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Research Article

PESTICIDE OCCURRENCE AND DISTRIBUTION IN CULTIVATED SOILS OF THE ARID REGION OF EL-HEJERA, OUARGLA PROVINCE AND CORRELATION WITH SOIL PROPERTIES

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ABSTRACT

This study deals with the assessment of the most used pesticides by farmers in the Saharan region of Ouargla. Based on collected survey data, sampling of the cultivated soils, physicochemical analysis, solid/liquid extraction and identification by thin layer chromatography and high performance liquid chromatography, the following results were obtained: pesticides used in 2015 are not existing in the extracts, like the case of vapcomic (abamectin 1.8% EC) and Metronate (methomyle 25%), this could be explained by the retention which is the overall result of a set of elementary processes, involving interactions with organic constituents and soil minerals. Also, pesticide residues were found outside their points of application, such as Pulsar and Score 250EC, these phenomena can be explained by the local pedo-climatic conditions and to difference in solubility and chemical nature.

Keywords: pesticides residues, cultivated soils, HPLC, El-Hejera.

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1. INTRODUCTION

Pesticide use worldwide has increased dramatically over the past two decades, coinciding with changes in farming practices and more intensive agriculture [1]. Advances in plant protection have contributed to increased yields and consistency of production. Easy to access and use, relatively inexpensive, phytosanitary synthetic products have proved to be very effective and reliable in a large number of cases, over large areas. Today the systematic use of these products is in continuous debate, with the growing awareness of the risks they can generate for the environment, and even for human health. The retention and degradation of pesticides in soils are not independent phenomena. Retention conditions, the availability of pollutants, and adsorption can play a protective role against biological degradation, which is particularly important for pesticides with the highest retention capacity [2,3]; drift and drainage [4,5] and erosion and atmospheric deposition [6].

Nevertheless, in some cases, experimental observations on the effect of adsorption may remain ambiguous. In order to study these phenomena we have carried out the following work: Extraction of pesticide residues in the El-Hejera station under different cultures and at different depths, physico-chemical analysis followed by solid/liquid extraction, chromatography on thin layer and high performance liquid chromatography. Multidimensional statistical analysis was also carried out using the R.3.5.2 software. Correspondence factor analysis (AFC) was also done for categorical variables after being coded.

2. RESULTS AND DISCUSSION

2.1. The physicochemical analyses

The physicochemical analyses results of the soil samples are presented in table 1. They showed that the soil of the DASE has a slightly alkaline pH, low humidity, an electrical conductivity which ranks it as saline soil, the rate of organic matter is low to medium and total limestone is revealed weak too.

Table 1. Soil physico-chemical analysis results

Culture and depth	pH (Hydrogen potential)	moisture %	Electrical conductivity dS/m	Organic matter %	C (total limestone %)
CM 20cm	7,4	25	2,77	2,322	1,95
CM 60cm	7,7	24	2,24		
CM100cm	7,4	25	2,30		
CC 20cm	7,4	20	2	1,687	2,33
CC 60cm	7,8	22	1 ,85		
CC100cm	7,6	23	2,34		
C oliv 20cm	7,5	10,36	2 ,54	1,264	2,34
C oliv60cm	7,4	11	2,33		
C oliv 100cm	7,4	11	2,54		
PD 20cm	7, 3	13,5	2,33	0, 528	1,92
PD60cm	7,6	20	1,98		
PD100cm	7,5	25	1,98		

CM : vegetable crops C oliv : Olive cultures CC : Cereal cultures PD : Date palm culture

2.2. Pesticide identification by TLC

TLC analysis revealed different spots with different retention factors (Rf) for the same extract, pesticides were partly identified based on retention factors of commercial pesticides compounds, they are presented in table 2, 3, 4 and 5. Based on the obtained results, it could be said that the extract of vegetable crops soil (depth 100cm) contains residues of trimol and some traces of Coragen 20 SC, Pulsar 25SC and roundup. Similarly, the extract of olive culture soil (100cm) contains residues of Cypermethrine and some traces of Pulsar 25SC, however, the extract of cereal culture soil (100cm) contains residues of Roundup and some traces of Pulsar25SC and Prosaro, while the extract of date palm culture soil (100cm) contains residues of Trimol, Cypermethrine, Pulsar 25EC, Score 250EC as well as Roundup.

Table 2. RF values of the extract of vegetable crops soil (100cm depth)

Sample spot's RFs (CM depth 100cm)	Trimol® spot's RFs	Coragen 20 SC® spot's RFs	Cypermethrine® spot's RFs	Pulsar25SC® spot's RFs	Prosaro® spot's RFs	Score 250 EC® spot's RFs	Roundup® spot's RFs
0.3 0,8 0,9	0,8 0,9 0,9	0.3	0.2 0.65 0.7	0,8	0,9	0.5	0.5 0,8

Table 3. RF values of the extract of olive culture soil (100cm depth)

Sample spot's RFs (oliv C depth 100cm)	Trimol® spot's RFs	Coragen 20 SC® spot's RFs	Cypermethrine® spot's RFs	Pulsar25SC® spot's RFs	Prosaro® spot's RFs	Score 250 EC® spot's RFs	Roundup® spot's RFs
0.45 0.85 0,98	0.75 0.88 0.9	0.75 0.99	0.45 0.85 0,98	0.35 0.85 0,98	0.45 0.98	0.45 0,98	0.8

Table 4. Rf values of the extract of the cereal culture soil (100cm depth)

Sample spot's RFs (CC depth 100cm)	Trimol® spot's RFs	Coragen 20 SC® spot's RFs	Cyperméthrine® spot's RFs	Pulsar25SC® spot's RFs	Prosaro® spot's RFs	Score 250 EC® spot's RFs	Roundup® spot's RFs
0.18 0.5 0,67	0.75 0.88 0,9	0.75 0,99 0,8	0.45 0.85 0.98	0.35 0,5 0,67	0.83 0,5 0,67	0.18 0,67	0.18 0,67

Table 5. Rf values of the extract of date palm culture soil (depth 100cm)

Sample spot's RFs (CC depth 100cm)	Trimol® spot's RFs	Coragen 20 SC® spot's RFs	Cyperméthrine® spot's RFs	Pulsar25SC® spot's RFs	Prosaro® spot's RFs	Score 250 EC® spot's RFs	Roundup® spot's RFs
0.5 0.83 0,98	0.83 0,98	1	0.30 0.83 0.99	1 0.5 0,67	0.20	0.98	0.83 0,67

2.3. HPLC analysis

The chromatograms shown in figures 1 and 2 represent the peaks of the pesticides residues that were extracted from the cultivated soils (CM, CC, Coliv and PD), and the chromatograms of the commercial pesticides compounds, respectively. It was found that some residues corresponding to the active ingredient are present in the majority of the analysed extracts, confirming their strong retention in the soil.

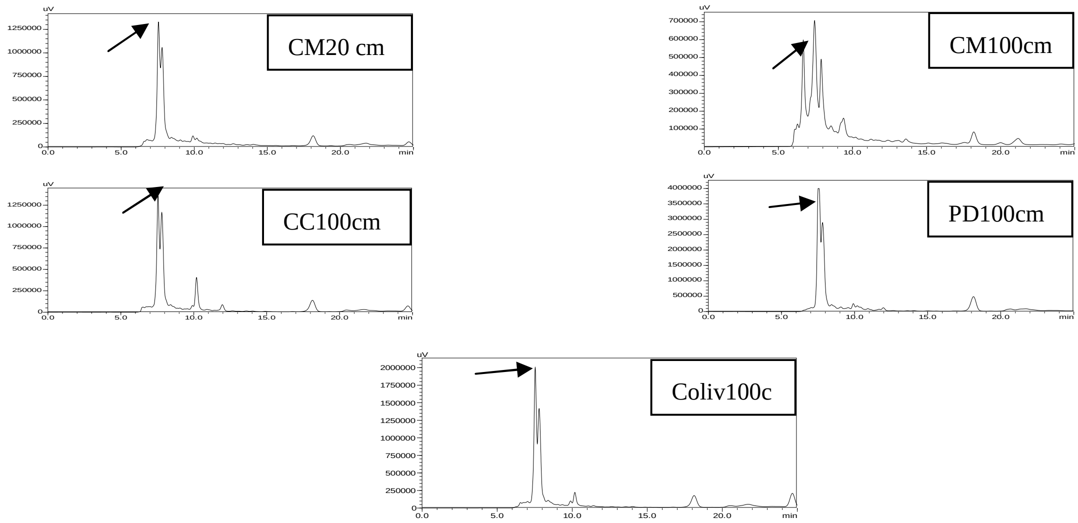

Fig.1. Chromatograms of the cultivated soils extracts

CM : vegetable crops, CC : Cereal cultures, C oliv : Olive cultures, PD : Date palm cultures

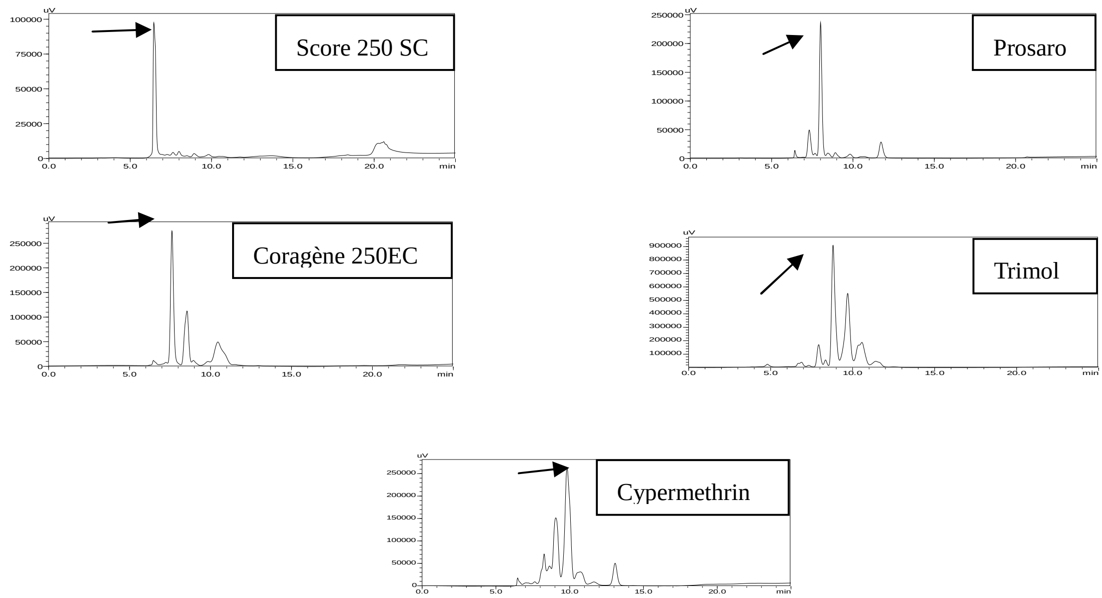

Fig.2. Chromatograms of the commercial pesticides used by farmers

CM : vegetable crops, CC : Cereal cultures, C oliv : Olive cultures, PD : Date palm cultures

These results confirm the results of TLC, where we obtained identical retention factors values in several extracts corresponding to the residues of molecules that were extracted from the cultivated soils (CM, CC, Coliv and PD). We found that some residues are present in the majority of our cultivated soils extracts, which could be explained by the presence of different peaks that have retention times Rt ranging from 7 to 8 minutes. It is important to note that our standard pesticides are not pure products which make it difficult to compare, but the active substance is predominantly present and corresponds to the major peack like the case of the insecticide pyrethroid or a metabolite with high retention in the soil.

2.4. Correlation study

According to the statistical analysis (Figure 3) it was found that pesticide molecules such as methomyl 25%, deltamethrin and pyrethroids are nonexistent in our extracts, this can be explained by the chemical or abiotic degradation that occurs by reactions including hydrolysis, redox and ionization [7]. Hydrolysis reactions are catalyzed by the presence of hydrogen or hydroxide ion, resulting in a highly pH-dependent reaction rate [8]. Generally, biological degradation is quantitatively more important than abiotic transformations, but these can be decisive for certain pesticides that are particularly recalcitrant to biodegradation. Pesticide molecules are divided into three groups according to their strong presence in soils (Figure 4).

Depending on its distribution, the nature of the involved surfaces, the biological activity and the physicochemical properties, various chemical and / or biochemical reactions can occur and lead to the transformation, or even the mineralization of the pesticide. Degradations of chemical and / or photochemical origin are most often considered minor [9]. However, there are many reports highlighting the importance of these degradation pathways [10,11].

Similarly, persistence is the result of a set of physicochemical and biological dissipation processes that decrease the concentration of the pollutant according to the kinetics of the pollutant and the environment [12,13]. As soon as they arrive on the ground, the organic pollutants are distributed in the three phases: solid, liquid and vapor, according to constants of desorption and volatilization adsorption equilibria. These constants are characteristic of each product but they are modified according to the pedoclimatic conditions. Thus, the concentration of pollutants in each of the phases is not fixed in time; it evolves over time as a function of the physicochemical conditions (temperature, moisture, pH, etc) and as a function of pollutant transformations and the evolution of interactions with soil constituents.

Other pesticide residues were found in locations outside their application sites, it is the case of Pulsar and Score 250EC, the presence of these residues outside their crop fields was explained by research work that would tend to show that their deposition near treated areas can reach levels of the same order of magnitude as drift deposits, or even be higher under certain conditions [14,15]. It can be also interpreted by the use of granules, micro-pellets or treated seeds which can also generate the emission of fine particles to the atmosphere that will be able to be deposited (or not) in the vicinity of the plot. In Germany, a major reference work [16] has made it possible to construct drop deposit tables according to the Leeward distance of the plot, and a method of classifying equipment to limit this "drift" [17]. These data explained the presence of these pesticides outside their culture medium. During processing, some of the product comes into contact with the surface of the soil constituents, while another part may remain in the soil solution.

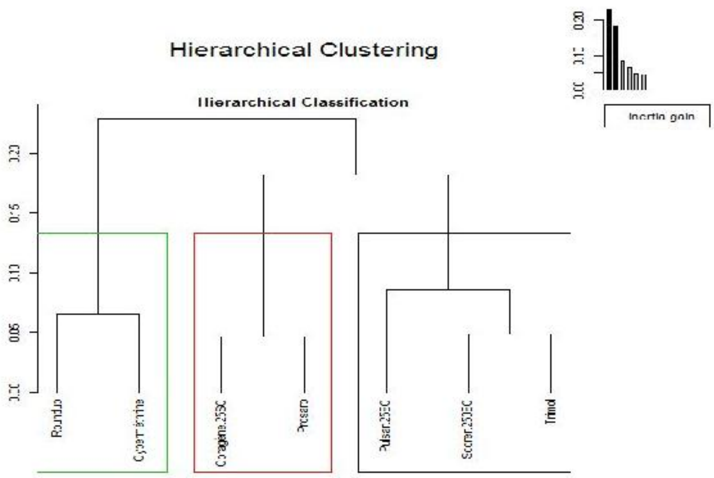

Fig.3. Profile representing groups of pesticides used on the site

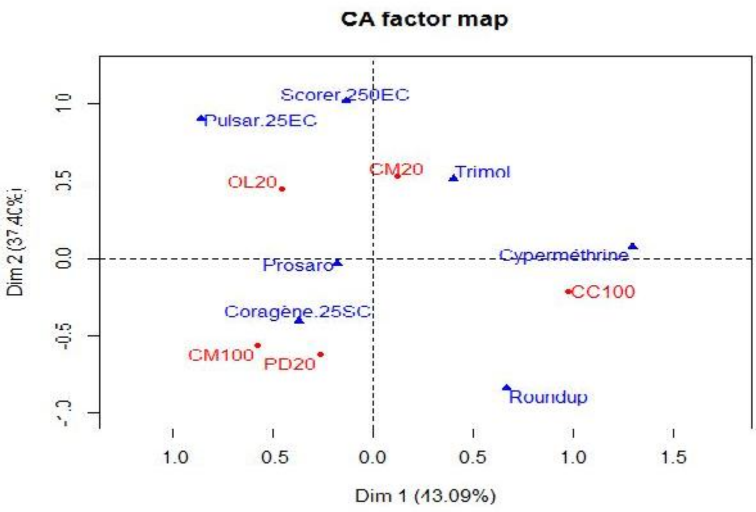

Fig.4. Profile representing the distribution of pesticides by crops

CM : vegetable crops CC : Cereal cultures OL : Olive cultures PD : Date palm culture

The canonical analysis was carried out with the aim of showing that there is a correlation between the different pedoclimatic parameters and the occurrence of the pesticide molecules (Figure 5). We noticed that moisture, pH and conductivity can play a role in the dissipation, retention and degradation of pesticides in the case of cypermethrin, trimol and score 250EC. The pH of our samples is between 7.2 and 7.7; the electrical conductivity values of our samples are ranging between 1.85dS / m and 2.77 dS / m giving it the saline class [18]. A decrease in retained amounts of ionizable pesticides is observed as pH increases [19]. Thus, for acidic pesticides, their dissociation into anions with the increase in pH results in a reduction of their retention by soils. This has been observed for various glyphosate [20] and bentazone [21,22].

According to the literature, a relationships between the adsorption coefficients of pesticides and certain properties of soils like carbon, clay or oxide contents, pH, exists [23-26].

El-Hejera region is known for high temperatures that can exceed 43, 66 ° C during summer, it should also be noted that the rainfall remains very low throughout the year (13.06 mm in January). The moisture varies between 11% for the cultivation of olives and 25% for vegetable crops; this can be explained by the fact that water demand of vegetable crops is more important. Soil moisture has an effect on the concentration of pesticides in the soil, on their DT50 half-life values (time required for 50% dissipation of the initial concentration), the more moist is the soil, the less persistent the product will be and therefore higher is its retention capacity and the more moist is the soil, the higher the concentration will be [27].

The results of the organic matter content of our soil samples revealed a rate of 2.32% for the soils of vegetable crops. According to scientific reports, a very general positive correlation exists between the retention and the organic matter content of soils with most pesticides [23; 24, 25, 28, 29]. Moreover, the adsorption of pesticides on organic matter is dependent on the polarity of the surfaces which is the case of our molecules which are mainly polar. This polarity is determined by the relative abundance of polar groups (nitrogen and oxygen functional groups) and apolar (carbon functional groups) [30,31].

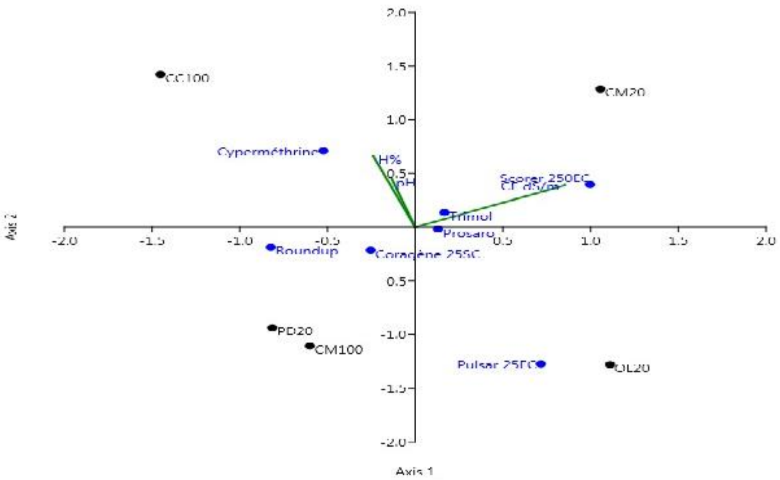

Fig.5. Influence of pedoclimatic parameters on pesticide dissipation.

CM : vegetable crops CC : Cereal cultures OL : Olive cultures PD : Date palm culture

3. EXPERIMENTAL

3.1. Study area and sampling

El-Hejera zone is located in the extension of the large basin of the north-eastern part of the Algerian Sahara. The climate is arid, with average to low rainfall, and very high potential evaporation. The regions of the Saharan depressions have long suffered from an excess of water, the origin of which is the rise of water from the Cornet water table [32,33].

Sampling was carried out on 10/12/2017 at 9:00 am, on a farm in El-Hejera, in the Saharan agriculture area (DASE), at different depths (20 cm, 40 cm, 60 cm, and 100cm) and under different crops: Vegetable crops, cereal crops, olives and date palms. It should be noted that the ambient temperature was between 12°C and 16°C. Soil samples and pesticides were immediately transferred to the laboratory.

3.2. Physico-chemical analyses

The analyses focused on: - The moisture content, the pH, the electrical conductivity, the organic matter and the total limestone, according to Aubert, [18] and Daoud and Halitim, [34].

3.3. Pesticide extraction and analysis

Solid/liquid extraction by Soxhlet was used. It is a method that involves mechanically agitating the samples in the presence of an extractant solvent; it is pure dichloromethane at atmospheric pressure and room temperature [35]. The samples were analysed first by thin layer chromatography (TLC) [36] and second by high performance liquid chromatography using an HPLC-RPC18 HPLC High Performance Liquid Chromatograph (SHIMADZU type HPLC-RP-C18) column, under the following operation chracteristics: A polar eluent acetonitrile, methanol. Oven: CTO 20A, Pump: LC 20AL, LC20AL (Shimadzu Scientific Instruments, Kyoto, Japan), UV-Visible Spectrophotometer (PRIM Advanced SCHOTT Instruments GmbH), Column: Shim-packVP-ODS (250mm x 4.6mm i.d 5μm), Incubator (Heidolph Instruments, Heizmodul type, Germany), Electrical analytical balance (Shanghai Sunrise Instrument precision 0.001g).

3.4. Multidimensional analysis

Multidimensional analysis was performed using R.3.5.2 software. Correspondence factor analysis (FTA) was also performed for qualitative variables after coding.

4. CONCLUSION

In conclusion, it could be suggested that understanding the behavior of phytosanitary products in the soil is essential for the risk assessment of their transfer to different compartments of the environment. This understanding will make it possible to implement a reasonable and sustainable use of these products without calling into question the economic sustainability of these activities.

Thus, in this work, our goal was the assessment of pesticide molecules in agricultural soils of El-Hejera region. The results let us deduce that the molecules of phytosanitary products undergo transformations or degradation which are the result of a set of processes like dissipation, physico-chemical and biological processes, which reduce the concentration of the pesticide according to the kinetic characteristics of the pesticide and the medium. However, more in-depth analyses are required to determine concentration of the residual pesticides found in agricultural soils, giving us the possibility to better evaluate the linked health hazards.

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