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Sorption–desorption equilibria of Deltamethrin in two contrasting agricultural soils of Loukkos North-west of Morocco

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Abstract

Loukkos perimeter is among the most important irrigated agricultural area in Morocco. The use of pesticides has made this region one of the first agricultural areas of our country in terms of the quantity of its production. However, excessive and random use of these chemicals could have adverse effects on human health and the environment, including groundwater. Deltamethrin is among the most used insecticides in this region, on several crops, including sugar beet and citrus. Excessive use of this insecticide presents a real risk to the deterioration of the groundwater quality, especially in the case of sandy soils. The aim of this research work was to investigate the adsorption and desorption processes of Deltamethrin in two contrasting agricultural soils (sandy and clayey soils) from the Loukkos perimeter using Batch equilibrium method. Freundlich model was used to describe the adsorption and desorption isotherms. Linear regressions were used to calculate the adsorption coefficients, used to assess these phenomena. The results showed that adsorption and desorption processes of Deltamethrin on soils were well described by the Freundlich model. The properties and the composition of the soils have great influence on the adsorption desorption mechanims of Deltamethrin. Results showed also that the irreversibility of the adsorption process is more important when the adsorption capacities of the soils and their clay content are higher. Our study showed a high risk of the presence of Deltamethrin in the Loukkos groundwater, particularly in sandy soils, which have low retention capacity due to their low content in clay and organic matter.

Keywords: Deltamethrin, adsorption, desorption, soils, Loukkos.

Etude d'adsorption-désorption de la deltaméthrine dans deux sols agricoles contrastés du Loukkos au Nord-Ouest du Maroc

Résumé

Le périmètre du Loukkos est l'un des plus importants périmètres agricoles irrigués du Maroc. L'utilisation des pesticides a pu faire de cette région l'une des premières zones agricoles de notre pays par la quantité de ses récoltes. Cependant, l'utilisation excessive et anarchique de ces produits chimiques pourrait avoir des effets néfastes sur la santé humaine et l'environnement, y compris les eaux souterraines. La deltaméthrine est parmi les pesticides les plus utilisés comme insecticide dans cette région, sur plusieurs cultures, dont la betterave à sucre, les agrumes. L'utilisation excessive de cet insecticide présente un risque réel de détérioration de la qualité des eaux souterraines, en particulier dans le cas des sols sableux. L'objectif de ce travail de recherche était d'étudier les processus d'adsorption et de désorption de cet insecticide dans deux sols agricoles contrastés du périmètre du Loukkos, à savoir des sols sableux et argileux, en utilisant la méthode d'équilibre Batch. Le modèle de Freundlich a été utilisé pour décrire les isothermes d'adsorption et de désorption. Des régressions linéaires ont été utilisées pour calculer les coefficients d'adsorption, utilisés pour évaluer ce phénomène. Les résultats ont montré que les processus d'adsorption et de désorption de la Deltaméthrine sur les sols étaient bien décrits par le modèle de Freundlich. Les propriétés et la composition des sols ont une grande influence sur les mécanismes d'adsorption et de désorption de cet insecticide. Les résultats ont également montré que l'irréversibilité du processus d'adsorption est plus importante lorsque les capacités d'adsorption, des sols et leur teneur en argile, sont plus élevées. Notre étude a montré un risque élevé de présence de la Deltaméthrine dans la nappe phréatique du Loukkos, en particulier dans les sols sableux qui ont une faible capacité de rétention en raison d'une faible teneur en argile et en matière organique.

Mots clés : Deltaméthrine, adsorption, désorption, sol, Loukkos.

توازنات الامتصاص والارتخاء لمبيد الدلتامثرين في تربة زراعية متباينة في حوض اللوكوس بشمال غرب المغرب

ملخص:

يعتبر حوض اللوكوس من أهم المناطق الزراعية المروية في شمال غرب المغرب. باستخدام المبيدات أصبحت هذه المنطقة من أولى المناطق الزراعية في بلادنا من حيث جودة وكمية منتوجاتها الزراعية. ومع ذلك، فإن الاستخدام المفرط والعشوائي لهذه المواد الكيماوية يمكن أن يكون له آثار ضارة على صحة الإنسان والبيئة، بما في ذلك المياه الجوفية. يعتبر الدلتامثرين من أكثر المبيدات الفلاحية المستخدمة، كمبيدات حشرية في هذه المنطقة، على العديد من المحاصيل، بما في ذلك الشمندر السكري والحمضيات وغيرها من الخضروات. يمثل الاستخدام المفرط لهذا المبيد خطرًا حقيقيًا على تدهور جودة المياه الجوفية، خاصة في بيئة ذات تربة رملية. كان الهدف من هذا البحث هو التحقيق في عمليتي الامتزاز والامتصاص لهذه المادة، دلتامثرين، في تربة زراعية متباينة في حوض اللوكوس، تربة رملية وتربة طينية، وذلك باستخدام طريقة التوازن الدفعي. تم استخدام نموذج Freundlich لوصف متساوي درجة حرارة الامتزاز والامتصاص، وتم استخدام الانحدار الخطي لحساب معاملات الامتزاز لتقييم هذه الظاهرة. أظهرت النتائج أن عمليات الامتصاص الامتزاز لمادة الدلتامثرين على التربة قد تم وصفها بشكل جيد بواسطة نموذج Freundlich لخصائص التربة وتركيبها تأثير كبير على آليات الامتزاز والامتصاص لدلتامثرين. أظهرت النتائج كذلك على أن قابلية عكس عملية الامتزاز تكون أكثر أهمية عندما تكون قدرات امتصاص التربة ومحتواها الطيني أعلى. أظهرت دراستنا وجود مخاطر عالية لوجود مادة الدلتامثرين في المياه الجوفية لحوض اللوكوس، خاصة في التربة الرملية ذات قدرة الاحتفاظ المنخفضة بسبب المحتوى المنخفض في الطين والمادة العضوية.

الكلمات المفتاحية: الدلتامثرين، الامتزاز، الامتصاص، التربة، اللوكوس.

Introduction

Loukkos perimeter is among the most important agricultural zones in Morocco covering an area of 256.000 ha, 147.300 ha of which are agricultural areas. With a Mediterranean climate and abundant water resources, the diversity of the soils and crops is important (Benicha et al., 2013). The basin receives an average annual rainfall estimated at 700 mm/m^2 and most of the farms are irrigated. In other terms, the perimeter is known for its intensive farming activity (Benicha et al., 2011, 2016; Daoudi et al., 2014), mainly in the sub areas of Laouamra, Zouada, Souaken, Dlalha, … (Hachimi and Maslouhi, 2016; El Falah et al., 2021).

The use of pesticides is becoming indispensable to intensify and i secure the production levels and face the increasing food demand from consumers and agri-industries (Benicha, 2005; El Bakouri et al., 2008). However, repeated, inappropriate and excessive uses of these chemicals, could contribute to an increasing risk of environmental contamination especially to groundwater (Benicha et al., 2011, 2013, 2016; Sarti et al., 2021).

Adsorption and desorption are the main physico-chemical mechanisms that characterize the behavior of a pesticide after its application in soil. They affect all other phenomena responsible for its dissipation such as degradation, persistence, volatilization, movement, and leaching. It is an important factor in predicting the level of contamination of the groundwater (Ismail and Maznah, 2006; Arias-Estévez et al., 2008; Li et al., 2011; Benicha et al., 2011, 2016; Vryzas, 2018).

Adsorption desorption isotherms are usually expressed by linear equations of Freundlich models. The Freundlich model or Freundlich adsorption isotherm is an empirical relationship suggested to link quantity of a gas adsorbed into a solid surface and the gas pressure. This model was subsequently used by different researchers for pesticide adsorption. Sorption - desorption capacity of pesticides in soils depend on both the physical, chemical and biological attributes of soils and the properties of pesticides (Benicha et al., 2005; Ismail and Maznah, 2006; Li et al., 2011). The importance of organic matter and particle size, for sorption, has been emphasized by many researchers (Huang et al., 1984; Barriuso et al., 1992; Gao et al., 1998; Benicha, 2005). Thus, knowledge of the pesticide adsorption-desorption characteristics of soils is important for predicting their mobility and fate in soil and water environments (Azejjel et al., 2008; Lunagariya et al., 2020).

Synthetic pyrethroids are among the most commonly used insecticides in agriculture (Burns and Pastoor, 2018) and their utilization has greatly increased in the last decades due to their effectiveness and low toxicity when compared to other insecticides (Yoo et al., 2016; Ross and Carr, 2019). Deltamethrin [(S)-a-cyano-3-phenoxybenzyl(1R,3R)-3-(2,2-dibromvinyl)-2,2-dimethyl-cyclo-propancarboxylate], is among pyrethroid insecticides commonly used in Morocco, especially in Loukkos area. It is a broad-spectrum insecticide used to control insects and aphids, fruit fly, thrips and cassid on several crops, including sugar beet, vegetables, citrus fruits (ONSSA, 2020). Deltamethrin is extensively used in agriculture because of its available under various commercial trade names and of its high activity neurotoxic properties (Hénault-Ethier, 2015; Cycoń et al., 2014; Singh et al., 2018). It is a non-systemic insecticide with rapid contact and ingestion actions (Guler et al., 2010; Utip et al., 2013; Shiavanoor and David, 2014). Deltamethrin degrades via hydrolysis, photolysis, and microbial actions and pathways. It is more persistent in soils with a high clay or organic matter content

(Roberts and Hutson, 1999; Tomlin, 2006, ASTDR, 2022) 3,5,9,27). Reported half-lives under aerobic laboratory conditions for Deltamethrin in sandy loam or silt loam soils range from 11 to 72 days (EPA, 1999; Tomlin, 2006). In another study, the half-life of Deltamethrin ranged from 5.7 to 209.0 days in four terrestrial field dissipation studies depending of soil type (EPA, 1999). Deltamethrin is considered relatively immobile in soils (EPA, 1999, ATSDR, 2022), so it has little potential to leach into groundwater due to its strong tendency to bind to soil organic matter that biodegradation can be stalled (Roberts and Hutson, 1999; Tomlin, 2006).

The wide use of this insecticide can have negative consequences on human health and environment by the presence of residues in food and in groundwater, which is used directly as drinking water in this region (Mestres and Mestres, 1992; Tang et al., 2018).

Accordingly, our objective aimed at assessing its environmental risk, particularly to the local shallow groundwater in the Loukkos perimeter. Actually, detailed studies of sorption of Deltamethrin in Moroccan soils will essentially help in predicting water contamination, as well as in improving the efficacy of this pesticide in controlling target organisms and minimizing the adverse effects on non-target organisms.

Aged residue of pesticides tends to be highly sorbed on the soil with a potential impact on the environment (Lesan and Bhandari, 2003; Benicha et al., 2005). As a result, they become biologically and chemically inert and are thus, effectively removed from the environmental system (INCHEM, 1984; Benicha et al., 2016).

Laboratory experiments were conducted to determine Deltamethrin sorption behavior to two different representative agricultural soils of Loukkos perimeter, using the standard batch equilibration technique. In this work, focus has been made on the potential of desorption of Deltamethrin from sorbed soils as well. The influence of soil properties such as soil organic matter and clay contents on the pesticide sorption was also examined.

Materials and methods

Chemicals

Analytical standard Deltamethrin (98.0% purity) was purchased from Sigma Aldrich. For the calibration curve, in HPLC analysis, a stock solution of 100 mg/L was prepared by diluting analytical grade Deltamethrin in HPLC grade methanol. Working standard solutions of 0.01 to 10.0 mg/L were prepared by appropriate dilution of stock solution with HPLC grade methanol. All standard stock solutions were freshly prepared and stored at - 4°C.

Sample preparation and soil properties

Two soils were selected from farmer’s fields located within Loukkos perimeter northwestern Morocco; one soil was selected from Zlaoula (latitude: 35°4'.12 ''N, longitude: 6°06'.47'' W), on the other side, the second soil type, was sampled from M'rissa (latitude: 35.015 ° 00'.55 ''N, longitude: 5.96 ° 57'.37'' W) (Figure 1). Composite samples were taken at random from a depth of 0 to 30 cm. In laboratory, they were air dried, crushed and sieved through 2 mm mesh screen.

Soils were analyzed within 2 weeks of sampling at the Regional Accredited Soil Laboratory of INRA of Tangier. Texture composition was determined using the Robinson Pipette method, pH was measured in water: soil (1:2.5) ratio, organic matter (OM) was assessed according to the Walkley & Black method (Walkley and Black, 1934), cation exchange capacity (CEC) was determined with the Metson method (Metson, 1957)

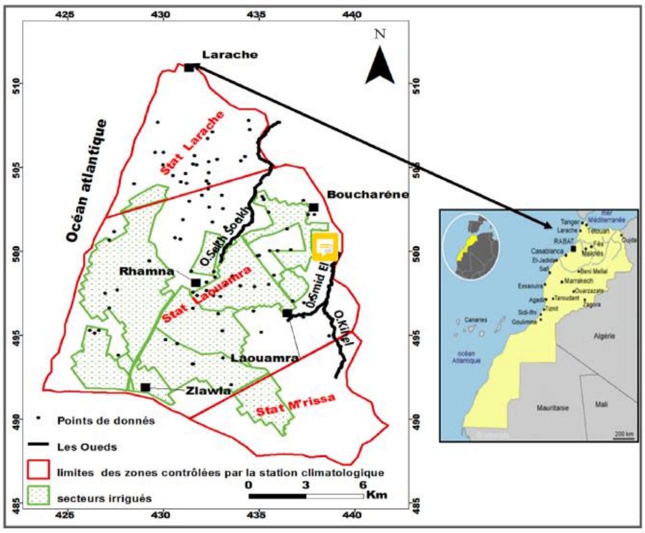


Figure 1. Geographical location of the Zlaoula and M’rissa soil sampling sites (Loukkos perimeter)

Adsorption desorption study

The study of the sorption kinetics is essential for the determination of the time required to reach sorption equilibrium. It also helps to determine, comparatively, the quantities of pesticides sorbed over time for a given initial concentration. Finally, it provides information on the mechanisms of sorption and the transfer of solutes from the liquid phase to the solid phase.

Equilibrium time and adsorption kinetic studies

For adsorption kinetics, 5g soil Samples (≤2mm size) were added to 20 mL conical centrifuge tubes containing 10mL 0.01M CaCl2 aqueous solution with Deltamethrin concentration of 10 mg/L. The tubes were shaken on a horizontal shaker at 200 rpm at room temperature. At predetermined time intervals of 0, 1, 2, 3, 4, 5, 6, 10, 22, 34, 48, 72 and 96 h, samples, in triplicate, were centrifuged for 5 min at 4000 rpm (Sigma centrifuge). 5mL of supernatant was collected and the Deltamethrin residues concentration was determined by HPLC after filtration through filter disc (0.45 µm). The kinetics data indicated that the sorption equilibriums for the two soils were basically achieved within 34 hours.

Adsorption isotherm experiments

Batch sorption experiments were performed in 50 ml centrifuge tubes, in triplicate, to avoid any inconsistency in experimental results. Each tube contained 10 g of soil and 25 ml of solution contained 0.01 M $CaCl_2$ and spiked with a specified volume of Deltamethrin stock solution, yielding initial working Deltamethrin concentrations ranging from 0.5 to 10.0 mg/L.

Desorption isotherm experiments

Desorption experiments were performed immediately after completion of the adsorption study. For this purpose, the soil (with the adsorbed Deltamethrin) was shaken for 34 h in 10 ml of 0.01M $CaCl_2$ solution. The aqueous supernatant was analyzed the same manner as in the sorption experiment. This desorption procedure was repeated four times for each soil. The amount of Deltamethrin adsorbed by the soil at each desorption stage, was calculated as the difference between the initial amount adsorbed and the amount desorbed.

After equilibrium, samples were taken and treated exactly as the samples of the sorption kinetic experiments. For each initial concentration, desorption started after the last adsorption step (96h). Each desorption step was conducted by replacing the supernatant with 0.01M, background solution and shaking for 34h. The fraction of Deltamethrin desorbed from the soils was calculated on the basis of the change in concentration in solution (before and after desorption).

HPLC analysis

Deltamethrin residue quantification was performed using isocratic HPLC apparatus equipped with a C18 Lichrosorb column (250×3.9mm; 5μm) and UV detector Shimadzu (LC-10ADvp) at 220 nm. The injection volume was 20μl and mobile phase was Methanol:water (80:20 v/v) at a flow rate of 0.9 mL/min. The samples were analyzed in triplicate.

RESULTS AND DISCUSSION

The soils are classified as clayey and sandy soils. Their characteristics are presented in in Table 1.

Table 1. Selected Physical and chemical characteristics of the studied soils:

Soil	Texture	Clay %	Silt %	Sand %	pH Water	pH KCl	OM %	CEC meq/100g
M'rissa	Clayey	61.2	17.3	21.5	7.10	6.80	1.87	40.24
Zlaoula	Sandy	5.1	8.9	86.0	7.30	6.90	0.57	2.80

Determination of adsorption and desorption kinetics

Sorption kinetic and equilibrium time

A preliminary sorption experiment was conducted to determine contact times required for sorption equilibrium to be reached. The results, presented in figure 2, indicate that sorption kinetic of Deltamethrin for both soils followed a biphasic pattern; fast sorption step during few hours (8 hours), during which high proportions/amount of Deltamethrin are retained (80%) for the clayey soil. The second step, however, is very slow and remained for several hours (up to 40 h) during which low amount of Deltamethrin was sorbed. The same tendency was obtained for the sandy soil, with however low sorption intensity as compared to clayey soil (Figure 2).

The kinetic curve of Deltamethrin sorbed onto two soils is illustrated in Figure 2. The concentration of Deltamethrin sorbed on the two soils increased rapidly at the initial stages and then slowed down until sorption equilibrium time is reached. The sorption equilibrium was basically achieved at approximately 34 h. The adsorption rate for M'rissa clayey soil was 74%, while it was only 38.5% for Zlaoula sandy soil.

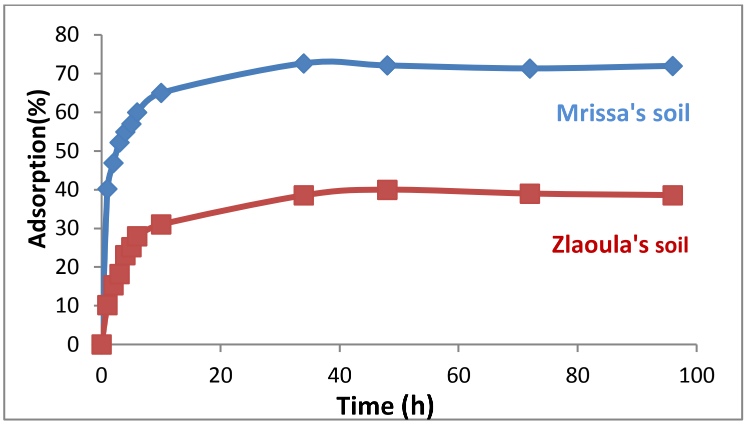


Figure 2. Adsorption kinetics of Deltamethrin in studied soils

The absorption kinetics data demonstrate clearly the possibility to differentiate between the two types of soils based on the quantities of Deltamethrin adsorbed at the equilibrium. Experimental data show a two-step reaction; the first step is relatively fast and takes place in less than five hours. This can be explained by the fact that during this first phase, the adsorption is controlled by the transfer of extra-granular material. This reaction is associated with the diffusion of the pesticide to the surface of the adsorbent (Barriuso et al., 2000; Yoo et al., 2016). The second phase is characterized by a slow adsorption of Deltamethrin. As in any porous media such as soil, this limitation of the adsorption rate, during this stage, is often attributed to the molecular diffusion of the pesticide to less accessible sites such as the micro-pores of the soil, the interfoliar space of clay minerals, or inside organic matter (Lesan and Bhandari 2003; Yoo et al., 2016). In his research dissertation, Jiandani (2015) also found a two phase or region adsorption process of selected pesticides including Deltamethrin.

Previous studies by Gilchrist et al. (1993) and Barriuso et al. (2000) suggested that the rapid phase is due to the adsorption of the pesticide to the most accessible sites, probably located on the outer surfaces of the soil particles.

During the last phase of the adsorption kinetics process the retained quantities of Deltamethrin remains constant indicating that the absorption equilibrium has been reached. For both types of soil, 34 hours of soil pesticide contact time were sufficient to reach complete absorption equilibrium. In addition, the adsorbed quantity of Deltamethrin at the equilibrium can be used as an indicative factor to differentiate between the two types of the soil;'s the largest amounts of the insecticide (74%) being by M'rissa soil, while only 38.5% was retained by Zlaoula soil.

These results show clearly that, the amount of Deltamethrin adsorbed increases with clay content; the richest the soil in clay fraction, the greater the proportion of the pesticides is retained. Thus, clay plays a fundamental role in the retention process of Deltamethrin as well as soil organic matter (OM) (Zhu and Selim, 2002; Ismail et al., 2013;

Adsorption isotherms

Sorption isotherms have been modelled according to the Freundlich model. It characterizes the sorption isotherms by two parameters: K_f reflecting the soil adsorbent power and n_f, the evolution of the accessibility of the pesticide to the soil available

binding sites. These parameters are calculated after linearization Freundlich equation (Calvet, 1989).

$$Q_{ads} = K_f\, C_e^{nf} \Longrightarrow \log Q_{ads} = \log K_f + n_f \log C_e$$

Where: n_f is up the distribution of adsorption sites and K_f is a function of the number of sites and the Ionic composition of the liquid phase.

The Freundlich constant (K_f) reflects the adsorbent affinity of a matrix with respect to the pesticide. The higher the value of K_f, the greater the adsorption. When n=1, the sorption isotherm is simplified in linear relation:

$$Q_{ads} = Kd.\ Ce$$

With Kd: the distribution coefficient (or partition coefficient) of the pesticide between the liquid phase and the solid phase.

The adsorption isotherms of Deltamethrin are shown in Figure 3 and the corresponding fitting parameters are presented in Table 2. Sorption of Deltamethrin fits well the Freundlich model for the two soils as indicated by the high linear regression coefficients (R^2=0.997 for sandy soil and R^2=0.977 for clayey soil). The adsorption isotherms of both soils are of L type according to the classification of Giles, suggesting high affinity of soils for Deltamethrin at low concentrations (Giles et al., 1960). The K_f adsorption coefficients varied between 3.914 and 1.503 and n_f coefficients ranged between 1.158 and 0.940 for clayey and sandy soil, respectively. The values of these constants increase therefore with clay and OM contents.

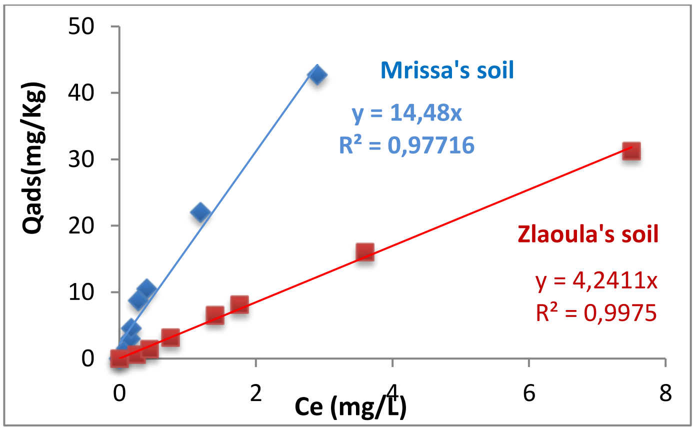


Figure 3. Deltamethrin adsorption isotherms for the two soils (Freundlich model)

Table 2. Fitting parameters of Freundlich model to the adsorption isotherms of Deltamethrin on M'rissa and Zlaoula soils

Soil Type	K_f	n_f	K_d	R^2
M'rissa	3,914	1,158	14,480	0,977
Zlaoula	1,503	0,940	04,240	0,997

The adsorption isotherms for both soils are well described by Freundlich model. The K_f values are significantly different from each other. Compared to M'rissa soil, the K_f value calculated for the Zlaoula soil was almost three times lower (Table 2). This finding

indicates that there is a significant effect of soil type on K_f values. Zhu (2002) reported Kf adsorption coefficient ranging from 11.8 to 146.94 according to soil type and concluded that soil organic matter and clay contents are positively correlated with Kf.

Ismail et al. (2013) reported that adsorption of Deltamethrin was higher in peat soil 431 1/kg: than silt clay soil (140 L/kg) which was reflected from respective higher Freundlich adsorption coefficient (Kf) values. Qualitatively, Zlaoula soil has the ability to retains Deltamethrin, but from a quantitative point of view, the retained amounts are low (low K_f value). This is directly related to soil organic matter and clay contents; these two soil constituents are the main parameters that play an important role in pesticide adsorption process (Spark and Swift, 1994; Guangyao et al., 2001; Benicha et al., 2016). Indeed, Zlaoula soil has low clay and organic matter contents as compared to those of M'rissa soil. Similar results on sorption of Deltamethrin were obtained by Arienzo et al. (1994). These authors found that the adsorbed amount of Deltamethrin decreases with decreasing soil organic matter content. Thus, the increase in the quantity of adsorbed Deltamethrin is associated with the increase in soil organic matter content (Coninck et al., 1998).

The fact that the calculated value of n_f parameter for Zlaoula's soil (n_f = 0.9401) is very close to 1, indicates that the adsorption of Deltamethrin is almost linear. This demonstrates that the amount of Deltamethrin adsorbed is directly proportional to the concentration of the solution at the equilibrium. So, all the sites of the adsorbent have the same potential energy and the K_f parameter corresponds to the partition coefficient K_d . which reflects the distribution of the pesticide between the solid phase (the soil) and the liquid phase of the soil. The higher the Kd value, the greater the affinity of the pesticide for the soil. In contrast, the adsorption of Deltamethrin by M'rissa soil is not linear ($nf > 1$). This means that the adsorption becomes slightly difficult with the increase of Deltamethrin concentration.

Desorption process

If the sorption process reduces the mobility of the pesticide, the sorbed molecules are not least potentially available and can be remobilized to the soil solution by desorption process. The desorption study is therefore important because it allows to obtain information on the reversibility of sorption process.

Determination of desorption kinetic

Figure 4 shows that the quantities of Deltamethrin desorbed in solution increase as a function of desorption time up to 16 h for the two types of soil. This desorption time seems optimal with the possibility to release the maximum amount of Deltamethrin in solution. Beyond this period, the quantities desorbed decrease for both soils. By comparing these results with those obtained for the adsorption kinetics, we found that an incomplete reversibility of adsorption occurs which corresponds to the hysteresis phenomenon (H). In many previous studies, similar H has been observed with other pesticides. The H could have several origins including the formation of irreversible chemical bonds (Lesan and handari, 2003; Ammoury, 2004; Shih, 2008; Ouoba, 2009; Benicha et al., 2016).

Desorption is expressed in terms of percentage (R) of deltamethrin adsorbed by the soil and is calculated as follows:

$$R = (C_0 - C).100/\ C_0$$

With C_0: the initial concentration of deltamethrin (mg/l)
C: the final concentration of deltamethrin (mg/l)

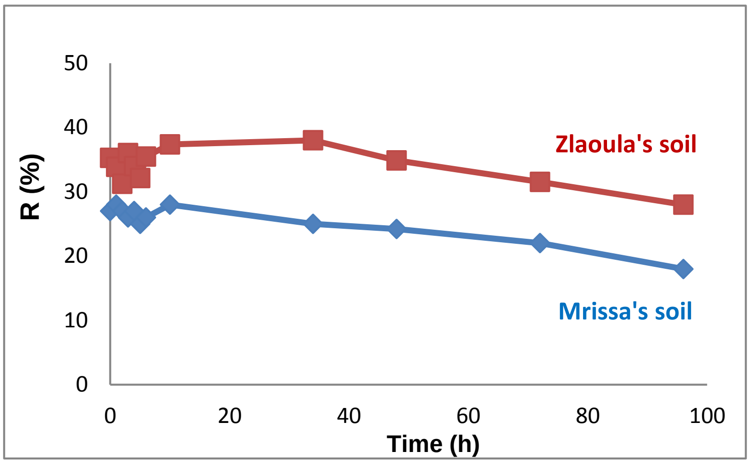
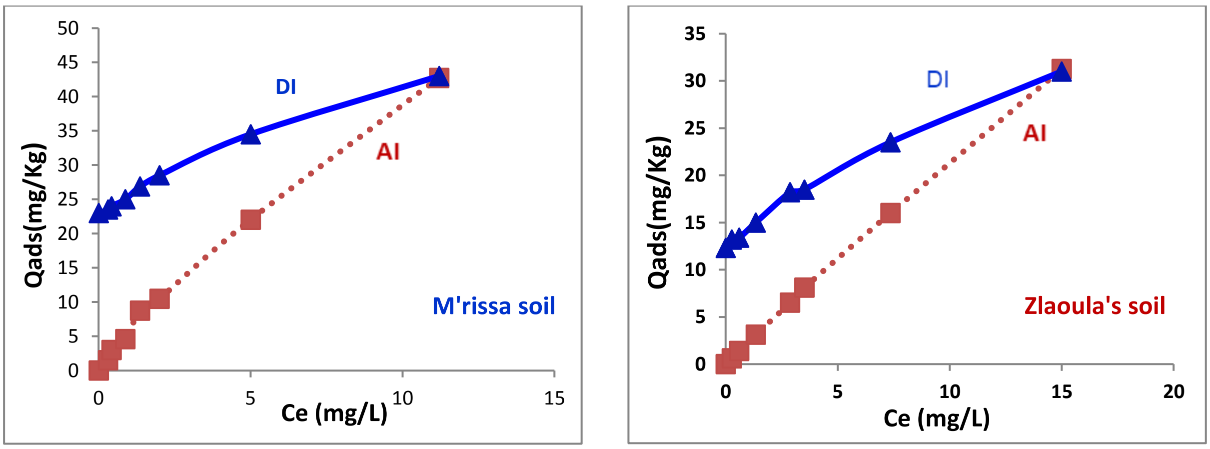


Figure 4. Desorption kinetics of Deltamethrin in Loukkos soils

Desorption or release characteristics of pesticides generally influences their leaching and bioavailability in soils (Mersie and Seybold, 1996). Soils are generally more retentive of pesticides during desorption than adsorption, a phenomenon known as **hysteresis**. Consequently, desorption parameters can be substantially different from that for adsorption.

Desorption isotherms

The desorption isotherms obtained are presented in figure 5. This figure showed also that soil behaved/act, as in sorption process, differently towards/in terms of Deltamethrin desorption: the sandy soil allowed desorption of high amount, while for the clay soil, the difference is smaller than what is occurring in sandy soil.



AI: Adsorption isotherm; DI: Desorption isotherm

Figure 5. Adsorption (AI) and Desorption (DI) isotherms of Deltamethrin in both soils

The discrepancy, observed between the isotherms of adsorption and desorption, reflects a hysteresis phenomenon highlighting not completely reversible nature of the adsorption of Deltamethrin by the soil. In many studies, this hysteresis phenomenon has been observed for pesticides (Pignatello and Huang, 1991; Lesan and Bhandari, 2003; Drori et al., 2005). The hysteresis observed can have several origins: the formation of irreversible chemical bonds, the trapping of pesticide molecules due to degradation (Koskinen and Harper, 1990; Weber et al., 1998; Lesan and Bhandari, 2003; Benicha et al., 2016).

Modelling desorption of Deltamethrin

As in the case of sorption process, Freundlich model was used for modelling the Deltamethrin desorption isotherms according to the following equation (Calvet, 1989):

$$Q = K_{fd}\, C_e^{nd} \Longrightarrow \log Q = \log K_{fd} + n_d \log C_e$$

Where:

- Q: the amount of pesticide remaining sorbed after each desorption, expressed per unit of weight of soil,
- Ce: Concentration in solution at equilibrium after desorption,
- K_{fd} and n_d are empirical coefficients.

Figure 6 shows that desorption isotherms are well described by Freundlich model with correlation coefficients $R^2 \geq 0.9976$ and 0.9952 for M'rissa (clay) and Zlaoula (sandy) soils respectively. The K_{fd} parameter makes account of the capabilities of desorption from soils and the n_d parameter reflects the degree of nonlinearity of the desorption isotherm. In other words, it reflects the variation in adsorption with the concentration (curvature). They were slightly modified upon altering the aging time of the Deltamethrin residues in the soil (Table 3).

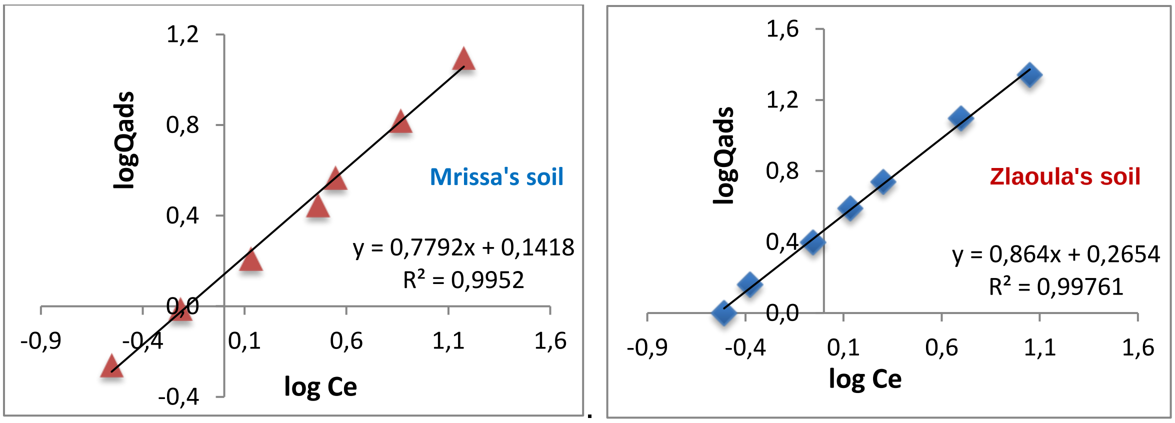


Figure 6. Deltamethrin desorption isotherms (Freundlich model)

In addition to the adsorption isotherms, desorption isotherms are also well described by Freundlich model. The desorption index (nf_d) is lower as compared to the adsorption one (nf_a).

This finding demonstrates that the desorption rate is inferior to the adsorption one. Thus, a fraction of the Deltamethrin remains adsorbed in both soils, even after the completion of the desorption process. This irreversibility between adsorption and desorption processes is the cause of the hysteresis phenomenon recorded for both soils (Fig. 5). As reported in previous studies, this irreversibility can be related to the

fact that the pesticide molecules stabilized as bound residues from gradually increase over time (Ismail and Maznah, 2006; Olvera-Velona et al., 2008; Benicha et al., 2016; Yoo et al., 2016). Hysteresis index (HI) is defined as the ratio HI=Nd/Na, where N_a and N_d are Freundlich N for adsorption and desorption, respectively. Cox et al. (1997) proposed a desorption hysteresis coefficient H, based on the ratio of desorption and adsorption isotherm parameters. As show in Table 3, the hysteresis index (HI), of Zlaoula soil is lower that of the M'rissa soil, which indicates a higher irreversible adsorption for Zlaoula soil.

Zhu and Selim (2002) reported strong deltamethrin hysteresis was observed for all soils as depicted by discrepancies of adsorption from desorption isotherms and conclude that deltamethrin is not susceptible to leaching losses from the zone of application. Zhu Selim (2002) reported the Kd values after 1-day sorption ranged from 13 to 98 ml/g soil. The adsorption and desorption processes are associated with other soil parameters such as pH and water content (Oudou and Hansen 2002). The higher ratio of deltamethrin dissipation observed in sandy soils, that characterized by a low content of organic matter and clay fraction, was connected with a higher availability of insecticide to bacteria as compared to silty soil (Cyon et al., 2013).

The modeling of the desorption isotherms of Deltamethrin makes it possible to calculate for the two soils, the hysteresis index HI (table 3). This index makes it possible to assess the more or less reversible character of the adsorption phenomena (O'Connor et al., 1980).

An hysteresis coefficient (H) was calculated (H = 1/ndes / 1/nads)= nad/ ndes for desorption. In general, hysteresis is defined only for H < 0.7 (Barriuso et al., 1994). When H decreases (n_{ads} decreases), the hysteresis increases, indicating a more irreversible adsorption (Gaullier, 2018).

The values of the hysteresis index obtained vary according to the two types of soil. Examination of the variation of the HI index shows that soil B has the lowest degree of hysteresis (highest HI), which results in more irreversible adsorption. Remember that this soil is characterized by the highest adsorption capacity, due to its high content of emeril and MO (Kd = 14.48 L/Kg). On the other hand, the adsorption of Deltamethrin on the sandy soil presents a clearly more hysteretic behavior (HI = 0.55) and therefore a more reversible adsorption. The retention capacity of this soil is therefore relatively low (Kd = 4.25 L/Kg).

These results indicate that the adsorption of deltamethrin is more irreversible as the adsorption capacity of the soil is high. Thus, the greater hysteresis obtained for M'rissa soil in this study could be explained by the establishment of irreversible bonds between Deltamethrin molecules and the sediment, especially with the organic matter (Mamy and Barriuso, 2007; Olvera-Velona et al., 2008).

Non-reversible sorption and hysteresis effects concern many pesticides (Koskinen and Harper, 1990; Pignatello, 2000). Increasing pesticide contact time or ageing affects adsorption and desorption processes, and generally desorption decreases with the residence time in soil (Pignatello, 2000; Mamy and Barriuso, 2007).

Table 3. Freundlich model parameters of the adsorption - desorption isotherms of Deltamethrin

Soils	nf_d	nf_a	HI
M'rissa	0.8640	1.1583	0.7260
Zlaoula	0.7752	0.9401	0.5523

The calculated HI values show that M'rissa soil exhibits the lowest hysteresis degree, which correspond to a higher irreversible adsorption. This type of soil is characterized by the highest adsorption capacity due to its high content in clay and OM (K_d = 14.48 L/Kg). On the other hand, the adsorption of Deltamethrin on Zlaoula soil exhibits a marked hysteretic behavior (HI=0.55), which corresponds to higher reversible adsorption (Figure 2).

Zhu et al. (2002) reported that strong hysteresis behavior of deltamethrin adsorption-desorption was observed for all soils studied as illustrated by the discrepancy between the adsorption and desorption isotherms. For many pesticides, it is generally accepted that sorption to soil increases as a function of pesticide-soil contact time; a phenomenon often termed aged or time-dependent sorption (Gevao et al., 2000; Reid et al., 2000; Beulke et al., 2004; Regitano et al., 2006; Benicha et al., 2016). Furthermore, there is substantial evidence to suggest that a fraction of aged pesticide residues can become irreversibly bound to the soil matrix (Dec et al., 1997; Mordaunt et al., 2005; Wanner et al., 2005; Benicha et al., 2016). This is why the desorption amount decreased with aging time. As a result, they become biologically and chemically inert and are thus, effectively removed from the environmental system (INCHEM, 1984). Irreversible sorption has been observed for many pesticides and is often suggested as a cause of hysteresis in laboratory studies (Celis and Koskinen, 1999; Benicha et al., 2005).

Conclusion

Understanding of the sorption mechanism is fundamental to predict the fate and distribution of Deltamethrin contaminant in the soil and its environment. Sorption measurements allow the evaluation of this insecticide in relation to its capacity to remain in the soil solution. Results presented here showed that Deltamethrin adsorption, for two contrasting Loukkos agricultural soils, is characterized by a fast and rapid phase followed by a slow one. The first phase is due to adsorption at readily available sites, while the second phase is due to slow molecular diffusion of Deltamethrin, which increased over time. This reaction seems to be linked to the diffusion of the pesticide molecules mainly through the soil micropores.

The equilibrium adsorption isotherms have shown a different adsorption capacity for each soil. M'rissa's soil exhibited high affinity for Deltamethrin compared to Zlaoula's soil. In addition, the adsorption capacity is proportionally correlated with clay content of the soil. The observed hysteresis between adsorption and desorption processes, reveals the irreversibility nature of Deltamethrin adsorption in both soils. This irreversibility is more pronounced, as the adsorption capacities of the soils and their clay contents are high. The *n* and *k* constants for Deltamethrin sorption on soils support our hypothesis, so Deltamethrin could present a high risk of ending up in groundwater when applied to sandy soils. In this sense, leaching or mobility as well as biodegradation studies should be carried out and options of remediation of soil environments contaminated with deltamethrin or other pesticides must be investigated and developed.

Conflict of interest

Authors declare that they have no conflict of interest.

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