011, the acceptable daily intake (ADI), and the acute reference dose (ARfD) are as follows:

$ARfD_{Dimethoate}$: (0.02) mg/kg bw, $ADI_{Dimethoate}$: (0 – 0.001) mg/kg bw/day [24]

$ARfD_{Dichlorvos}$: (0.01) mg/kg bw, $ADI_{Dichlorvos}$: (0 – 0.004) mg/kg bw/day [33]

The high concentrations of pesticides residues in soil may have effects on soil fertility and ecosystem vitality, as well as the safety of plants grown in the soil, which may indicate that their residues in cucumbers, tomatoes, and beans may exceed MRL and the exposure to these residues by farmers and consumers may be higher than ADI and ARfD.

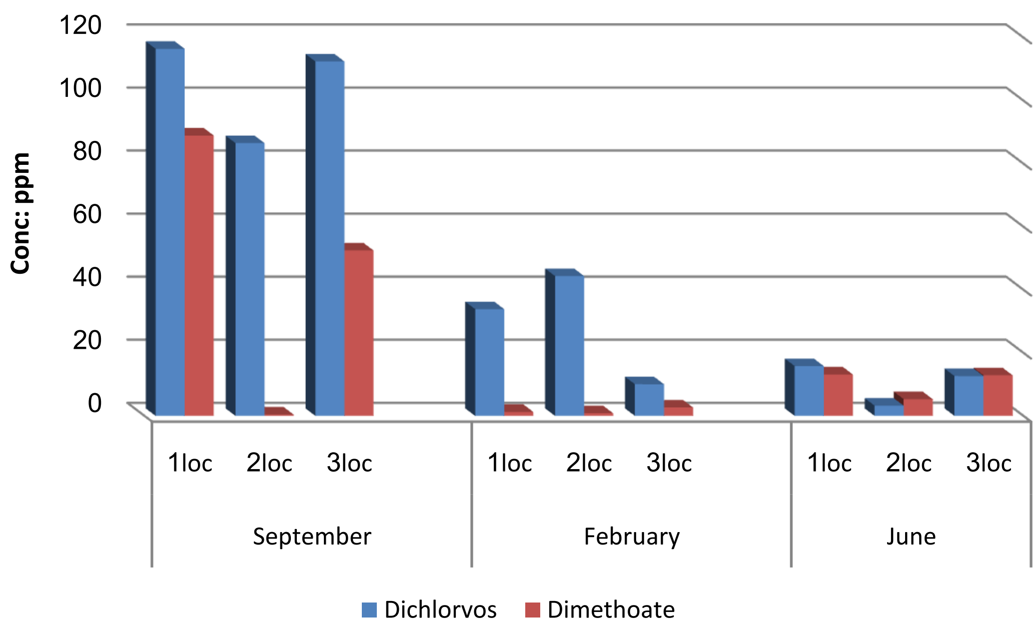

Figure 5: comparison between the two pesticides concentrations

Conclusion and Recommendations

This study shows that green house soils in Burj Islam were contaminated by the two pesticides Dimethoate and Dichlorvos residues and their concentrations were high, which confirms the intensive use of them and the risk of accumulation in soil and accessibility to drinking water of nearby Wells.

We therefore recommend the application of these chemicals under the management and supervision of the institutions of the ministry of agriculture and the ministry of local administration and environment. The institutions concerned should provide environmental awareness courses to farmers. Besides, observational programs should be established to evaluate the contamination by pesticides, particularly organophosphorus pesticides, in various environmental media.

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