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African Journal of Agricultural Research

Full Length Research Paper

Reputation effect of the moral hazard on contract farming market development: Game theory application on rice farmers in Benin

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A good reputation is the basis for rice farmers to survive and gain trust from buyers in a competitive business environment. However, due to the existence of information asymmetry between buyers and rice farmers, the moral hazard problem is the key obstacle that impedes the benefits of related shareholders and hinders the efficiency of contract farming negotiations. It is crucial to design a control mechanism to avoid the negative impact of the moral hazard. This paper studies the principal and agent relationship between rice farmers and buyer in contract farming negotiation. Because of the influence of information asymmetry, many buyers have suffered from being cheated by rice farmers who fail to comply with the terms of the contract or provide fraudulent products in practice. These frequent cases will function to deteriorate any long-term relationships between rice farmers and buyers. The study focuses on the analysis of the causes of moral risks and the effect of reputation on moral risk utilizing repeated game theory. The purpose of this paper is to help both rice farmers and buyers effectively avoid moral hazards and achieve a win-win situation in contract farming negotiation. The result show that the rice farmer in contract farming practices has the incentive to maintain his reputation in order to gain more profits in the future. That also accounts for the reasons why the rice farmer will invest more to improve the customer's service level, caring about the quality of product and the comments of finished contractor customer, to keep a longer farmer-buyer relationship. The rice farmer in contract farming practices has the incentive to maintain his reputation in order to gain more profits in the future and this means that contract farming can be developed with great success in Benin.

Key words: Contract farming negotiation, moral hazard, reputation model, game theory, rice

INTRODUCTION

In Benin, rice producers face enormous funding challenges (Odountan et al., 2018). The levying of

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customs duties when transporting agricultural products to the market and the payment of market taxes are factors that influence the profitability of production. To address this situation, producers could use contract farming (Arouna et al., 2015). Contract farming is seen as a potential solution to overcome agricultural production constraints for resource-poor farmers (Arouna et al., 2017). Nevertheless, for a long time there has been one serious problem impeding the development of contract farming, that is, the lack of trust between farmers and buyers. There are many factors that influence the relationship between the farmers and buyers in contract farming practice. One of them is the moral hazard, which refers to the egoistic behaviors of farmers after making a deal with the buyers. Buyers do not have any insurance that the contract is flawless. Moreover, the insurance process is not well developed in the agricultural sector in developing countries, particularly in Benin, where buyers depend on farmers as the buyers usually forgo the common sense step of taking some precautionary measures.

In contract farming negotiation, buyers and farmers have a motivating force to take part in social contracts to build up volumes exchanged and to lessen the vulnerability that builds exchange costs which further decreases interest in esteemed included resources (Bezabeh Ali, 2018). This is most obvious among firms giving extension services and ranch input supply to farmers (Anim, 2010). The farmers who will adulterate the agreement and deliberately commit bribery are the root cause of the moral hazard. The underlying reason for the moral hazard is information asymmetry, which means the rice farmers have more information about the quality and cost of the rice, while buyers know less. In the practice of contract farming, the rice farmers usually will exploit their knowledge of the quality of product, production and transportation costs, and so on to take advantage of buyers. There are two types of information asymmetry: The first is adverse selection which occurs before the coalition between buyer and farmers, whereas the other is the moral hazard which happens after the deal.

This paper will focus on defining the problem of the moral hazard between the rice farmers and buyers in contract farming practice and on a potential solution to the problem. One popular way is to introduce the concept of establishing a corporate reputation to track the past behavior of the rice farmers. A corporate reputation is an overall evaluation that reflects the extent to which people see the farming as substantially “good” or “bad” (Dowling, 2004). A good reputation is valuable because it can enhance trust and confidence so that the buyer feels that it is safe to buy products and service from this farmer. This outcome can also benefit the farmers in their markets and various researches have also shown that farmers with good reputations are better able to attain and sustain superior profits over time.

The primary research question in this paper examines the expected profits of the farmers and the buyers that depend on two factors. One is the type of farmers, and the other is the reputation of the farmers with the buyer. For example, does the farmer always benefit from cheating or not? To answer this research question, we will examine the contract farming practice where the reputation mechanism exists and check the influential mechanism. In this paper, we will set the reputation model of the farmer in contract farming practice. We first characterize the situation that the type of farmer is not common knowledge and, then, demonstrate that, even though cheating has a direct benefit to the farmer, it can sometimes hurt the farmer, buyer, or both if the contract continues in the long run. Furthermore, we show the impact of reputation. In addition, we illustrate that the farmer will always choose to be honest when the mechanism of reputation works. In a typical game-theoretic view of the relationship between farmer and buyer, each player acts in order to maximize his own profit (rational player) without taking into account the overall optimal relationship. Thus, incentive is offered to influence the behavior of the other player. Such an incentive is reputation.

LITERATURE REVIEW

In contract farming, the buyer and farmers commit in advance to exchange the product. In addition, the buyer can provide credit, inputs, monitoring, or is directly involved in part of the production process. Contract farming has been claimed to have a positive impact on local economies by improving the welfare of rural households, but the relationship between farmers and buyer could be switched (Arouna et al., 2017).

Apart from the problem of direct observability of possible frauds by farmers, reputation mechanisms and the activation of bilateral sanctions by individual farmers do not have any chance to deter such abuses (Mazé, 2009). As a potential motivation, reputation could encourage the farmer to improve the quality of his practice during the contract process. Since the time of Adam Smith, reputation has been considered to be a very important mechanism to ensure the implementation of a business contract, but only recently, it has been widely used in combination with game theory (He and Sommer, 2006). In management practice, the motivation of reputation is also very popular and has brought new management thinking to the creation and maintenance of a good reputation. The farmer who cares about his reputation will be responsible for his behavior, even when there is no explicit motivational contract. Farmers would work hard to increase the level of reputation, hoping that they would gain more in the future.

Some researchers have pointed out the important effect of reputation on incentive mechanisms and have begun to associate the farmer’s reputation and incentives

to build a complete model (Cai and Weng, 2014).

According to Watanabe et al. (2017), the assentions in the contract farming may be ensured by trusted and rumored social standards that provide self-enforcement, leading to the desired behavior. Such research points to the idea that the reputation of the agricultural market could be used as a replacement for an explicit contract.

Reputation was first introduced by Fama (1980). Following this, Kreps, Milgrom, Roberts, and Wilson established the KMRW reputation model based on the repeated game (Kreps and Wilson, 1982; Milgrom and Roberts, 1982). When both parties in the game only care about the immediate benefits, the optimal strategy is to not return the product because it is not beneficial for either party. In the setting of the repeated game, reputation provides implicit motivation for contracts; the player would like to compromise by giving up short term benefits to choose coordinate equilibrium.

Zheng (2013) and Lyu et al. (2016) also proves that, when the payoff of one player is not known by the other, this player has incentive to build good reputation to exchange for long run profits.

Thus, we specifically develop a model to investigate the effect of reputation on the profit of the rice farmers.

CONSTRUCTION OF THE MODEL

Within the context of a repeated game, we consider a market in which both the farmers and the buyers are clients, which is quite popular in the real exercise. There are two probable types of farmers: probability *p* indicates he has a respectable reputation and 1− *p* probability indicates that his reputation is immoral. The selling price of the rice is P_s and the unit cost is *C*; the value of the rice to the buyer is denoted as V_b, as $V_b > P_s$; otherwise, the buyer does not have the incentive to buy the product (rice). Moreover, there are two arrangements which the farmers could make regardless of which type it is, which are either to provide an honest deal or a dishonest deal.

The cost of rice farmers with a respectable reputation or an immoral reputation to act honestly or dishonestly is designated as follows: C_{HR} and C_{DR}, C_{HI} and C_{DI}. “H” denotes the rice farmer who chooses to be honest while “D” denotes the rice farmer who chooses to be dishonest. “R” denotes the type of rice farmer who is respectable, while “I” denotes the type of rice farmer who is immoral. The rice farmer of low reputation will have more management costs and more future risk; additionally, the rice farmer with an immoral reputation is more familiar with cheating the buyer, therefore,

Assumption 1: $0 < C_{HR} < C_{HI} < C_{DI}. < C_{DR}$.

The information asymmetry in contract farming application is reflected by the fact that the rice farmer knows his own type, while the buyer lacks this knowledge. As shown in Figure 1, if the rice farmer with a respectable reputation chooses to be honest, and the buyer thinks that the rice farmer will not cheat him, the buyer will, therefore decide to make a deal. The revenue of the rice farmer is: $P_s - C - C_{HR}$, and the revenue of the buyer is $V_b - P_s$. If the buyer thinks that the rice farmer is cheating him, and the buyer decides not to make a deal with the rice farmer, then the rice farmer with a respectable reputation will suffer from loss: $-C_{HR}$. Similarly, we could conclude the payoff of buyer and rice farmer when the type of rice farmer is immoral in Figure 2.

Assumption 2: Suppose the unit value of the product provided by the seller within some periods values T, which is a function of rice farmer’s service level λ, the rice farmer’s real strength θ and the uncertainty in contract farming market application, so we have:

$$T = k\lambda + h\theta + \mu,$$

where λ is the private information of the rice farmer, T is the common knowledge of both the rice farmer and buyer, besides θ and μ following nominal distribution, with means equal to 0 and variance equals σ_θ^2 and σ_μ^2 respectively.

Assumption 3: If the times that the buyer makes a contract with the rice farmer is kept at a constant φ, then the profits of the buyer is $\pi^b = \varphi T$.

Assumption 4: The sequence is as follows: first, the buyer will decide how many times to contract with this farmer, then the rice farmer will decide the deal level.

The rice farmer mainly profits from the commission from purchasing times φ, which implies that βφ, which is the cost of the service provided by the rice farmer is c(λ), $c'(\lambda) > 0$, $c''(\lambda) > 0$. $c(\lambda) = (b\lambda^2)/2$, while the income of the rice farmer is $\pi^F(\lambda) = \beta\varphi - (b\lambda^2)/2$.

MODEL ANALYSIS

The introduction of the deal level of a rice farmer aims to diminish the risk of the buyer, to keep the benefits of the buyer and guarantee the efficiency of the contract market. Therefore, the optimal deal level to maximize the total profits in the contract farming market should be:

$$max_\lambda^T = \pi^b + \pi^F(\lambda)$$

$$max_\lambda^T = \varphi T + \beta\varphi - (b\lambda^2)/2 \rightarrow \lambda = \varphi k/b$$

Since the first decision, the buyer is to choose the contract times from a specific rice farmer, and, the next time, the rice farmer will decide the deal level. Rice farmer will take the following arrangements:

$$max_\lambda^T = \beta\varphi - (b\lambda^2)/2 \rightarrow \lambda' = 0$$

$$T = \beta\varphi - b\lambda \rightarrow \lambda'' = 0$$

When the contract deal is a first time contract, and the farmer knows that the probability to sign another contract scheme with the buyer another time is low, the rice farmer will choose dishonesty to maximize his own profits, regardless of whether he is generally honest or dishonest. Moreover, the buyer will not make a deal with the rice farmer after considering that; thus, this contracting market does not exist. Nevertheless, in the case of repeated contract application whereby the rice farmer signs a contract with the same buyer, the buyer will make the decision based on past contract experience. As the repeated game changes the restriction mechanisms, the payoff for both parties will be divergent, so a new equilibrium will exist.

In the first time contracting, when the buyer thinks that the rice farmer has a respectable reputation, the expected payoff of the buyer is:

$$(V_b - P_s)\, P_1 + (-P_s)\,(1 - P_1) > 0,$$

With P_1 the probability that the rice farmer was regarded to have a respectable reputation at the first time, only when $P_1 > P_S / V_b$, will

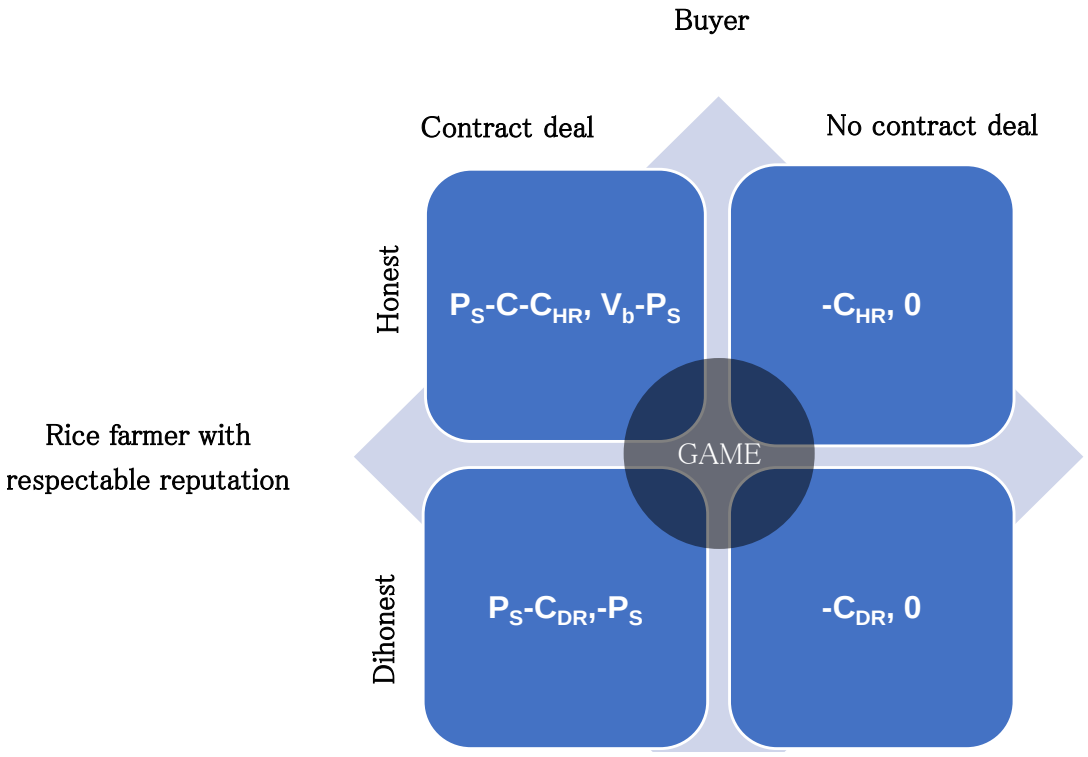

Figure 1. The payoffs of the rice farmer with respectable reputation R.

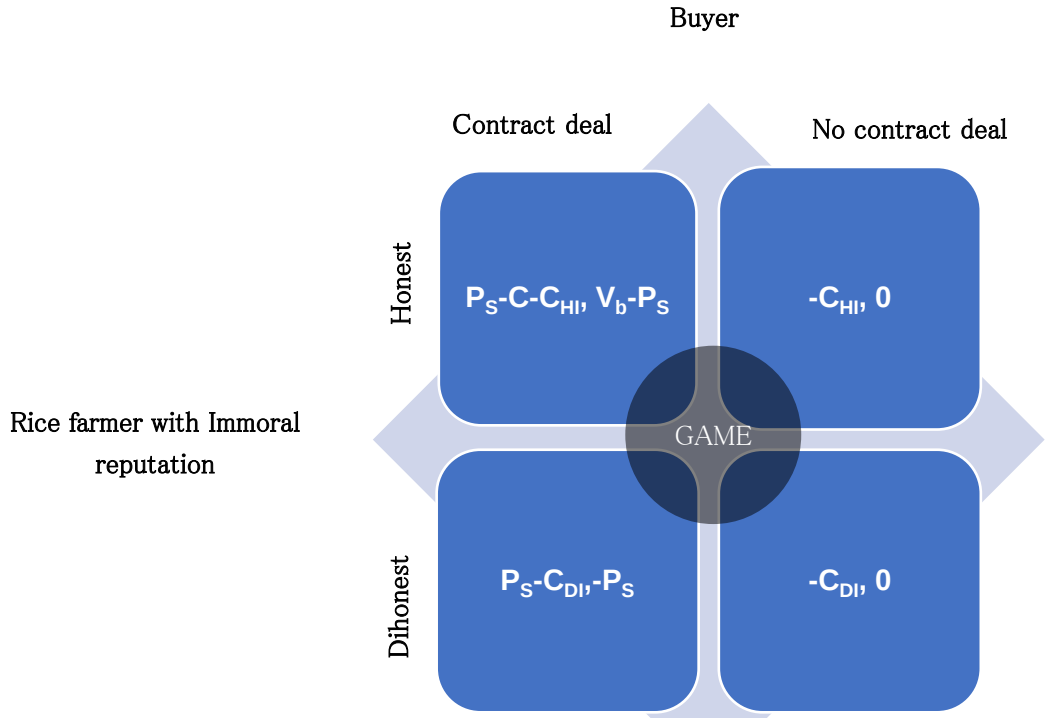

Figure 2. The payoffs of the rice farmer with the immoral reputation I.

the buyer decide to make a deal with rice farmer.

We propose that $P_1 > P_S/V_b$, represents the payment at the first-time contracting scheme of rice farmers to collect the rice by the buyer, in which he may introduce a discount rate Z, which will be

counted in the next contract scheme application. This is especially true if the rice farmer has an immoral reputation, and will cheat the first time, then his payoff is high as $P_s - C_{DI,}$ yet this also induces the buyer to confirm the type of rice farmer. Now, if at the next contracting scheme, the rice farmer will choose to be honest after considering the behavior of the buyer, then $- C_{DI} < - C_{HI.}$

The total payoff of the rice farmers is:

$X_1 = (P_s - C_{DI}) (1+Z) + (-C_{HI})$

Considering the case when the seller of immoral reputation first tries to hide his type to gain the credibility of the buyer, in order to garner more profits in the following contract scheme, then the strategy of the buyer is (Contract deal, Contract deal), and the total payoff of the rice farmer is:

$X_2 = (P_s - C - C_{HI}) (1+Z) + (P_s - C_{DI})$

When the rice farmer chooses to not cheat at the first deal contract, then $X_2 > X_{1,}$ and we have:

$X_2 - X_1 = (C_{DI} - C - C_{HI}) (1+Z) + (P_s + C_{HI} - C_{DI}) > 0,$

then the threshold value ψ_I of rice farmer with immoral reputation when deciding which strategy to take is:

$$\psi_I = \frac{P_S - C}{C + C_{HI} - C_{DI}}$$

We could also calculate the corresponding threshold value ψ_R of the rice farmer with a respectable reputation when he decides which strategy to follow.

From the assumption that $C_{DR} - C_{HR} > C_{DI} - C_{HI}$, we could conclude that $\psi_R > \psi_I$. As long as there exists one $\psi_I > \psi$, whatever the type, the rice farmer will choose to be honest in order to gain long term profit.

DISCUSSION

The study inferred that the rice farmer in contract farming practices has the incentive to maintain his reputation in order to gain more profits in the future. That also accounts for the reasons that the rice farmer will invest more to improve the customer's service level, caring about the quality of product and the comments of finished contractor customer, to keep a longer farmer-buyer relationship. If a farmer has to continue with contractual rice production and marketing relations, this will depend on his attitude and reputation. Bad behavior reflects a bad reputation and has an effect on the survival of the contractual relationship. These results confirm Bartling et al. (2008) study. The author explores in his study how an agent's record, that is, his performance with other principals in the past, affects the actual and optimal design of contracts in one-shot interactions; and have shown that information about past behavior can have a crucial effect on optimal contract design.

Jackson and Kalai (1998), in the study titled "False reputation in a society of players", lead to the conclusion that the agents can observe the play in all previous periods. This would mean that previous behaviors in a previous relationship are determinative in future decisions and the preservation of trust. Kim and Park (2013) concluded in their study that only good reputation can win the trust of buyers. According to these two authors, trust had significant effects on purchase and word-of-mouth intentions; and depends on the reputation of agricultural companies. The rice farmer in contract farming practices has the incentive to maintain his reputation to preserve the trust of the buyers.

Conclusion

As there is lack of a well-designed evaluation system targeted at the contract farming practice market, the problem of the moral hazard cannot be avoided or resolved. The integrity between trade partners is the basis of contract item, so it is necessary to appeal to all partners participating in contract farming, both buyers and rice farmer, as well as the government, to work methodically to push for the development of an evaluation system based on reputation to connect the profits of farmers with their reputations, and to increase the cost of irregular actions in the contract farming practice market. The rice farmer in contract farming practices has the incentive to maintain his reputation in order to gain more profits in the future and this means that contract farming can be developed in Benin with great success.

CONFLICTS OF INTEREST

The authors have not declared any conflict of interests.

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Sorption-desorption isotherms of diuron alone and in a mixture in soils with different physico-chemical properties

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Herbicide mixture is a widely used weed control practice in many agricultural areas. However, interactions between the herbicide mixture and soil may alter the soil dynamics. This research evaluated the effect of the physicochemical properties of the soils in the application of diuron alone and in a mixture with hexazinone, by means of sorption-desorption Freundlich isotherms. ^{14}C-diuron sorption (isolated and mixed) was evaluated by batch equilibration at five concentrations of diuron (0.14, 0.16, 0.19, 0.26 and 0.39 µg mL^{-1}) and hexazinone (0.03, 0.06, 0.13, 0.19 and 0.26 µg mL^{-1}), corresponding to the recommended field dose (D) of D/4, D/2, D, 2×D and 4×D, respectively, in five soils cultivated with sugarcane. The sorption of the diuron applied separately and in mixture presented Freundlich sorption coefficient (K_f) values in the range of 1.47 to 5.08 and 0.59 to 3.77 µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}, respectively. The lowest desorption values were found for Clay-1 soil (72.5% clay), with 6.01 and 5.87% for diuron isolated and blended, respectively. Diuron sorption was slightly higher when applied alone rather than in the herbicide mixture, and this sorption correlated positively with the clay content of the soils, regardless of the application form. The disponibility of diuron improved in mixture of hexazinone in soil, which can increase its absorption and control efficiency; on the other hand, the transport of herbicide can rise. Future researches about the transport, runoff or leaching are required for complete information of the behavior of this mixture of herbicides in soil.

Key words: Retention process, sorption kinetics, hysteresis, commercial mixture.

INTRODUCTION

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is a non-ionic, phenylurea herbicide, moderately persistent ($t_{1/2}$ = 75.5 days) and with low water solubility (42 mg L^{-1} at 25°C) (Giacomazzi and Cochet, 2004; PPDB, 2018). It is

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recommended for the control of eudicotyledons and dicotyledons in pre- and post-emergence of weeds, with registration for pineapple, cotton, coffee, sugarcane and citrus crops (Rodrigues and Almeida, 2011). As a non-ionic herbicide, diuron remains in its molecular formula in soil solution (Rocha et al., 2013). When applied in isolation, its sorption is influenced by the organic carbon (OC) content of the soil, being moderately hydrophobic (Alva and Singh, 1990; Ahangar et al., 2008). However, when the soil has higher OC than clay contents, the contributions of the mineral surfaces in the sorption of the diuron can be masked, because the herbicide has a relatively greater sorption affinity for the organic fraction than the mineral fractions in the sorption (Green and Karickhoff, 1990).

The retention of herbicides in the soil is a process influenced by the physicochemical properties of the herbicide and the soil, such as texture, pH, cation exchange capacity (CEC), OC content, among others. The sorption of the herbicide molecules present in the soil solution to the active parts of the soil particles is one of the most important processes of the herbicide behavior in the soil, as it limits the transport by leaching and volatilization (Cáceres-Jensen et al., 2013). However, the herbicide-soil interaction may interfere with the microbial biodegradation processes and the bioavailability of herbicides to be absorbed by plants (Smernik and Kookana, 2015).

The sorption process depends on the accessible surface of the soil particle and the sorption characteristics, which involve chemical and physical bonding of the herbicide molecule to the surface of the soil colloids (Cáceres-Jensen et al., 2013). For a better understanding of this process, several sorption studies have been performed with diuron applied alone. For example, Wang and Keller (2009) found that clay fractions K_f (Freundlich sorption coefficient) and K_{foc} (organic-C normalized K_f value) were, respectively, 18.0 and 6.9 times higher for diuron, in relation to sand fractions, as clay content increased in the soils studied, due to the increased K_f values in clayey soils. Rocha et al. (2013) observed high correlations of diuron sorption with OC and soil CEC, where K_f values varied by 8.53 times more for the soil with the higher versus lower OC contents. Inoue et al. (2008) found low mobility for the isolated diuron (precipitation up to 40 mm), which was associated with the highest clay content (56%) and low OC (1.6%). However, the application of diuron in a mixture may exhibit distinct behavior in the soil when compared with the isolated molecule (Sousa et al., 2018).

When in mixture, the herbicides can present competitive sorption (Martins and Mermoud, 1998; Pateiro-Moure et al., 2010); it is possible to have effective additivity, synergism and antagonism (Bonfleur et al., 2015) or behavior in soil similar to when herbicides are applied alone (Mendes et al., 2016a). This information is incomplete in literature, because of the complex interactions of herbicides in soil. So, many studies are realized with the herbicides alone. However, few studies have considered the interaction of the diuron mixture with other herbicides and their influence on soil sorption. The current research evaluates the effect of the physicochemical properties of soils and the application of diuron (isolated and in a mixture with hexazinone) on the sorption-desorption Freundlich isotherms.

MATERIALS AND METHODS

Soil

The five soil types used in the experiments were collected in sugarcane fields in the region of Piracicaba, São Paulo, Brazil, at Iracema farms, from 0.00 to 0.10 m deep layer, with a pre-cleaning layer of vegetation covering the soil. The soil samples were air-dried, sieved on a 1.7-mm mesh and stored at room temperature in labeled plastic bags. The main physicochemical properties of the soils are shown in Table 1.

Herbicide

The radiolabeled diuron herbicide (phenyl-14-C(U)) (DuPont, Wilmington, DE, USA) showed a radiochemical purity of 98.7% and specific activity of 2.43 MBq mg^{-1}. For non-radiolabeled hexazinone herbicide (DuPont), the chemical purity was 99.5%.

Sorption-desorption studies

The method was established according to the OECD-106 standard 'adsorption-desorption using a batch equilibrium method' (OECD, 2000). Five concentrations of diuron (0.14, 0.16, 0.19, 0.26 and 0.39 µg mL^{-1}) and hexazinone (0.03, 0.06, 0.13, 0.19 and 0.26 µg mL^{-1}) were used, corresponding to a recommended dose (D) of field of D/4, D/2, D, 2×D and 4×D, respectively. Each experimental unit consisted of a 50 mL Teflon tube with a screw cap, in duplicates. Aliquots of 5 g soil were weighed in duplicate in the tubes and 10 mL of 0.01 mol L^{-1} $CaCl_2$ was added resulting in a soil-solution ratio of 1:2 (m v^{-1}). In the sorption studies, 120 µL aliquots of radiolabeled solutions containing ^{14}C-diuron isolated and with hexazinone non-radiolabeled (analytical standard) were transferred to separate vials containing 10 mL of the scintillation solution for the determination of the initial concentration, to be used later in the Teflon tubes. The initial concentration of ^{14}C-herbicides was determined after 15 min, by liquid scintillation counting (LSC) with a Tri-Carb 2910 TR LSA counter (LSA PerkinElmer, Waltham, MA, USA).

In duplicate, 10 mL of the radiolabeled concentrations of all solutions were added to the Teflon tubes containing 5 g of soil samples. The tubes were agitated in a horizontal tabletop shaker in a dark room (20 ± 2°C) for 24 h to achieve the equilibrium concentration (data not shown). At the equilibration concentration, the tubes were centrifuged (Hitachi CF16RXII centrifuge, Hitachi Koki Co., Ltd., Indaiatuba, SP, Brazil) at 755 *g* for 15 min, and 1 mL aliquots of the supernatant from each tube were transferred in duplicate, to scintillation vials containing 10 mL of the scintillation solution. LSC analysis was then performed to determine the concentration of the ^{14}C-herbicides solution, by counting the radioactivity. The amount of herbicide sorption was calculated, using the difference between the initial concentration and the concentration in the supernatant after equilibration (Mendes et al., 2017).

Desorption studies were performed immediately after sorption,

Table 1. Physicochemical properties and geographical coordinates of the sugarcane areas of soils used in the studies in Piracicaba, São Paulo, Brazil.

Property	Soil classification - symbols*				
	Clay-1	**Clay-2**	**Loam-1**	**Loam-2**	**Sand**
Texture	Clay	Clay	Loamy sand	Loamy sand	Sand loam
Sand (%)	18.2	12.2	58.2	56.1	88.6
Clay (%)	72.9	75.4	30.2	32.7	10.1
Silt (g %)	8.9	12.4	11.6	11.2	13.0
pH ($CaCl_2$)	5.09	4.45	5.93	5.11	4.96
P (mg dm^{-3})	60	24	19	6	20
S (mg dm^{-3})	19	79	7	11	4
K ($mmol_c$ dm^{-3})	6.4	3.1	1.4	2.2	0.4
Ca ($mmol_c$ dm^{-3})	32	28	78	23	16
Mg ($mmol_c$ dm^{-3})	28	26	60	14	6
Al ($mmol_c$ dm^{-3})	0.01	1	0.01	0.01	1
H+Al ($mmol_c$ dm^{-3})	38	71	9	23	22
SB ($mmol_c$ dm^{-3})	66.4	57.1	139.4	39.2	22.4
CEC ($mmol_c$ dm^{-3})	104.4	127.8	148.3	62.6	44.4
V (%)	64	45	94	63	50
OC (%)	1.8	1.0	1.2	1.6	2.0
Latitude (S)	22°34'58.8"	22°35'49.2"	22°42'15"	22°41'19.8"	22°14'21.6"
Longitude (W)	47°33'58.8"	47°35'15.6"	47°32'16.8"	47°31'57"	47°43'6"
Altitude (m)	623	601	533	521	860

*According to Soil Taxonomy and Brazilian Soil Science Society (EMBRAPA, 2013). Latossolo Vermelho eutrófico (Clay-1) [Oxisol Typic Hapludox], Latossolo Vermelho Amarelo distrófico (Clay-2) [Oxisol Typic Hapludox], Nitossolo Háplico eutrófico (Loam-1) [Nitosol Eutrophic], Argissolo Vermelho Amarelo eutrófico (Loam-2) [Udult soil] and Neossolo Quartzarenico órtico (Sand) [Typic Quartzipsaments]. BS: sum of bases; CEC: cation extend capacity; V: base saturation; OC: organic carbon.
Source: Department of Soil Science – ESALQ/USP, Piracicaba, SP, Brazil.

under the same conditions. Such that, $CaCl_2$ solution (10 mL, 0.01 mol L^{-1}) was added to the Teflon tubes containing the soil and the radiolabeled herbicide sorbed from the sorption experiment. The tubes were agitated in a horizontal tabletop shaker in a dark room (20 ± 2°C) for 24 h to reach the equilibrium concentration. After re-equilibration, the tubes were centrifuged. Then, 1 mL aliquots of the supernatant were pipetted in duplicate to scintillation vials containing 10 mL of the scintillation solution, before analysis by LSC. The desorbed amount was calculated as the difference between the radioactivity sorbed in the soil and the remaining supernatant (Mendes et al., 2017).

Sorption-desorption model

Sorption coefficients, K_f and 1/n, were calculated from the slope and intercept of the Freundlich equation: $C_s = K_f \times C_e^{1/n}$; where C_s is the concentration (mg g^{-1}) of herbicide sorbed onto the soil after equilibration; K_f is the Freundlich equilibrium constant (µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1}); C_e is the herbicide concentration (mg L^{-1}) after equilibration, and 1/n is the degree of linearity of the isotherm. The equilibrium constant K_{foc} sorption standard for the OC content of the soil was adjusted by using the following equation: $K_{foc} = (K_f/(\%OC)) \times 100$. The desorption coefficients, K_f and 1/n, were determined in a similar way to the sorption coefficients, using a plot of the amount of the remaining chemical sorbed at desorption versus the equilibrium concentration. The hysteresis coefficient (H) for the sorption-desorption isotherms was calculated according to the following equation: $H = (1/n_{desorption})/(1/n_{sorption})$, where $1/n_{sorption}$ and $1/n_{desorption}$ are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively (Barriuso et al., 1994).

Statistical analysis

The non-linear regressions of sorption and desorption of diuron isolated and mixed were adjusted by the Freundlich models, as described previously. Pearson's correlations (*r*) were evaluated for the K_f values of the herbicide in both forms of application with the physical and chemical properties of the five soils, and only the clay content showed a significant correlation with the K_f when compared with the t test ($p < 0.01$, $n = 5$). Figures were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software, Inc., Point Richmond, CA, USA).

RESULTS AND DISCUSSION

Sorption isotherms of diuron alone and mixture

The Freundlich equation adequately described the sorption of diuron alone and when mixed with hexazinone ($R^2 \geq 0.94$). The K_f values of diuron ranged from 1.47 to 5.08 µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} when isolated and 0.59 to 3.77 µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} when in mixture with hexazinone, for the same soils (Table 2). The K_{foc} values were between 73.50 and 445.00 and 29.50 and 367.00 µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for the diuron alone and in mixture with hexazinone, respectively. The sorption was increased in soils in 1.56 times for the diuron isolated and 1.64 times for the application of the diuron in mixture, concerning the

Table 2. Freundlich sorption parameters for the diuron alone and a mixture with hexazinone in the five soils with different physico-chemical properties.

Herbicide	Soil[a]	$K_{f\ (sorption)}$ ($\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$)	$K_{foc\ (sorption)}$ ($\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$)	$1/n_{(sorption)}$	R^2	Sorption (%)
Diuron alone	Clay-1	5.08 (4.97-5.18)[b]	282.22 (276.11-287.78)	0.51 ± 0.01[c]	0.97	89.33
	Clay-2	4.45 (4.16-4.71)	445.00 (416.00-471.00)	0.49 ± 0.03	0.98	88.33
	Loam-1	3.00 (2.91-3.09)	250.00 (242.50-257.50)	0.47 ± 0.01	0.99	81.54
	Loam-2	2.74 (2.67-2.79)	171.25 (166.87-174.37)	0.48 ± 0.01	0.99	76.79
	Sand	1.47 (1.28-1.70)	73.50 (64.00-85.00)	0.50 ± 0.05	0.94	56.32
Diuron in a mixture	Clay-1	3.77 (3.72-3.82)	209.44 (206.67-212.22)	0.43 ± 0.01	0.99	88.65
	Clay-2	3.67 (3.58-3.74)	367.00 (358.00-374.00)	0.44 ± 0.01	0.99	87.35
	Loam-1	1.92 (1.90-1.93)	160.00 (158.33-160.83)	0.34 ± 0.01	0.96	79.95
	Loam-2	1.92 (1.85-1.99)	120.00 (115.62-124.37)	0.38 ± 0.02	0.95	75.75
	Sand	0.59 (0.58-0.60)	29.50 (29.00-30.00)	0.16 ± 0.01	0.96	53.99

[a]Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments. [b]Number in parentheses are confidence intervals of the mean, $n = 2$. [c]Mean 1/n value ± standard deviation of the mean.

increase of CO content in soils by 69%, a growing effort for sand soil for clay-1 (Table 1).

The closeness of the K_f values indicated similarity in the sorption between the forms of application of the herbicide diuron, isolated or in mixture with hexazinone, considering the conditions of the present study. In corroboration with this results, Mendes et al. (2016a) also did not find differences between the application modes (alone and in mixtures), for the mesotrione mixture with S-metolachlor + terbuthylazine. Correlating the retention of herbicides with soil leaching, Reis et al. (2017) noted the application mode of diuron (alone and in combination with sulfometuron-methyl + hexazinone) did not influence diuron mobility along the soil, proving the herbicide presented low mobility in the soils. Furthermore, the soil texture had no impact on diuron leaching. However, higher percentages of the diuron in mixture with hexazinone than diuron applied alone were found in the leachate in the clayey soil. On the other hands, when in combination with the same mixture (diuron in mixture with sulfometuron-methyl + hexazinone), Mendes et al. (2016b) noted negligible diuron in the leachate (0.19%), due to the higher affinity with OC present in the upper layers of the profile of a dystrophic "Argissolo Vermelho-Amarelo distrófico - PVAd" (Yellow Red Argisol-Oxisol) (0.52% OC and 81.6% clay).

The sorption of diuron applied isolated was 56.32% for soil with low clay content (10.1%) and reached 89.33% when in soil with high clay content (72.9%) (Table 2). For the mixed diuron, the results were similar but relatively slightly lower, presenting sorption of 53.99% for the sand and 88.65% for the Clay-1. These data are in agreement with the results found for the K_f values, described earlier. On the other hand, Sousa et al. (2018), studying the sorption of the diuron alone and in combination with the hexazinone, found that the mixture had on average twice the sorption with respect to the diuron alone. The same authors state that the sorption variations of these herbicides when mixed may be related to soil OC quality, so that being that material of origin, decomposition and structure of the organic matter of the soil can exert different influences on the sorption of herbicides. The addition of organic compounds to the soil in the research of Sousa et al. (2018) may increase the retention capacity of these herbicides when mixed, differing from the present study.

The $1/n_{sorption}$ values were lower than 0.51 and 0.44 for the application of diuron alone and mixture with hexazinone, respectively; this indicated an L-type isotherm ($1/n < 1$), with a non-linear and concave slope relative to the abscissa (Giles et al., 1960) as shown in Figure 1. Then, the sorption rate decreased with increasing herbicide concentration, where this increase in herbicide concentration in the soil solution reduced the availability of the sorption sites. Chaplain et al. (2008), Rocha et al. (2013) and Giori et al. (2014) also found a similar L sorption isotherm trend for the diuron applied alone, indicating the influence of soil sorption sites filling with diuron sorption.

Correlation of diuron (isolated and in a mixture) sorption with soil physicochemical properties

Among the physicochemical properties of the studied soils, only the clay content was positively correlated with the K_f of diuron sorption in both forms of application (Figure 2). Thus, with a 10% increase in the clay content of the soil, the K_f values were increased by 1.67 $\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ for the diuron alone and by 0.77 $\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ for the diuron in a mixture with hexazinone (Figure 2). The sorption values for the diuron alone were slightly

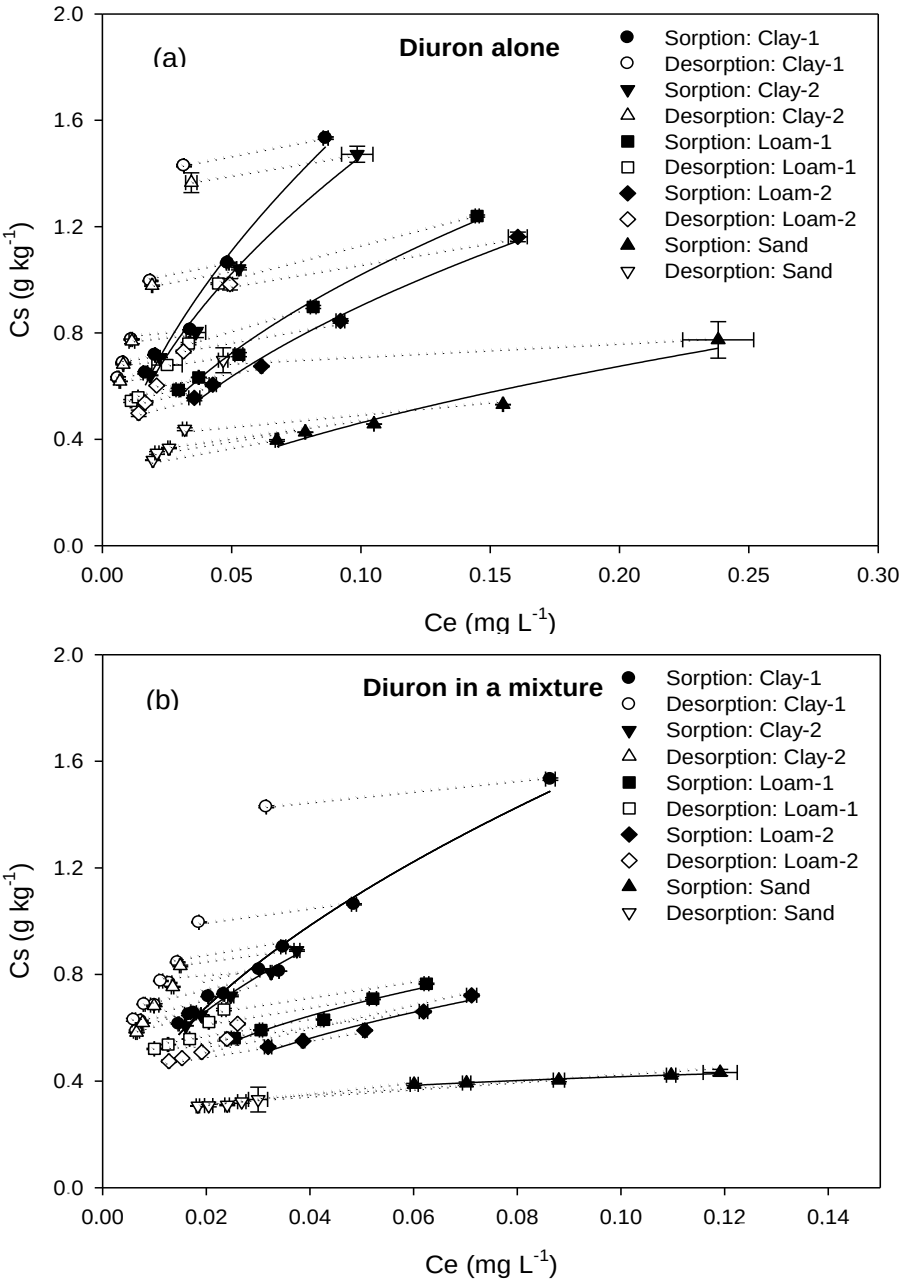

Figure 1. Freundlich sorption (●, ▼, ■, ♦, and ▲) and desorption (○, Δ, □, ◊, and ▽) isotherms of diuron alone (a) and in a mixture with hexazinone (b) in the five soils with different physico-chemical properties. Error bars represent standard error of the mean (*n* = 2) of Ce (equilibrium concentration) and Cs (soil concentration). Symbols may cover error bars. Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments.

higher than the mixture. This increase in clay content in the soil directly reflects more diuron sorption and may affect the availability of the herbicide in the soil solution. Namely, we believed there could be less herbicide bioavailable for biological degradation, and it be less absorbed by the target plants, reducing weed control efficiency and increasing the persistence of the product in more clayey soils.

The effect of clay content is more pronounced when diuron is applied alone. Fernández-Bayo et al. (2008) also found a positive correlation between the clay content and the specific surface area of the soils studied with diuron sorption. Sorption of diuron may be proportional to the number of active sites in the soil. This behavior may

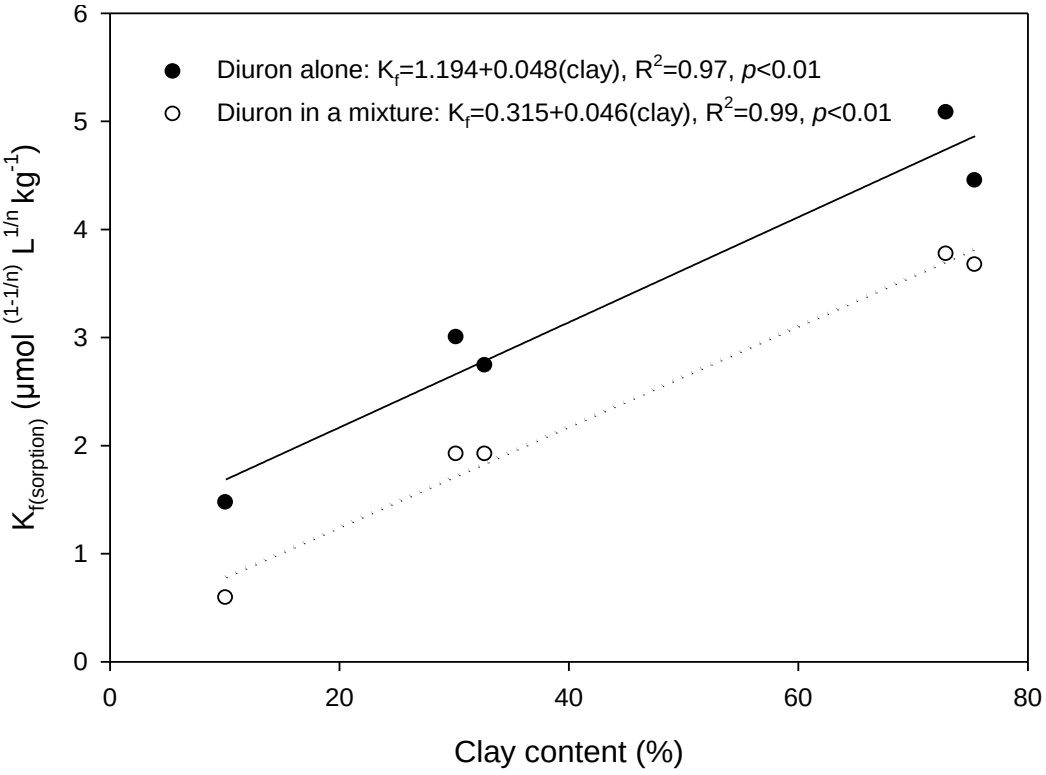

Figure 2. Relationship between the Freundlich sorption coefficient - K_f (µmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) mean of diuron applied alone and in a mixture with hexazinone, and the clay content (%) of five soils with different physicochemical properties.

explain the diuron sorption, which, due to its polarity, potentially binds to clay minerals sites; the greater the area of contact with the soil, the higher the sorption capacity. According to Oliveira and Reginato (2009), these adsorptive forces are highly relevant to herbicides with low solubility and polarity, such as diuron, and are also characterized by interactions of intermolecular forces, such as van der Waals and non-ionizable H bridges (neutral).

Several studies noted a positive correlation between diuron sorption and OC content in soils (Ahangar et al., 2008; Liu et al., 2010; Umali et al., 2012; Cáceres-Jensen et al., 2013). This fact is related to the low solubility of the herbicide and the greater affinity of the molecule with the hydrophobic compounds (Chaplain et al., 2008). For hydrophobic compounds, such as diuron, sorption is more influenced by organic compounds when the OC content in the soil is greater than 2.0% (Reddy and Gambrell, 1987). Like in the present study, soils presented a variation in the CO content between 1.0 and 2.0%, indicating that in this range the CO content of the soils had little effect on the sorption of the diuron alone and in the mixture. However, for diuron alone, Giori et al. (2014) found a correlation between herbicide sorption and soil OC (0.76-2.6%), as well as Sousa et al. (2018), who verified a correlation of diuron sorption both alone and in mixture with hexazinone, considering a greater range of OC (1.46-27.77%). This indicates that the type of organic material present in the soil can alter the retention dynamics of the herbicides in the soil, whether isolated or mixed. The sorption of diuron can also be correlated with the pH, due to the polarity of the molecule, despite being a non-ionic herbicide (Rodrigues and Almeida, 2011; Rocha et al., 2013). As mentioned by Chaplain et al. (2008), when there is a correlation between sorption and pH, K_f increases as the pH decreases, as also found by Liu et al. (2010) and Araujo and Melo (2012). However, in the pH range of arable soils, such as in this study (pH 4.45-5.93), in sugarcane cultivation areas for this soil property, there was no correlation with sorption.

Desorption isotherms of diuron alone and in mixture

The K_f values for diuron desorption ranged from 3.13 (Loam-1) to 9.47 µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (Sand) when applied alone and from 4.42 (Clay-1) to 7.22 µmol$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (Sand) in a mixture (Table 3). Therefore, the behavior of diuron in soils, regarding the application forms, corroborated the sorption data. For desorption of the isolated diuron and mixture, the Freundlich's isotherms were suitable (R^2 > 0.87) (Table 3). In both application modes, the $1/n_{desorption}$ values were less than 1, indicating

Table 3. Freundlich desorption parameters and hysteresis coefficient (H) for the diuron alone and a mixture with hexazinone in the five soils with different physicochemical properties.

Herbicide	Soil[a]	$K_{f\ (desorption)}$	$K_{foc\ (desorption)}$	1/n (desorption)	R^2	H	Desorption (%)
		($\mu mol^{(1-1/n)} L^{1/n} kg^{-1}$)					
Diuron alone	Clay-1	7.45 (7.16-7.71)[b]	413.89 (397.78-428.33)	0.49 ± 0.01[c]	0.96	0.96	6.01
	Clay-2	6.66 (6.21-7.09)	666.00 (621.00-709.00)	0.47 ± 0.01	0.99	0.96	6.24
	Loam-1	3.13 (3.08-3.16)	260.83 (256.67-263.33)	0.40 ± 0.01	0.93	0.85	9.34
	Loam-2	4.79 (4.65-4.90)	299.37 (290.62-306.25)	0.53 ± 0.01	0.99	1.10	11.57
	Sand	9.17 (8.55-9.68)	458.50 (427.50-484.00)	0.86 ± 0.02	0.95	1.72	16.01
Diuron in a mixture	Clay-1	4.97 (4.62-5.22)	276.11 (256.67-290.00)	0.42 ± 0.02	0.97	0.98	5.87
	Clay-2	4.42 (4.33-4.49)	442.00 (433.00-449.00)	0.40 ± 0.01	0.98	0.91	6.60
	Loam-1	1.87 (1.83-1.91)	155.83 (152.50-159.17)	0.28 ± 0.01	0.90	0.82	10.13
	Loam-2	2.02 (1.98-2.05)	126.25 (123.75-128.12)	0.34 ± 0.01	0.89	0.89	12.13
	Sand	7.22 (7.05-7.38)	361.00 (352.50-369.00)	0.21 ± 0.02	0.87	1.17	17.39

[a]Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments. [b]Number in parentheses are confidence intervals of the mean, $n = 2$. [c]Mean 1/n value ± standard deviation of the mean.

L type isotherms, as also observed for the sorption. The desorption history values (H < 1) were lower than the sorption. Namely, less herbicide returned to the soil solution (Figure 1), as likewise found in some soils studied by Liu et al. (2010). However, in the present study there was more desorption of the diuron when applied in isolation (H > 1) to the Loam-2 and Sand soils, as well as in Sand with the diuron in mixture with hexazinone, respectively, when compared with the other soils. Such behavior was possibly due to the low soil CEC (44.4 for Sand and 62.6 $mmol_c\ dm^{-3}$ for Loam-2) relative to the other soils tested, thereby having fewer sorption sites for herbicide retention.

In general, there was an increase of 10.00 and 11.52% in the desorption of the diuron isolated and in the mixture, respectively, when the soil profile was changed from Clay-1 soil to sand (Table 3). That is, in soils with comparatively higher clay content, less herbicide returned to the soil solution, with 6.01% desorption for diuron isolated and 5.87% for diuron mixture, in the soil Clay-1. These data confirm a correlation of the clay content with diuron sorption, where the clay proportion was 72.9% for Clay-1 and 10.1% for sand, respectively. In this sense, Rocha et al. (2013) found elevated diuron desorption values in "*Latossolos vermelhos"* with low clay content (27%) and OC (0.8%), which can be attributed to the poor interaction of herbicide with a soil surface.

Conclusion

Diuron sorption was similar when isolated compared to the application of the herbicide in the mixture (Table 2).

For soils with comparatively high clay content and low OC content, the clay fraction had a marked influence on diuron sorption. The desorption of diuron was most pronounced in soils with relatively low clay content, for both forms of application. The application of this herbicide may not affect the transport through leaching, due to the little effect on the retention process. The results of this study contribute to the information regarding the positive correlation between diuron retention and soil clay fraction. In this context, knowledge of the physical and chemical properties of the soil is essential before recommending this herbicide in weed management. Therefore, regardless of the mode of application, in soils with low OC content the availability of herbicides in the control of dying plants can be higher than in soils with high OC content. In this same sense, soils with higher clay content can retain more diuron isolated and in mixture, interfering in the control dynamics of these herbicides in the soil. Herbicide transport studies, such as surface runoff, are encouraged to complement the retention findings, especially in the tropical soil conditions, with various rainfall indices, and for a widely used herbicide, such as diuron.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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