



UNIVERSITÀ DEGLI STUDI DI PADOVA

Department of Agronomy Food Natural Resources Animals
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Second Cycle Degree (MSc) In Sustainable Agriculture

**Mulching and soil organic amendments: Effect on the adsorption-
desorption of herbicides**

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1. ABSTRACT

Conservative tillage practices and application of organic amendments to soil improves its fertility and its present and future agronomic value. These practices increase the organic matter content in soil and can modify its physical, chemical, biological and hydrological properties (OM, bulk density, soil structure, porosity, etc.). Consequently, they can modify the behaviour and environmental fate of herbicides in soil. In this thesis project we studied the adsorption-desorption of three herbicides (S-metolachlor, foramsulfuron, and thien carbazono-methyl) on wheat straw mulch at three different decomposition rate (M1, M2 and M3) and size particle (M1 crop residue milled (MM1)), and in two soils non-amended (S1 and S2) and amended with MM1 (S1+MM1 and S2+MM1) as well as the properties of herbicides, mulches and soils that effected the adsorption-desorption of these compounds. Adsorption-desorption isotherms were obtained by the batch equilibrium technique and fitted to Freundlich model. The K_f values for S-metolachlor ($1.3 < K_f < 65.8$) increased in the order: $S1 < S2 < S1+MM1 < S2+MM1 \ll MM1 < M1 < M2 < M3$ according to the increase in OC and/or DOC content of the adsorbents. This order was the same as observed for foramsulfuron ($0 < K_f < 34.3$) except on MM1. The adsorption of thien carbazono-methyl ($0.01 < K_f < 1.10$) increased in the order: $S1 \sim S1+MM1 < S2 < S2 + MM1 = M3 < M2 \sim M1 < MM1$. The desorption K_{fd} values varied between 3.39 and 65.1 for S-metolachlor, 0 – 26.3 for foramsulfuron, and 0.19 - 7.65 for thien carbazono-methyl. In general, K_{fd} values were higher for mulches than for soils (unamended and amended). CO and COD play an important role in adsorption-desorption of the 3 compounds; however, CO was the most important variable controlling the K_f , K_{fd} , of S-metolachlor, K_d of foramsulfuron and K_f of thien carbazono-methyl. DOC was the one that controlled the desorption K_{fd} of the thien carbazono-methyl.

2. INTRODUCTION

For decades, man has produced food through a system dominated by growing the same crops year after year, by using large quantity of chemical pesticides and fertilizers. Application of these compounds to crop increases its production, however, it also carries several dangers. Excess uses of pesticides may result in a series of problems related to both loss of their effectiveness in the long run and certain externalities like pollution (soil, water and air) and human health hazards, it also increases the production cost (Sabur and Molla 2001).

In many places around the world, the soil has already suffered long-term damage, and water resources are often overused or polluted by fertilizers and pesticides (Silva et al. 2019) (Li et al. 2014) (Herrero-Hernández et al. 2017) (Sousa et al. 2018) (Robson R.M. Barizon et al. 2020). These negative effects have heightened awareness of the fact that agriculture does more than produce food, animal feed and energy, it also impacts the climate and the health of the ecosystem. In some parts of the world, a growing number of innovative farmers are taking a different path, moving toward a farming system that is more sustainable — environmentally, economically and socially (<https://yali.state.gov/sustainable-farming-practices-and-efficient-resource-management/>).

Some of sustainable practices need for the food production and preservation of the ecological system are minimal use of fertilizers and pesticides, application of organic amendments to soil, mulching, cover crops, rotating crops, integrated pest management, reduced or eliminating tillage. These practices increase the soil productivity while minimizing harmful effect on the climate. The application of organic residues to soil as organic amendments has been proposed as alternative for mineral fertilizers (Luo et al. 2018). Among the organic residues applied to soil as organic amendments are from agriculture (crop residues, straw, green compost), livestock (manure and slurry), urban waste and agro-industrial activities (wine, beer, mushroom cultivation). On the other hand, many research papers have identified several benefits of conservation tillage with respect to soil physical, chemical and biological properties as well as crop yield (Gil-Ribes et al. 2017) (FAO 2016) (Gabriel et al. 2019) (Trail et al. 2016) (Thierfelder, Matemba-Mutasa, and Rusinamhodzi 2015). Cover crops have also been shown to increase crop yields, increase soil organic matter (OM) content, prevent leaching of nutrients, attract pollinators, etc. Reduced or no tillage, crop residue

management, direct sowing, and crop rotation are the pillars of conservation tillage (FAO 2016).

However, it should be also highlighted that the application of pesticides to soil under these sustainable practices might modify the dynamics of these compounds in the soil and consequently their environmental fate (Alletto et al. 2010) (Carpio et al. 2021) being it object of study in this thesis.

2.1. Pesticides

Pesticides are the chemicals (natural or synthetic) employed in agriculture to control pests, weeds and diseases in plants. Nearly 45% of the yearly food production is lost due to pest infestation. Because of loss, effective pest management by using wide range of pesticides is needed to reduce pest and to speed up the crop production (Sharma et al. 2019). It is generally accepted that pesticides play an important role in agriculture development because they can reduce the losses of agriculture products and improve the affordable yield and quality of crops (Tudi et al. 2021). Due to emergency to increase the food production and control insect borne diseases, to reduce malnutrition, the development of pesticides increased during the Second World War. Worldwide pesticide production increased at a rate of about 11% per year, from 0.2 million tons in the 1950s to more than 5 million tons by 2000. Currently, three billion kilograms of pesticides are used worldwide every year (Tudi et al. 2021). Asia continent occupies first place in percentage of pesticides used in world with 52.8% followed by America with 30% and Europe stands in third place with 13.7% (Figure 1). While 1% of pesticides are effectively used to control insect pests on target plant, the large amount of remaining pesticides contamination has polluted the environment and caused negative impacts on human health (Ivanova et al. 2016) Pesticides are classified attending different terms such as chemical classes, functional groups, modes of action, and toxicity. However, the most common classification of pesticides is focused on the target pest, including fungicides, insecticides, herbicides, rodenticides, acaricides, bactericides, molluscicides, etc. For example, fungicides are used to combat against fungi, insecticides against insects, herbicides are used to kill weeds, etc. (Tudi et al. 2021). At European level, the use of fungicides and bactericides, accounted for the most proportion of total pesticides (46%) in 2016, seconded by herbicides, haulm destructors and moss killers (29%) and followed by

insecticides and acaricides (11%), and other plant protection products (14%) (Figure 2, data shown is received from the 20 EU member states).

Pesticides (total) + (Total) by continent,
Average 1990 - 2019

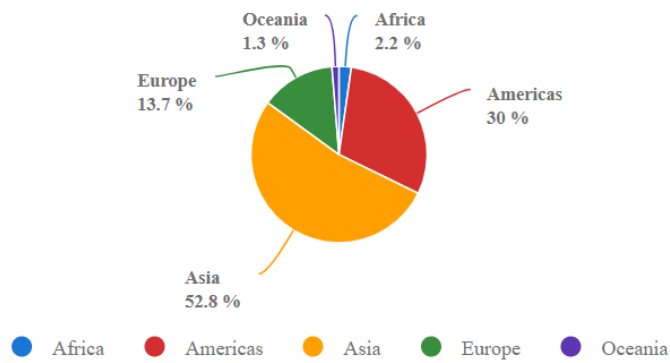


Figure 1. Percentage of pesticides used around the world by continent wise
(Source : www.fao.org/faostat)

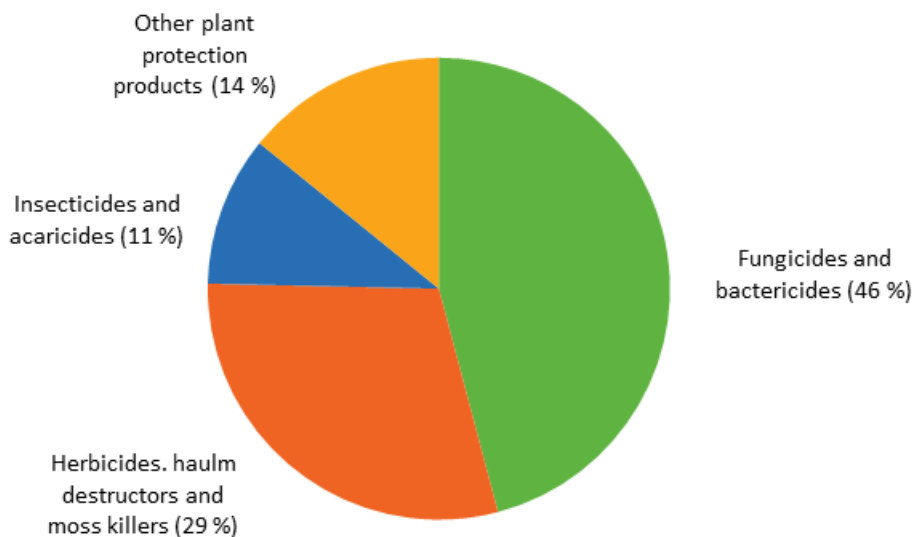


Figure 2. Percentage of total volume pesticides sales by category (2016) (Source: <https://ec.europa.eu/eurostat/web/products-eurostat-news/-/DDN-20181015-1>)

The experimental part of this memory has been carried out by using compounds with herbicide activity. Herbicides are cheap, efficient and easily available, the chemicals used for

combating the weeds or inhibiting their growth. There is a wide range of compounds with herbicide application, some of these compounds have inorganic composition (e.g., arsenic acid, borax, copper sulfate, etc.) while other have an organic composition (e.g., butachlor, alachlor, paraquat, diquat, diuron, nitralin, 2,4-D, etc.). Some of them have a selective mode of action (e.g. propanil, EPTC, 2,4-D, etc.) while others are non-selective (e.g. paraquat, glyphosate, sulphuric acid, sodium arsenate, etc.) (Kaur et al. 2019). In this memory, three are the target herbicides: S-metolachlor, foramsulfuron and thiencazone-methyl. These three compounds are used in control of weeds in maize, the main crop of the present experiment carried out at laboratory scale within a project set up at field scale (See Materials and Methods Section).

2.2. Pesticide behaviour in the environment

When pesticides are applied to a target plant or soil, they have the capacity to enter into the environment. On entering into the environment, pesticides may undergo three main processes that control the behaviour and fate of pesticides in the soil: accumulation, elimination, transfer or movement (Figure 3) (Singh 2012).

1. Processes responsible for the **accumulation** of pesticides in soil: This type of processes implies the passage between two media without undergoing any chemical transformation allowing the pesticide to retain the function for which it was designed. Within this group are the **adsorption-desorption** processes (objective of this memory).
2. Processes responsible for the **elimination** of pesticides in soil: They are photochemical, chemical or biological processes that involve a transformation of these compounds giving place others with different function, toxicity and behaviour than the originals. Within these processes are the **degradation** phenomena (non-objective of this memory).
3. Processes responsible for the **movement** of pesticides in soil: Like the accumulation processes do not involve any chemical transformation of the pesticide, but they differ in significant displacement type of process of the pesticide relative to its initial position. Within these processes are the phenomena of **leaching, runoff and volatilization** (non-objective of this memory).

These processes depend in turn on the physio-chemical properties of the soil and pesticides as well as on environmental factors (Marín Benito 2011).

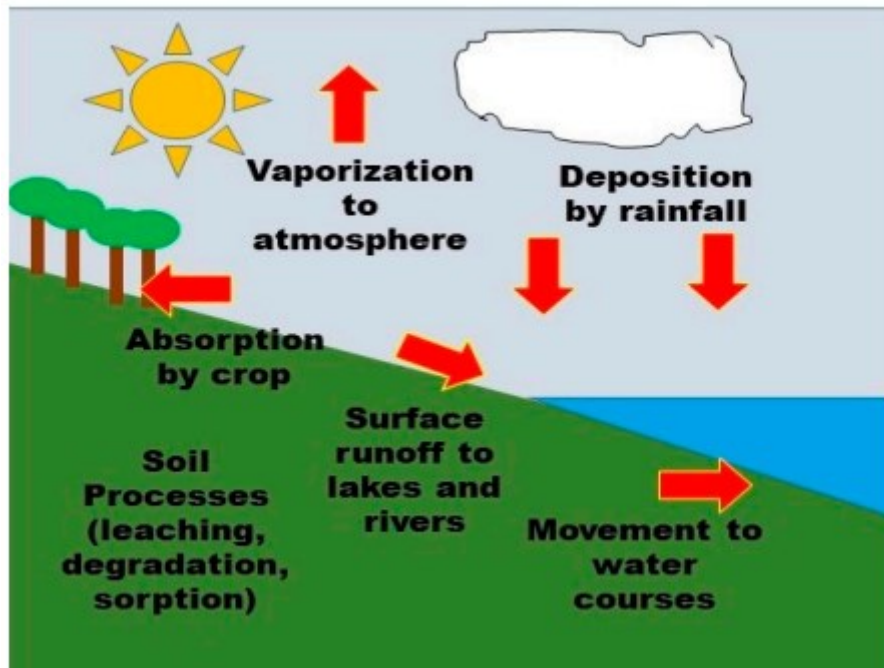


Figure 3. Pesticide behaviour in the natural environment (Tudi *et al.* 2021)

2.2.1 Accumulation processes: *Adsorption*

It is a physicochemical process that largely governs the environment fate of pesticides in the soil (Gavrilescu 2005). It is a process by which the molecules of a solute (adsorbate) pass from the aqueous phase to the surface of a solid that acts as a sorbent (adsorbent) (Calvet 1989). In this case, the pesticide molecule would be the adsorbate and the soil particles those of the adsorbent. Adsorption is closely related to the specific surface and to the physicochemical properties of the soil particles and consequently to their size. When pesticides are used, only a small scale of applied pesticides plays a defensive role to fight against plant diseases. In contrast, excess of pesticides penetrates into the soil, resulting severe soil and water pollution.

Soil adsorption process depends on various factors including the physicochemical soil properties (mainly structure, humidity, texture, pH, clay and organic matter contents) (Kah and Brown 2007), pesticide characteristics (solubility in water, hydrophobicity, polarity, etc.) and external forces (temperature, rainfall, agriculture practices, etc.) (Gavrilescu 2005). Adsorption occurs because of an attraction between the pesticide and soil components. The adsorption interactions of pesticide in soil may involve either the mineral or organic

components of soil or both. In soils that have high organic matter (OM) levels (>5%), pesticides adsorption depends mainly on organic matter content with the nature of organic matter having generally little influence on the adsorption process (Marín-Benito, Andrades, et al. 2012) (Djurovic et al. 2009). In soils with low organic matter contents, the adsorption of pesticides often depends on active components of the inorganic fraction, which is predominantly the clay fraction. An increase in clay content results in increasing adsorption of some pesticides (Djurovic et al. 2009). Non-polar compounds are mainly adsorbed by hydrophobic partitioning, so OM content is generally the dominant soil parameter determining their adsorption (Gavrilescu 2005). Typically, organic-soluble pesticides are more attracted to clay particles and to organic matter in soil than water-soluble pesticides. Pesticides molecules with positive charge are more tightly adsorbed to negatively charged soil particles. A pesticide that adsorbs to soil particles is less likely to move from the application site than a chemical that does not adsorb tightly to the soil (Pesticide characteristics-UF/IFAS EDIS). In contrast, pesticides that are highly soluble in water dissolve easily in this mean. Such pesticides are not strongly adsorbed on soil being more likely their movement in soil surface by runoff or through the soil dissolved in water than less-soluble pesticides. The climatic factors that influence the adsorption of organic compounds in soils are the temperature and moisture content of the soil linked to the rainfall events. It is often assumed that adsorption is an exothermic process, whereby an increase in temperature leads to decreased adsorption and increased desorption rates (Pierzynski et al. 2020), whilst the soil moisture content affects to the pesticides' adsorption through their solubility in water previously explained.

2.2.2 Accumulation processes: *Desorption*

Desorption process is the phenomenon through which the adsorbate is released from the surface of the adsorbent. The mechanism of desorption of the compound will depend mainly on the adsorption energy. The higher this energy, the more difficult will be the desorption of the pesticide and vice-versa. So, we can speak of a reversible adsorption and an irreversible adsorption to a greater or lesser degree depending on whether there is a total or partial desorption of the adsorbed molecules, respectively (Silburn 2020). The adsorption-desorption process is considered of great interest among all the processes involved in the evolution of pesticide in the soil mentioned above, since they directly or indirectly influence

the magnitude and effect of all of them by conditioning the amount of pesticide available in the soil. It is easy to understand, therefore that adsorption hinders leaching, volatilization and even biodegradation by microorganisms, since they cannot degrade the pesticide if it is not bioavailable. It has been shown that substrates that are not accessible to microorganisms are not attacked or attacked more slowly (Marín Benito 2011). While, on the contrary, desorption favours these processes to occur.

2.3. Agriculture practices and its influence on pesticides' behaviour

As previously cited, soil and pesticide characteristics play a key role in the behaviour of pesticides in soil. This memory pays additional and special attention to the influence of external parameters related to the agriculture practices in the main processes that control the dynamics of pesticides in soil (adsorption-desorption processes).

2.3.1. Tillage and no-tillage practices

Cultivation is defined as 'the tilling of land', 'the raising of a crop by tillage' or 'to loosen or break up soil'. Other terms include 'improvement or increase in (soil) fertility'. All these definitions indicate that cultivation is synonymous with tillage or ploughing. Cultivation (tillage) is a practice that has been introduced from Europe to other countries by farming pioneers. The principle of cultivation is to turn the soil into a fine tilth to provide the ideal environment for seeds to germinate. Cultivation was also a traditional form of weed control.

Tillage is used to soften the soil and prepare a seedbed that allowed seed to be placed easily at a suitable depth into moist soil using seed drills or manual equipment. This results in good uniform seed germination. Wherever crops grow, weeds also grow and compete for light, water and nutrients. Every gram of resource used by the weed is one less gram for the crop. By tilling their fields, farmers are able to shift the advantage from the weed to the crop and allow the crop to grow without competition early in its growth cycle with resulting higher yield, with the help of soil nutrients and minerals required for the growth of the crop are released by exposure of organic matters to air. Incorporating previous year crop residues into the soil help the release and available of soil amendments to the root.

The collective conservation tillage includes direct drilling, no-tillage, minimum tillage/ ridge tillage, each practice includes specific relation to conservation goal of some nature. Usually, covering 30% of soil surface by residues defines the lower limit of classification for conservation tillage, but influences the other conservation objectives that include

conservation of time, fuel, earthworms, soil water, soil structure and nutrients. This shows that residue levels alone do not appropriately describe all conservation tillage practices (Santel 2012).

In conservation tillage practice, there is an increase in soil organic matter in the soil surface, emission of greenhouse gases such as CO₂ is reduced, decreases the soil loss from wind and water erosion, increase the water infiltration rate and reduces the evaporation, it promotes soil aggregation, increases the soil water and nutrient holding capacity (FAO characterized). Closely related to conservation tillage practices are the concepts of cover crops and mulching (Busari et al. 2015).

Cover crops

Cover crops reduces erosion, increases soil nutrients and moisture availability, and helps to regulate the pest, weeds and brings a host of other benefits to fields. Cover crops play a major role in chemical properties effected by soil carbon content such as soil pH, cation exchange capacity, availability of nutrients, buffering capacity and in physical properties as soil structure, soil aggregation is improved. It also includes economic benefits like reduces the production cost, cut fertilizer cost (for example, legume cover crops boost atmospheric nitrogen fixation and cut the N fertilizer need for succeeding cover crop), reduce the need for herbicides and other pesticides, increase profits and even create new source of income protect water quality, help safeguard personal health conserve soil health and their benefits accumulate over a long term (González-Sánchez et al. 2017). Cover crop purposely not grown for market purposes, but ploughed under and incorporated into the soil, at that moment these cover crop may be referred as green manure crops, sometimes these cover crops are also called as catch crops, by using appropriate herbicides on cover crops are killed on the soil surface before they mature (Kaye and Quemada 2017).

Mulching

Mulching is defined as the practice of covering upper layer of soil with materials to minimize the loss of moisture, balance the soil temperature mainly in the root zone and maintains the evaporation loss. An important function of the mulching is to minimize the first stage of drying that helps to obtain minimum moisture status, cools the soil, also reduces the seedling mortality and improves the crop stand. Mulch is also used for various purposes to control

weed growth, reduces the wind and water erosion, increases soil fertility, protect the plant from insect pest and disease attack, maintain soil thermal throughout the cropping season and increases the crop production. Plastic-film and crop residues are the most common materials used as mulching in agriculture (Ghouse 2020). Crop residue mulching is easy to handle and defined as technology at least 30% of the soil surface is covered with crop residues (organic matter) of the previous crop at the time of crop emergence, chopping of the crop residue is required and applied in thin layers of 8 -10 depth and suitable for medium duration crop. Straw mulching is one of the most popular methods among the farmers because of its low cost, easy availability and soil friendly.



Figure 4. Plastic-film mulching (left) and straw mulching (right) type in maize cultivation (Ghouse 2020)

Effect of conservation tillage practices in pesticides' behaviour

It is widely studied the behaviour of pesticides in soil under conventional tillage practices being less known the impact in this behaviour of the previously cited conservation agricultural practices. Conservation tillage systems may prompt significant changes in physicochemical and hydraulic soil properties, soil temperature and humidity, the abundance of faunal and microbial populations and biological activity, etc., directly or indirectly affecting the behaviour of pesticides in the soil over time (Lionel et al. 2010). Figure 5 explains about the main changes in soil tillage properties due to tillage practices and their effect on the mechanisms involved in pesticide fate. Cover crop purposely not grown for market purposes, but ploughed under and incorporated into the soil, at that moment these cover crop may be referred as green manure crops, sometimes these cover crops are also called as catch crops, by using

appropriate herbicides on cover crops are killed on the soil surface before they mature (Kaye and Quemada 2017).

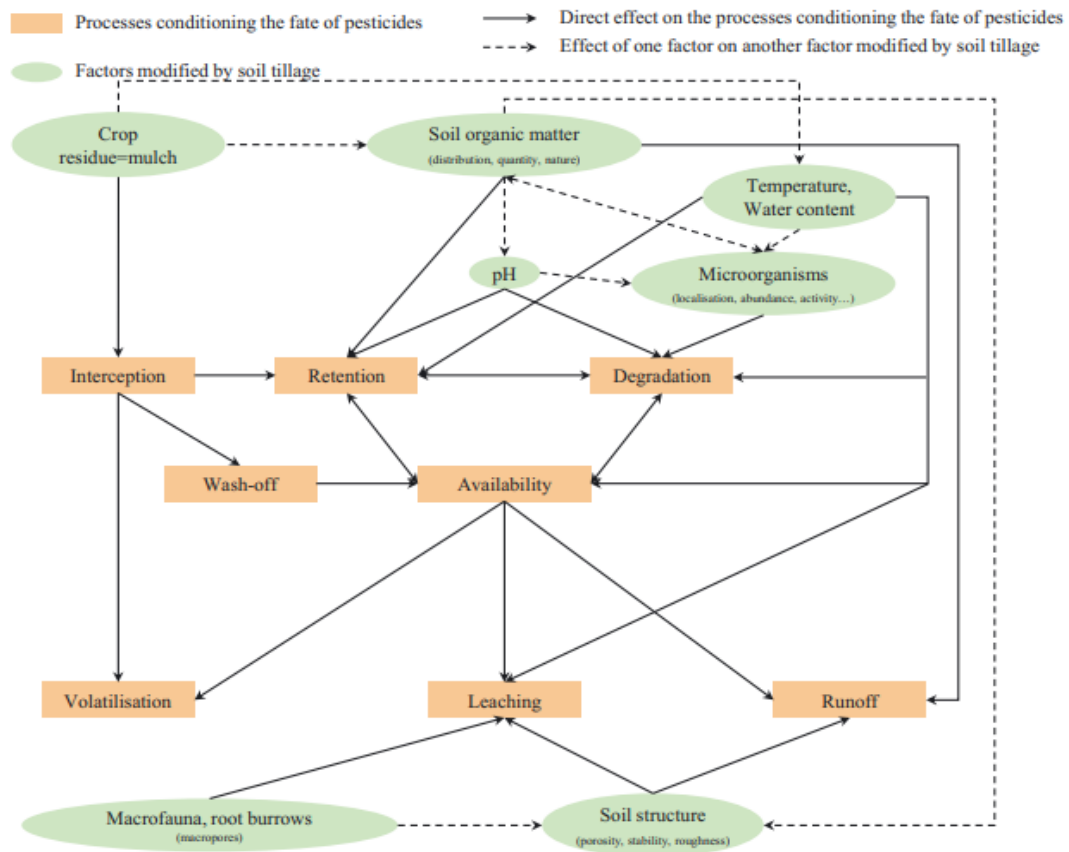


Figure 5. Relationship between the soil factors modified by tillage operations and the processes conditioning the fate of pesticides in soil, water and air.

It is generally expected that conservation tillage systems such as no-tillage improve macropore connectivity. This increases pesticide leaching and is the main drawback of conservation agriculture practices. In turn, mulch is a lignocellulosic material and could modify pesticide leaching in soils by the adsorption-desorption and degradation of these compounds, with these processes depending on mulch evolution and pesticide properties, as indicated for other materials of a similar nature (Amami et al. 2021)(Cassigneul et al. 2018)(Aslam et al. 2013) (Cassigneul et al. 2016) .Therefore, a better understanding of the adsorption-desorption processes of pesticides is called for in conservation tillage systems. It

is especially important for herbicides that play a key role in controlling the weeds competing with crops for soil resources because no mechanical destruction of weeds is carried out under conservation tillage systems. In this sense, selective and non-selective herbicides are applied to control the weeds for the corresponding crop and chemically eliminate the cover crops, respectively. This memory should be extended wide range to improve our understanding and extrapolate the impact of these conservation agriculture practices on the fate of S-metolachlor, foramsulfuron and thiencazone-methyl.

2.3.2. Application of organic amendments to soil

In modern agriculture, it is very frequent the application of organic amendments to soil to preserve its fertility and its present and future agronomic value. This practice seeks to exploit all the nutrients (micro and macronutrients) that the organic amendments contain, mainly its high OM content, to maintain or raise it in soils with low OM content (<2%). Moreover, these residues improve or maintain the soil's physical and hydrological properties, since they decrease bulk density, increase water-holding capacity, cation exchange capacity, the aggregation and structural stability of the soil, and its global porosity, together with the modification of pore size and connectivity. In addition, organic residues improve gas and water exchange in the soil, the exploratory capacity of plant root systems, and the development of the soil's bacterial flora. All this helps to protect the soil against physical processes such as run-off or erosion, and improve the revegetation of degraded soils (Kranz et al. 2020). On the other hand, some authors have also reported that soil amendments may be considered a way of capturing carbon dioxide from the atmosphere (Spokas et al. 2009) (Zhang et al. 2012).

Effect of organic amendments in pesticide's behaviour

The combined application of pesticides and organic residues in soils modifies the physicochemical behaviour, mainly through their adsorption-desorption by the amended soils (Carpio et al. 2021). Organic amendments increase soil OC content, and this parameter is the most relevant factor influencing the adsorption process and the affinity of hydrophobic pesticides by soils as previously explained in Section 1.2.1 (Zolgharnein et al. 2011).

In this sense, the addition of organic amendments to soil could lead to a greater or lesser degree of pesticide immobilization in the amended soil. This effect has consequences for

pesticide degradation, persistence or mobility, enhancing a pesticide's subsequent chemical, physical, and biological transformation or degradation, decreasing generally its transport through the soil profile, and consequently reducing groundwater pollution in some cases (Marín-Benito et al. 2009; Carpio et al., 2021). However, it could also affect the final concentration bioavailable for absorption by the targeted weeds.

A recent study revealed that 83% of the soils in European Union have been contaminated by one or more residues of pesticides (Silva et al. 2019). The increasing contamination of surface and ground water is probably due to deficient pesticide management, and increase by precipitation and/ or irrigation that give rise to the runoff or leaching process of these compounds through soil (Robson R M Barizon et al. 2020). In this context, numerous references report the ability that organic amendments have to adsorb pesticides having been also assessed frequently the application of organic residues as organic amendments as strategy to control water contamination (Marín Benito et al., 2016).

2.4. Study of pesticide adsorption-desorption processes in soil

One of the most used experimental techniques to evaluate the adsorption of pesticides by soil is the determination of their adsorption isotherm. It establishes the relationship between the amount of the pesticide (adsorbate) (C_s) absorbed by the soil (adsorbent) at different initial concentrations (C_i), and the equilibrium concentration (C_e) in contact with this one at a constant temperature. The amount of adsorbate adsorbed is determined under equilibrium conditions as the difference between the amount initially present in the solution (C_i) and that in the equilibrium solution (C_e) after putting in contact a known amount of adsorbent (m) and a volume (V) of the adsorbate solution of concentration C_i . To calculate the amount absorbed (C_s) per unit mass of adsorbent the following expression is used:

$$C_s = (C_i - C_e) \times \frac{V}{m} \quad [\text{eq. 1}]$$

Giles et al. (1960) classified the adsorption isotherms in water solution in 4 different types according to their geometric shape (Figure 6).

L-type adsorption isotherm (Langmuir): It is characterized by a decreasing slope when adsorbate concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. Such adsorption behaviour could be explained by the high affinity of the

adsorbent for the adsorbate at low concentrations, which then decreases as concentration increases (Ayawei, Ebelegi, and Wankasi 2017).

S-type adsorption isotherm (cooperative adsorption): Initially its slope increases with adsorbate concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled. This type of isotherm indicates that at low concentrations the surface has a low affinity for the adsorbate, which increases at higher concentrations.

C-type adsorption isotherm (partition constant): this type of isotherm occurs when the adsorbent has the same affinity for the solute as for the solvent. It is characterized by the existence of a linear relationship between the amount of solute adsorbed and that in the equilibrium solution at all concentrations. This type of isotherm has been observed in the adsorption of hydrophobic molecules by soils, organic matter or humic acids of the soil (Sánchez et al. 2003, Filipe et al 2009).

H-type adsorption isotherm (high affinity): this type of isotherm occurs when the adsorbent has a high affinity for the solute, so that at low concentrations everything is absorbed and the equilibrium concentration will be close to zero. Once the adsorbent surface is saturated, the excess solute will remain in solution. This results in an isotherm with an initial vertical shape and finally parallel to the axis of concentrations (Hinze 2001).

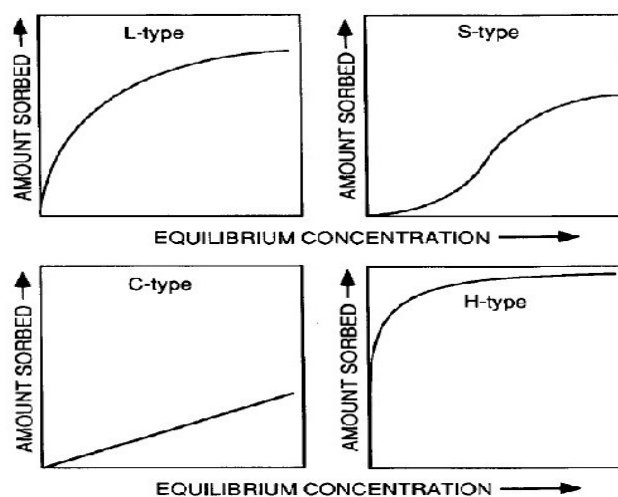


Figure 6. Types of adsorption isotherms according to Giles et al. (1960) classification

Modelling of pesticide adsorption-desorption in soil

There are several models that have been developed for the interpretation of the experimental result of the adsorption isotherms. One of the most used is described by Freundlich isotherm model. It is used to describe heterogeneous surface equations such as the heterogeneity of the adsorbent surface, the adsorption energy and the exponential distribution of the adsorption point. Freundlich isotherm model (Freundlich, 1909) is described by following equation.

$$C_s = K_f C_e^{1/n} \quad [\text{eq. 2}]$$

Where C_s ($\mu\text{g g}^{-1}$) is the amount of pesticide adsorbed per unit mass of adsorbent, C_e ($\mu\text{g mL}^{-1}$) is the equilibrium concentration of the pesticide in solution, and K_f ($\mu\text{g}^{1-nf} \text{mL}^{nf} \text{g}^{-1}$) and n are two characteristic constants of the adsorption capacity of pesticide by the soil that are determined from the equation 2 linearized as follows:

$$\text{Log } C_s = \text{log } K_f + n_{fd} \text{ log } C_e \quad [\text{eq. 3}]$$

The n coefficient is related to the surface heterogeneity and the diversity of the energy's associates with the adsorption reaction. If $1/n > 1$, the sorption process shows cooperative sorption; if $1/n = 1$, Freundlich model is equivalent to linear model indicating low heterogeneity among the sites of the adsorbent if $1/n < 1$, the relative sorption decreases when the concentration increases being it characteristic of an L-type adsorption isotherm (Maqueda et al. 2017)(Aslam et al. 2013). The coefficient K_f is the amount of pesticide adsorbed for a $C_e = 1 \mu\text{g mL}^{-1}$ and represents the adsorption at low concentration level. For higher level of concentration, it is usually determined the distribution coefficient (K_d , mL g^{-1}) as follows assuming that all pesticides removed from the solution is adsorbed by the soil:

$$K_d = C_s / C_e \quad [\text{eq. 4}]$$

Thus, K_d (a partition coefficient) is a ratio of solid phase to solute concentrations in solution at equilibrium conditions. High values of K_d (of the order of 100 or more) indicate that, at any given time, the majority of the pesticides is adsorbed to the soil surface and hence is less likely to move in soil, but it does not indicate the strength (reversibility) of that sorption. The K_d values are often determined over a range of concentrations at a constant temperature.

The desorption of a pesticide previously adsorbed on a soil is studied by successive washing of the soil with water and measuring the concentration of pesticide in the equilibrium solution. Freundlich's model is valid for the interpretation of experimental results of the desorption process in the form of next equation:

$$C_s = K_{fd} C_e^{n_{fd}} \quad [\text{eq. 5}]$$

where C_s ($\mu\text{g g}^{-1}$) is the amount of pesticide that remains adsorbed per unit mass of adsorbent after each desorption, C_e ($\mu\text{g mL}^{-1}$) is the equilibrium concentration of the pesticide in the solution, and K_{fd} ($\mu\text{g}^{1-n_{fd}} \text{mL}^{n_{fd}} \text{g}^{-1}$) and n_{fd} are two constants' characteristic constants of the pesticide desorption process on the soil. Analogously to the adsorption process, the values of these two constants are determined from the linear form of equation 5, which has the following form:

$$\text{Log } C_s = \text{log } K_{fd} + n_{fd} \text{ log } C_e \quad [\text{eq. 6}]$$

The interaction between a pesticide and the soil does not always occur through weak or reversible links, but on the contrary, they are retained by strong and irreversible bonds that prevent complete desorption. When the desorption data do not match those of the adsorption isotherm, the isotherms obtained show hysteresis of the desorption in a greater or lower degree. Due to this non-singularity effect, the desorption curve does not end at the zero-adsorption point when the equilibrium concentration approaches zero, and the effect is an apparent increase in the constant K_{fd} in relation to the constant K_f . Different authors (Sciences n.d.)(Ghezzi et al. 2014) have indicated the irreversibility of the adsorption process of the compound as a potential cause to explain the non-singularity of the adsorption isotherms and have proposed a hysteresis coefficient (H) (Barriuso et al. 1994) as a measure of this irreversibility that is quantified by the expression:

$$H = \frac{n_f}{n_{fd}} \quad [\text{eq. 7}]$$

According to Barriuso et al. (1994), the adsorption is reversible the more similar the constants n_f and n_{fd} are, and the more irreversible the greater n_f with respect to n_{fd} are, speaking of no hysteresis (reversible adsorption) when $n_f / n_{fd} = 1$, positive hysteresis when the n_f / n_{fd} ratio > 1 and negative hysteresis when $n_f / n_{fd} < 1$.

3. OBJECTIVES

The objectives of this study were to assess: i) the adsorption-desorption of three herbicides on wheat straw mulch at different decomposition degree, and in unamended soils and soils amended with this crop residue, and ii) the influence of mulches, soils and herbicides' properties on the adsorption-desorption processes of these compounds.

4. MATERIALS AND METHODS

4.1. Experimental field design

A field experiment was set up on experimental plots of 81 m² located in the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Spain (40°55'56" N latitude and 5°52'53" W longitude). The design consisted of a total 12 experimental plots randomly distributed in 4 treatments, resulting from the combination of 2 tillage systems and 2 different soils (S1 and S2), and each of them with three repetitions. The tillage systems corresponded to a conventional tillage with a cultivator (25-28 cm) (S1+CT and S2+CT) and to the non-tillage of the soil (S1+NT and S2+NT) in a monoculture maize system. The soil is kept bare after maize harvest on plots S1+CT and S2+CT while winter wheat is used as a cover crop on plots S1+NT and S2+NT during the fallow period. Wheat is sown by direct sowing on the maize crop residues, destroyed by glyphosate, cut and deposited on the soil surface covering 65-75% of it before the direct sowing of the new maize cycle.

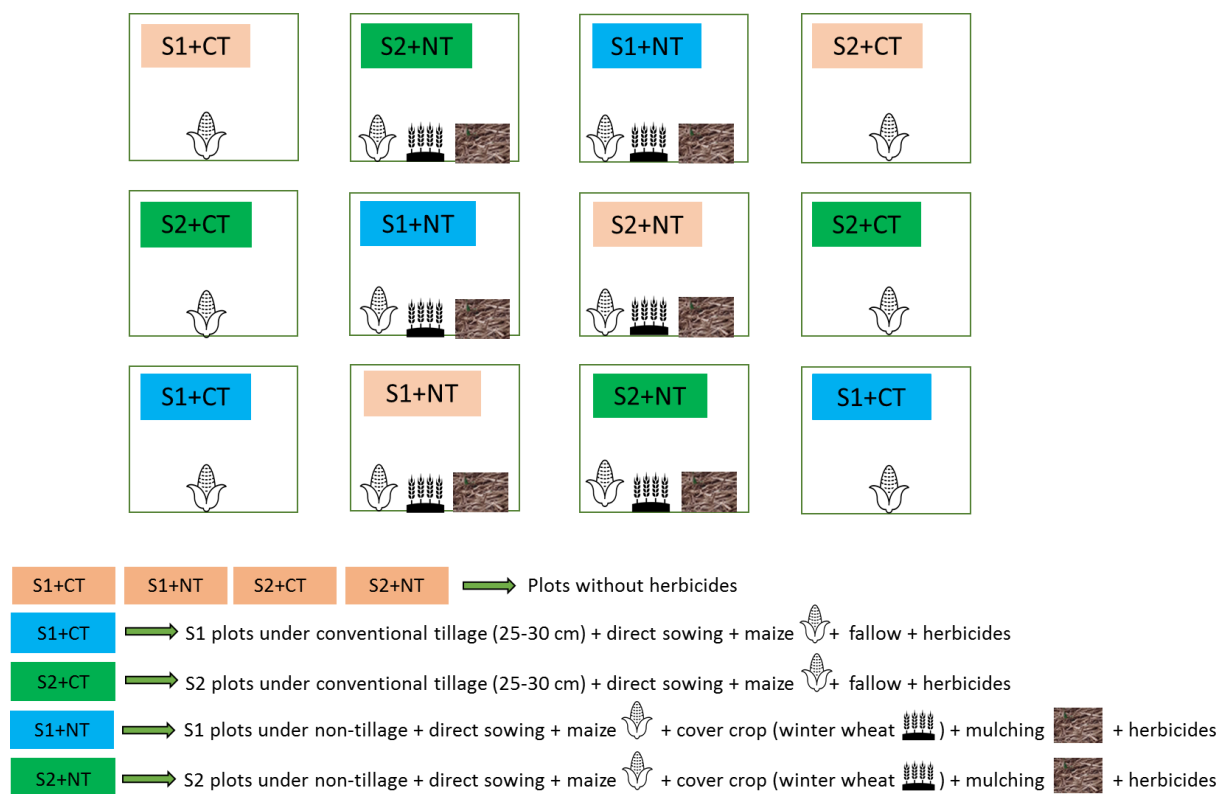


Figure 7. Experimental field design



Figure 8. Muñovela experimental farm belonging to IRNASA-CSIC, maize growing in plots with and without mulch



Figure 9. Direct sowing of the seeds

4.2. Mulches and soils: sampling and processing for herbicides' adsorption-desorption study

The studies of this memory were carried out at laboratory scale by using mulch and soil samples taken from the field experiment. The soil selected to carry out the field experiment was a Eutric-Chromic Cambisol (IUSS Working Group WRB, 2015) with sandy-loam texture (80.4% sand, 4.7% silt, and 14.9% clay). The soil corresponded to a single agriculture soil, but

with different physicochemical surface properties (0-10 cm) resulting therefore two different soils, S1 and S2.

Soil samples (S1 and S2) were collected from the respective experimental field plots at a depth of 0-10 cm before their treatment with any herbicide (Figure 10). Multiple sub – samples (a total amount of 5 kg) of S1 and S2 were taken from the equivalent plots, mixed and homogenized. Then, they were air-dried and sieved (< 2 mm) for the adsorption – desorption study of target herbicides (S-metolachlor, foramsulfuron, and thienencarbazone-methyl) under laboratory conditions

Straw mulch samples were taken from S1+NT and S2+NT plots non-treated with herbicides at three different dates after winter wheat destruction and its deposition on the soil surface (Figure 12). Therefore, mulch samples corresponded to three mulch decomposition degrees. The mulch sampling dates were on 2 June 2020 (just after deposition of mulch on soil surface) (mulch 1, M1), on 8 July 2020 (\approx 1 month after deposition of mulch on soil surface) (mulch 2, M2) and on 18 August 2020 (\approx 2.5 months after deposition of mulch on soil surface) (mulch 3, M3)). Multiple sub-samples (a total amount of 500 g) of each mulch type were collected, mixed, air-dried and cut in pieces of 2-cm length for adsorption-desorption studies. Mulch 1 was also milled (< 1 mm) (MM1) for additional adsorption studies. The amended soils (S1+MM1 and S2+MM1) were prepared by uniformly mixing S1 and S2 with MM1 (10% w/w on dry weight basis). The physicochemical characterization of mulches and soils (unamended and amended) samples was carried out by standard analytical methods (Carpio et al. 2020; Sparks 1996) and it is shown in Table 1. Among the different mulch types, M1 is characterized by the highest dissolved organic carbon (DOC) content compared to the other three mulches whereas MM1 showed the lowest DOC content varying, therefore, in the order $M1 > M2 > M3 > MM1$. M1, M2 and M3 mulches showed a similar organic carbon (OC) content being it lower for MM1. In the case of soils, S2 is characterized by a higher OC and DOC content, N total and pH than S1. The total OC content in the unamended S1 and S2 soils was 0.69% and 1.01%, respectively, and about 9-11.3-fold greater in amended than in non-amended soils (S1 and S2). Moreover, the DOC content was higher in S1+MM1 (5.81%) and S2+MM1 (5.96%) than in S1 (0.140%) and S2 (0.144%). Soils pH varied between 5.85 (S2+MM1) and 7.67 (S2).

Table 1. Main characteristics of mulches, unamended and MM1-amended soils

Sample	pH	OC (%)	N (%)	C/N	DOC (mg/g)
M1	5.38±0.04	44.57±0.05	1.21±0.03	36.78±0.78	125±3
M2	5.43±0.02	44.11±0.26	1.56±0.06	28.29±0.90	114±4
M3	6.09±0.07	44.52±0.06	1.53±0.02	29.12±0.48	66.0±1.4
MM1	6.49±0.05	41.69±0.11	2.22±0.03	18.78±0.18	55.8±17.5
S1	6.81±0.13	0.69±0.02	0.09±0.00	7.93±0.17	0.140±0.026
S2	7.67±0.09	1.01±0.06	0.12±0.01	8.27±0.30	0.144±0.013
S1+MM1	6.15±0.09	6.26±0.31	0.13±0.01	47.19±1.8	5.81±0.10
S2+MM1	5.85±0.09	11.43±0.96	0.14±0.01	79.63±2.5	5.96±0.25



Figure 10. Soil sample collected from the field



Figure 11. Soil 1 (left) and soil 2 (right)



Figure 12. Mulch samples (M1, M2 and M3) collected from the field at different dates (different decomposition degree)

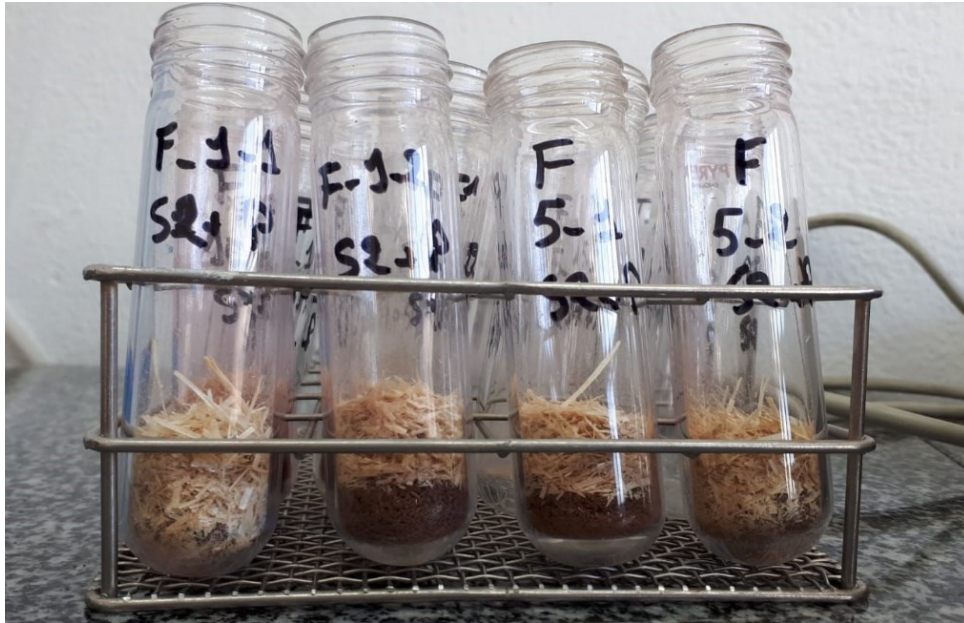


Figure 13. Soil + mulch samples

4.3. Herbicides

Studies included in this memory were carried out with the analytical standard of the herbicides S-metolachlor, thien carbazono-methyl and foramsulfuron (>98.5% purity) supplied by Sigma Aldrich Química S.A (Madrid).

S-metolachlor

Metolachlor was registered with the EPA in 1976. Metolachlor is a pre-emergent, selective herbicide used for general weed control in many agricultural food and feed crops (primarily maize, soybeans and sorghum), and on lawns and turf, ornamental plants, trees, shrubs and vines, rights of way, fencerows and hedgerows, and in forestry (Table 2). S-metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(2S)-1-methoxypropan-2-yl] acetamide) is a favourable alternative to metolachlor, physical and chemical equivalent to metolachlor but it is enriched with the S-isomer that increases its herbicidal activity in susceptible plants.

Table 2: Dose of S-metolachlor 960 applied as pre- and post-emergence

Timing	Weeds controlled	Dose/ha
Pre-plant surface (up to 30 days before planting)	Annual grasses, broadleaf perennial weeds	1.19-1.67 L
Pre-plant incorporated	Nutsedge, annual grasses and broadleaf weeds.	1.19-1.67 L
Pre-emergent	Annual grasses, broadleaf weeds including triazine tolerant weeds	1.19-1.67 L
Early Post Emergent (spike to 2-leaf stage)	Annual grasses and broadleaf Weeds including triazine tolerant weeds	1.19 – 1.67 L
Post- Emergent (3 to 6-leaf stage) (hybrid and silage corn only)	Annual grasses and broadleaf weeds including triazine tolerant weeds	1.19 – 1.67 L

Chemical formula of S-metolachlor is $C_{15}H_{22}ClNO_2$ and its molecular weight is 283.8 (Figure 14). It is a liquid that is white to tan in colour. S-metolachlor has a vapor pressure of 3.7 mPa at 20°C, a boiling point and a melting point of 334°C and -61.1°C, respectively.

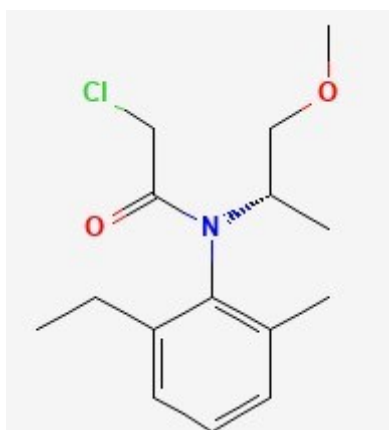


Figure 14. Chemical structure of S-metolachlor

S-metolachlor is a non-ionic compound with a relatively high solubility in water (480 mg L⁻¹ at 20°C) and it is classified as moderately leachable this herbicide frequently found on the surface and ground water (US EPA – Pesticides – Fact Sheet for Metolachlor). Its adsorption

and desorption do not show pH sensitivity (PPDB, 2021). The organic matter content is the main soil property that controls S-metolachlor adsorption process with K_f and K_{foc} values of 3.63 mL g^{-1} and 200.2 mL g^{-1} , respectively. The half-life (DT_{50}) value of S-metolachlor has estimated range from 10 to 221 days under laboratory conditions and from 3.55 to 55.7 days in field conditions (PPDB, 2021). Ground application is the most common use method of this herbicide, although aerial and chemirrigation application methods also are permitted.

Foramsulfuron

Foramsulfuron (1-(4,6-dimethoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl)-5-formamidophenylsulfonyl]-urea) is a post-emergence sulfonylurea herbicide for the control of a large number of grass species and certain broadleaf weeds in maize. Foramsulfuron has the chemical formula of $C_{17}H_{20}N_6O_7S$ and a molecular weight of 452.4 (Figure 15), melting point at 194.5°C and decomposes before boiling. It is a yellow-brownish solid, fine-grained granule with weak aromatic odour. Foramsulfuron has a vapour pressure of $4.20 \times 10^{-9} \text{ mPa}$ at 20°C , its solubility in water (g L^{-1} at 20°C) depends on the pH: 0.037 (pH 5), 3.293 (pH 7) or 94.577 (pH 8).

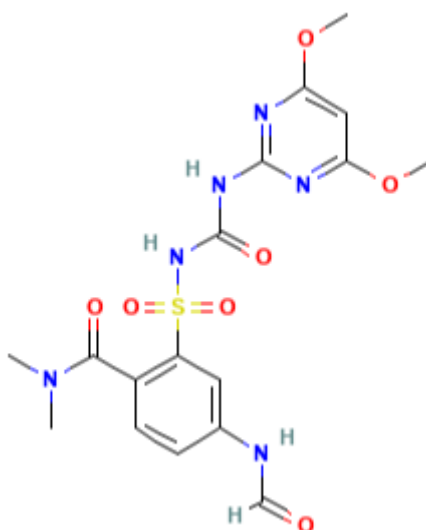


Figure 15. Chemical structure of foramsulfuron

Foramsulfuron at an application rate of 30-40 g ha, offers a minimum of 90% weed control on most grassy weeds, and a wide selection of broadleaf weed species, foramsulfuron is expected to have very high mobility based upon an estimated K_{oc} of 10. Sulfonylurea

herbicides, such as foramsulfuron, are more mobile in soils with lower organic matter and soils with pH > 8.5 (alkaline soils). Considering the moist soil surface, volatilization is not expected to be an important fate process based upon an estimated Henry's Law constant of $5.7 \times 10^{-12} \text{ Pa m}^3 \text{ mol}^{-1}$. Foramsulfuron is stable to photolysis in soil and water, if released into water, foramsulfuron is not expected to adsorb to suspended solids and sediment based upon the estimated K_{oc} . Foramsulfuron has a reported DT_{50} value of 25.4 days at typical conditions and 25.5 days at 20°C in laboratory conditions (PPDB, 2021).

Thiencarbazone-methyl

Thiencarbazone-methyl is an herbicide applied for the selective control of grasses and broadleaf weeds primarily in maize. The active ingredient belongs to the chemical class of sulfonyl-amino-carbonyl-triazolinones and acts as an inhibitor of the ALS-enzyme (Acetolactase synthesis). The compound can be applied at the pre-emergence and the post-emergence timing (Figure 16). The use rate depends on the application timing and may vary from 22 – 45 g a.i. ha⁻¹ in pre-emergence applications and 10 – 15 g a.i. ha⁻¹ in post-emergence applications (Santel 2012). Sequential treatments are possible as long as the maximum seasonal dose of 45 g a.i. ha⁻¹ is not exceeded.

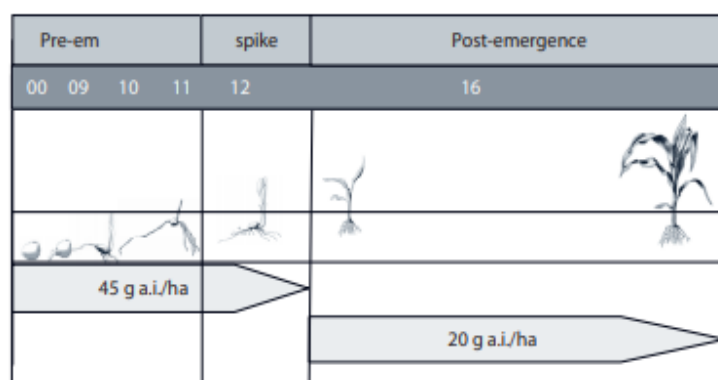


Figure 16. Crop development stages, application timings and maximum use rate of thiencarbazone-methyl in maize

Thiencarbazone-methyl has the chemical formula of $C_{12}H_{14}N_4O_7S_2$ and a molecular weight of 390.4 (Figure 17). The melting point of the compound is 205°C and it decomposes before boiling. It has a vapour pressure of $8.8 \times 10^{-11} \text{ mPa}$ at 20°C, its solubility in water is 436 mg L⁻¹.

The DT₅₀ value of thien carbazone-methyl is about 11.6 days at typical conditions and its range is between 51.5 and 55 days at 20°C under laboratory conditions. Thien carbazone-methyl is stable to photolysis in soil and water. If released into water, thien carbazone-methyl is not expected to adsorb to suspended solids and sediment based upon the estimated K_{oc} is 100 mL g⁻¹ (US EPA- Pesticides- Fact Sheet).

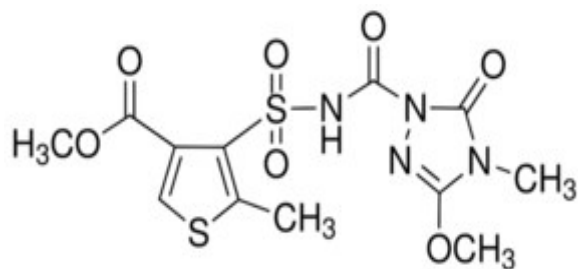


Figure 17. Chemical structure of thien carbazone-methyl

Thien carbazone-methyl obtained its first registration 2008 in Romania and then was registered in important maize producing countries of Europe and other parts of the world. This herbicide controls weeds through by inhibiting photosynthesis in the target plant. It disrupts membranes and inhibits photosynthesis in plants by blocking the ALS enzyme which is necessary for plant growth. Thien carbazone-methyl is taken up into the plant through the roots. Plants that do happen to emerge from the soil, die after being exposed to sunlight. It also works on foliar contact causing rapid desiccation.

4.4. Adsorption-desorption experiment

Adsorption experiment

Adsorption-desorption isotherms of herbicides by the mulch at different decomposition degrees (M1, M2, and M3) size particle (milled M1, MM1), and by the unamended (S1 and S2) and MM1-amended soils (S1+MM1 and S2+MM1) were obtained using the batch equilibrium technique. Duplicate dry mulch samples of 0.1 g or soil samples of 5 g were equilibrated with 10 mL of a Milli-Q ultrapure water solution of each herbicide at concentrations of 1, 5, 10, 15, 20 and 25 mg L⁻¹. The suspensions were agitated at 24.0 ± 0.1°C for 24h in a thermostatted chamber with intermittent shaking for 2 h at 3 h intervals.

Preliminary experiments revealed that contact for 24 h was long enough for equilibrium to be reached. The suspensions were subsequently centrifuged at 5045 g for 30-40 min, and the equilibrium concentrations of herbicide were detected by mass detector coupled high performance liquid chromatography (HPLC-MS) (see section 3.6). The amount of herbicide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. Calculations were based on the assumption that no degradation of herbicides occurred during the adsorption studies. Distribution coefficients (K_d) were also determined.

Desorption experiment

The desorption isotherms of the herbicides were studied in mulch and soil samples initially treated with 25 mg L⁻¹ solutions of each herbicide during the adsorption study in four sequential withdraw-replace steps. In each desorption step, after adsorption equilibrium had been reached, a 5 mL aliquot was withdrawn from the solution and immediately replaced by 5 mL of Milli-Q water. The resuspended samples were shaken as indicated above, after which the suspensions were centrifuged and the desorbed herbicide was calculated as the difference between that initially adsorbed and the amounts desorbed measured by HPLC-MS (see section 3.6).

Preparation of solutions (Stock solution and standard solutions)

An individual stock solution of 1000 mg L⁻¹ of each herbicide (S-metolachlor, foramsulfuron and thien carbazon-methyl) was prepared in methanol. These stock solutions were used to prepare four intermediate aqueous solutions of 50 (one per herbicide) and 20 mg L⁻¹ (one containing the 3 herbicides). Aqueous solutions of 1, 5, 10, 15, 20, and 25 mg L⁻¹ of each herbicide were prepared from the corresponding 50 mg L⁻¹ intermediate solution to be directly applied to the mulches, unamended or amended soils. Standard solutions of 0.01, 0.05, 0.1, 0.25, 0.75, 1 and 2 mg L⁻¹ were prepared from the combined 20 mg L⁻¹ intermediate solution to build the calibration curve for the quantitative determination of herbicides. The standard solutions were prepared in the corresponding aqueous matrix (M1, M2, M3, MM1, S1, S2, S1+MM1, or S2+MM1) previously prepared to avoid the matrix effect in the quantification process.

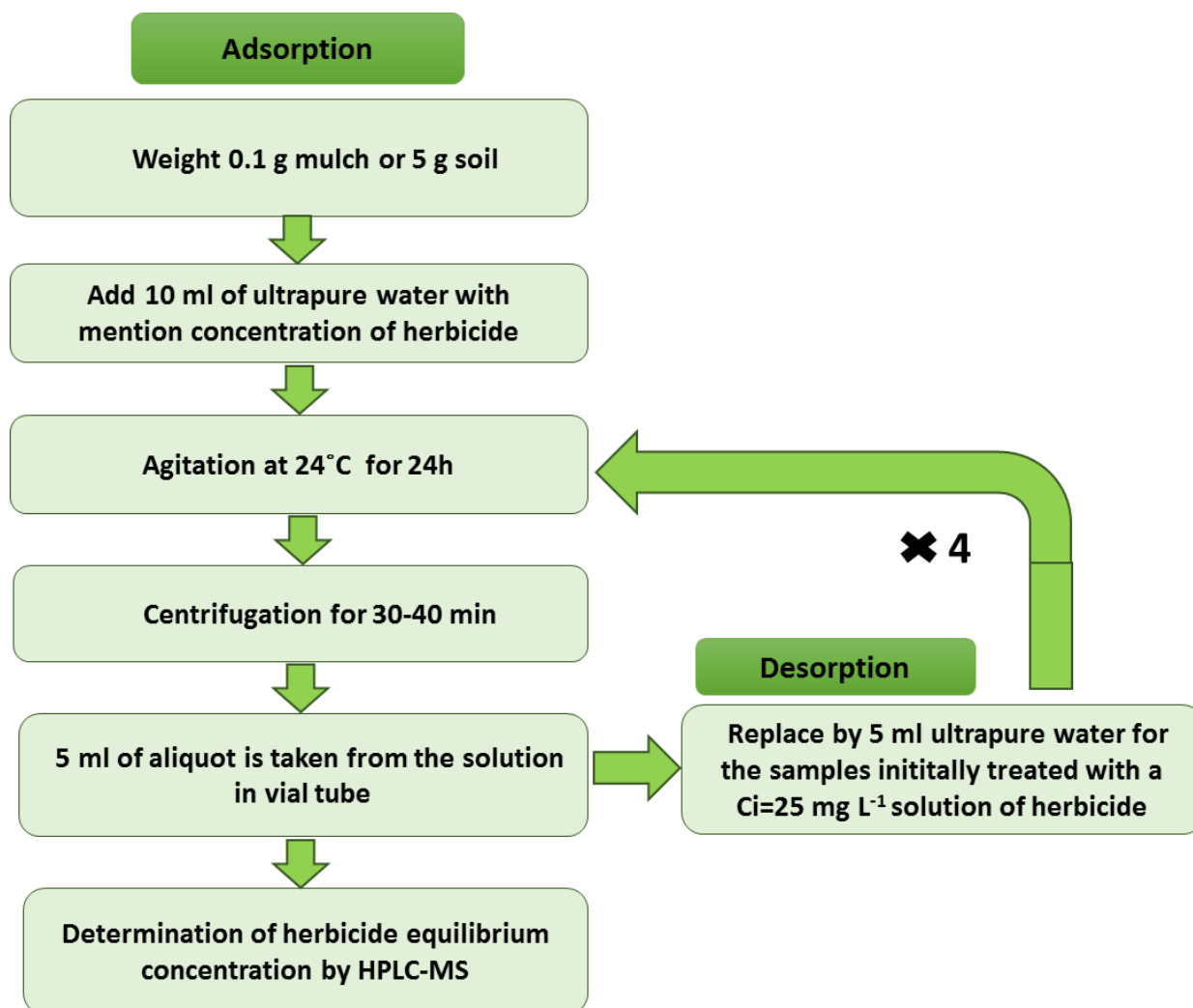


Figure 18. Schematic representation of the adsorption-desorption experiment

4.5. Analytical determination of herbicides

Herbicides were quantified by using a Waters HPLC-MS (Waters Assoc., Milford, USA) (Figure 19). The separation column used was a Phenomenex Luna PFP2 of 150 mm × 4.6 mm id, and 3 μm of particle size. The mobile phase used for the optimal separation and quantification of the three herbicides was methanol: water + 5mM ammonium formiate (80:20). The mobile phase flow rate was 0.4 mL min⁻¹, the cone voltage was 20V for the three herbicides and the injection volume was 20 μL. Herbicide determination was carried out by monitoring the corresponding positive molecular ion (m/z) [M+H⁺] 284.79 (S-metolachlor), 391.39

(thiencarbazono-methyl), and 453.44 (foramsulfuron). Under these measurement conditions, the retention times of foramsulfuron, thiencarbazono-methyl and S-metolachlor were 3.8, 5.6 and 11.3 min, respectively (Figure 20).



Figure 19. HPLC-MS

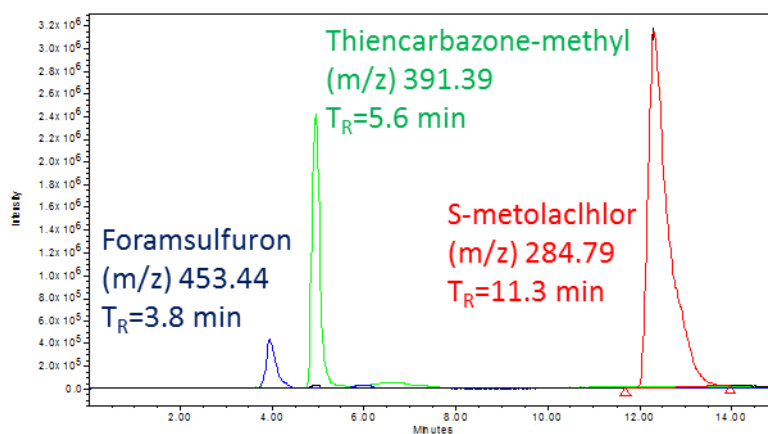


Figure 20. Chromatogram of foramsulfuron, thiencarbazono-methyl and S-metolachlor

4.6. Data analysis

The adsorption and desorption data for the herbicides were fit to the linearized form of the Freundlich equation: $\log C_s = \log K_f + n_f \log C_e$ or $\log C_s = \log K_{fd} + n_{fd} \log C_e$, where C_s ($\mu\text{g g}^{-1}$)

is the amount of adsorbed herbicide, C_e ($\mu\text{g mL}^{-1}$) is the equilibrium concentration of herbicide in solution, and K_f or K_{fd} ($\mu\text{g}^{1-n_f} \text{g}^{-1} \text{mL}^{n_f}$) and n_f or n_{fd} are the Freundlich adsorption or desorption coefficients and nonlinearity coefficients, respectively. Distribution coefficients, K_d (mL g^{-1}), were also calculated from the relationship C_s / C_e for C_e of $25 \mu\text{g mL}^{-1}$. Values of K_f or K_d normalized to 100% OC were determined as $K_{foc} = 100 K_f / \%OC$ or $K_{doc} = 100 K_d / \%OC$, respectively. Standard deviation (SD) was used to indicate variability in the adsorption and desorption coefficient values among replicates. Simple and multiple linear regression models were used to relate adsorption- desorption and adsorbent and herbicide characteristics. The Stat graphics Plus Version 5.1 software package was used.

5. RESULTS AND DISCUSSION

5.1. Adsorption of the herbicides by mulches and soils

S-metolachlor

Figure 21 includes the adsorption-desorption isotherms of *S-metolachlor* by mulches (M1, M2, M3, and MM1), unamended soils (S1 and S2) and soils amended with milled mulch (S1 + MM1 and S2 + MM1). Adsorption of the herbicide on mulches and soils was well described by the Freundlich equation over the range of the initial concentrations assayed (0-25 $\mu\text{g mL}^{-1}$) with r^2 values ≥ 0.92 . The K_f and n_f parameters determined from this equation are shown in Table 3.

S-metolachlor adsorption behavior showed a wide variety in the type of isotherm that better described it which depended on the adsorbent (Figure 21). The adsorption isotherms were of L-type ($n_f < 1$) for *S-metolachlor* adsorbed on M3, S1, S2, S1+MM1, S2+MM1 (with a total adsorption of the herbicide at concentrations $\leq 10 \mu\text{g mL}^{-1}$), and MM1 (L-C type) showing a high initial affinity of the adsorbent for the herbicide. S-type isotherms ($n_f > 1$) were obtained for M1 and M2 (close to C-type for M2), indicating a strong competition for adsorption sites by water molecules at low herbicide concentrations. These results indicate different mechanisms of adsorption for this hydrophobic herbicide in function of the adsorbent. The varied type of adsorption isotherms observed for *S-metolachlor* is in accordance with previous results reported by other authors. (Aslam et al. 2013) obtained adsorption isotherms almost linear ($n \geq 0.9$) for *S-metolachlor* on maize mulch residues decomposed under laboratory and field conditions. (Marín-Benito et al. 2021) reported adsorption isotherms in general of L-type for *S-metolachlor* on soil non-amended and amended with green compost and pelletised organo-mineral manure fertilizer whereas (Peña et al. 2013) observed C-type isotherms for *S-metolachlor* adsorption on soils amended with both oiled and de-oiled two-phase olive mill wastes.

The K_f values obtained for the adsorption of *S-metolachlor* by soils and mulches ranged between 1.34 and 65.8, corresponding the highest K_f values to mulches (43.7 – 65.8) and the lowest ones to unamended soils (1.34 – 2.00). These results are in agreement with the results of Cassigneul et al. (2018) who observed that the adsorption of *S-metolachlor* was significantly lower on soil than on mulch from different cover crop residues. The K_f values for this hydrophobic herbicide increased in the order: S1 < S2 < S1+MM1 < S2+MM1 << MM1 <

M1 < M2 < M3 according to the increase in OC and/or DOC content of the adsorbents (Tables 3 and table 6). OC is reported to be the most important soil component affecting the adsorption of S-metolachlor (Alletto et al. 2013) (Marín-Benito et al. 2021). The application of MM1 to unamended soils increased the K_f values up to 4.5 times in S1+MM1 and up to 6.4 times in S2+MM1. Mulch decomposition degree had also influence in the adsorption of S-metolachlor by increasing the K_f values with the decomposition of this adsorbent from 45.6 (M1) to 65.8 (M3) according to the decrease in DOC (M1 > M2 > M3) (Table 3) Other authors have also reported a positive impact on the adsorption of S-metolachlor and other herbicides on mulches of different nature with their decomposition degree (Aslam et al. 2013)(Cassigneul et al. 2015)(Cassigneul et al. 2016)(Cassigneul et al. 2018). However, the particle size of the freshest mulch (M1) did not show a significant effect in the adsorption of S-metolachlor that showed similar K_f values for M1 and MM1 although slightly lower for MM1 because of its lower OC and DOC content.

K_d distribution coefficients determined at an initial concentration of 25 mg L⁻¹ to compare with the adsorption behavior at low concentrations (K_f values) (Table 3) varied in the same sense as the K_f constants for unamended and amended soils but some changes were observed for mulches. The K_d values ranged from 0.41 to 68.4 and they followed the order: S1 ~ S2 < S2+MM1 ~ S1+MM1 << M3 = MM1 < M1 < M2. K_d values were lower (1.1 - 8.4 times) than K_f values for M3, MM1, S1, S2, S1+MM1, and S2+MM1 whereas they were 1.4 times higher for M1 and M2 as would be expected from the shape of the isotherms, L-type and S-type, respectively. The K_d values obtained in this study for S-metolachlor on mulches, unamended and amended soils are in accordance with those reported by other authors on these three types of adsorbents (Alletto et al. 2013)(Aslam et al. 2013)(Marín-Benito et al. 2021)

The simple correlation coefficients (r) showed in Table 3 revealed the existence of a highly significant positive correlation between K_f and K_d adsorption constants and the OC content for the adsorption of the most hydrophobic herbicide, S-metolachlor, by mulches, unamended and MM1-amended soils. On the basis of the determination coefficient, r^2 , OC would account for 94.3% or 87.2% of the variance of the adsorption of S-metolachlor by mulches and soils expressed by K_f and K_d , respectively. This indicates the influence of the mulch and soil OC content (natural or from MM1) in the adsorption of this highly hydrophobic herbicide, and it is in agreement with lower CV values found for the K_{foc} and K_{doc} compared to

its respective CV for K_f and K_d parameters (Table 3). There was also a significant ($p < 0.05$) or highly significant ($p < 0.001$) positive correlation between DOC content of the adsorbents and K_f and K_d values of S-metolachlor, respectively (Table 7). Previous studies have also reported an increasing in the adsorption of metolachlor by amended soils with a high DOC content in solution (Marín-Benito et al. 2021)(Singh 2003). No relationship was observed between S-metolachlor adsorption constants and adsorbents' pH. These simple relationships indicate that both OC and DOC are the main variables involved in the adsorption of S-metolachlor on the different adsorbents at low (K_f) and high (K_d) herbicide concentrations in solution. However, it should be noted that OC content explained a higher variability in K_f values ($r^2 = 94.3\%$) than DOC (68.9%) whereas the opposite effect was observed for the variability of K_d values (97.6% explained by DOC vs. 87.2% explained by OC).

The results were also subjected to multiple linear regression analysis by combining two or more variables to determine the relative importance of mulch and soil parameters when they vary simultaneously. Table 7 shows the multiple lineal regression models for the adsorption of herbicides by mulches, unamended and MM1-amended soils, which gave rise (in some cases) to a higher adjusted r^2 than the simple relationships. For S-metolachlor, a highly significant relationship ($p < 0.001$) was revealed by the equation between the K_d adsorption constant and the variables OC and DOC. The coefficient of determination, r^2 , accounts for a percentage of variability in the K_d of 97.8% that is, slightly higher than that explained when only the OC or the DOC content is considered as the responsible variable. This equation indicates that DOC had a higher positive effect than OC on S-metolachlor adsorption at high concentrations in solution that is in agreement with the simple relationships previously explained. A highly significant relationship ($p < 0.001$) was also revealed by the equation between the K_f adsorption constant and the variables OC and DOC (Table 7) although its r^2 value (93.8%) explained a lower percentage of the variability in the K_f than that explained by the OC as unique variable (94.3%). However, it is important to highlight that the model combining OC and DOC shows a negative influence of DOC on the adsorption of S-metolachlor at low herbicide concentrations (K_f) that supports the increasing of K_f values observed with the decomposition of the mulch.

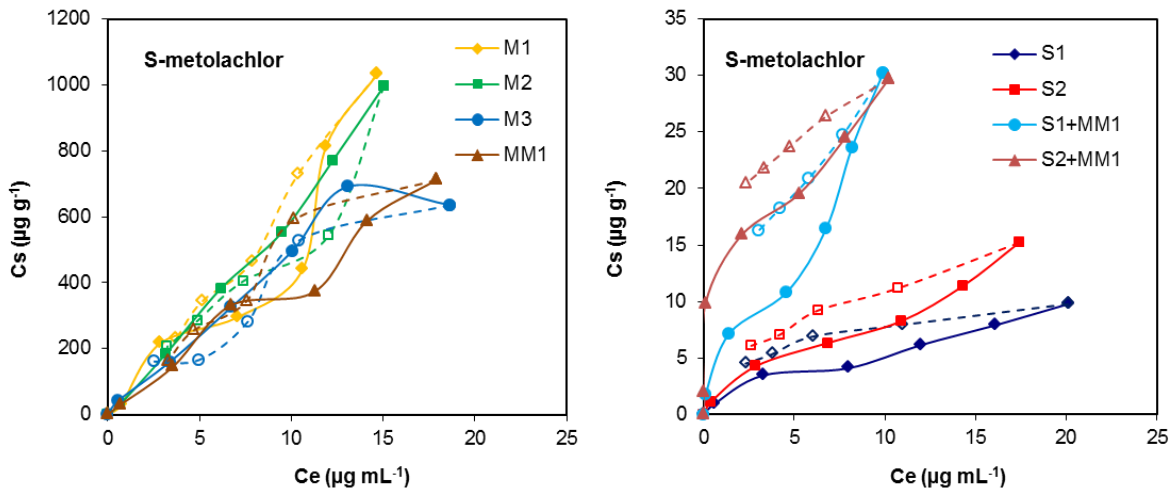


Figure 21. Adsorption-desorption isotherms of S-metolachlor by mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1+MM1 and S2+MM1). Closed symbols and continuous line correspond to adsorption and open symbols and dashed line correspond to desorption.

Table 3. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of S-metolachlor by mulches, unamended and MM1-amended soils, distribution coefficients (K_d), K_f or K_d normalized to 100% OC (K_{foc} , K_{doc}), and hysteresis coefficients (H).

Sample	$K_f \pm SD^a$	K_{foc}	$K_d \pm SD^a$	K_{doc}	$n_f \pm SD$	r^2	$K_{fd} \pm SD$	$n_{fd} \pm SD$	r^2	H^b
M1^c	45.58 ± 3.37	102.3	62.55 ± 8.95	140.3	1.10 ± 0.07	0.950	55.31 ± 37.63	1.08 ± 0.25	0.988	1.01 ± 0.17
M2^c	49.69 ± 16.13	112.7	68.42 ± 0.37	155.1	1.10 ± 0.10	0.999	65.06 ± 57.54	0.93 ± 0.30	0.943	1.18 ± 0.25
M3^c	65.77 ± 0.79	147.7	39.04 ± 3.69	87.7	0.84 ± 0.03	0.983	64.13 ± 8.69	0.79 ± 0.05	0.884	1.06 ± 0.10
MM1^d	43.73 ± 8.54	104.9	39.05 ± 2.33	93.7	0.96 ± 0.08	0.989	60.83 ± 19.25	0.89 ± 0.08	0.952	1.08 ± 0.18
S1^e	1.342 ± 0.01	194.5	0.41 ± 0.01	59.4	0.63 ± 0.01	0.976	3.39 ± 1.81	0.36 ± 0.14	0.985	1.77 ± 0.71
S2^f	2.00 ± 0.06	198.0	0.65 ± 0.01	69.4	0.65 ± 0.01	0.985	3.69 ± 1.30	0.48 ± 0.10	0.988	1.35 ± 0.27
S1+MM1^g	6.05 ± 2.16	96.6	1.60 ± 0.46	25.6	0.59 ± 0.20	0.961	8.81 ± 1.64	0.52 ± 0.09	0.973	1.13 ± 0.20
S2+MM1^h	12.89 ± 1.35	112.8	1.53 ± 0.18	13.4	0.34 ± 0.07	0.921	16.19 ± 0.58	0.26 ± 0.01	0.991	1.32 ± 0.30
CV (%) ⁱ	89.82	31.1	109.5	62.72						

^a SD = standard deviation of replicates. ^b $H = n_f/n_{fd}$. ^c M1, M2 and M3 = mulches at different decomposition degree. ^d MM1 = milled M1.

^e S1 = unamended soil 1. ^f S2 = unamended soil 2. ^g S1+MM1 = soil 1 amended with 10% of MM1. ^h S2+MM1 = soil 2 amended with 10% of MM1.

ⁱ CV= coefficients of variation.

Foramsulfuron

Adsorption-desorption isotherms of foramsulfuron by mulches, unamended and MM1-amended soils are included in Figure 22. Foramsulfuron adsorption on mulches and soils was well described by the Freundlich equation with r^2 values ≥ 0.91 (Table 4). Similar to S-metolachlor adsorption behavior, different isotherm types defined the adsorption of foramsulfuron on the studied adsorbents.

L-type isotherms ($n_f < 1$) were observed for foramsulfuron on MM1, S1+MM1 and S2+MM1 indicating that the percentage of this herbicide adsorbed by these three adsorbents decreased with increasing solution concentration, suggesting a decreasing adsorbing sites on the adsorbent surface at higher solution concentration. Anyway, it should be highlighted that in MM1 and S2+MM1 ($n_f = 0.94$) the type of isotherm is close to C-type ($n_f = 1$) characterized by a similar affinity of adsorbent by water and foramsulfuron molecules. In contrast, S-type isotherms ($n_f > 1$) were obtained for foramsulfuron on S2, M1, M2 and M3 whereas no herbicide adsorption was determined on S1. Similar to S-metolachlor, different mechanisms of adsorption in function of the adsorbent would explain this variety on adsorption isotherm type for this highly water-soluble herbicide.

Lower K_f values were obtained for the adsorption of foramsulfuron compared to that of S-metolachlor by mulches and soils. These K_f values ranged from 0 to 34.3 increasing in the order: S1 < S2 < S1+MM1 < S2+MM1 < M1 < M2 < M3 < MM1. This order was the same as previously indicated for S-metolachlor except for MM1 that was the mulch with the highest K_f value for foramsulfuron whereas it was the adsorbent with the lowest affinity by the most hydrophobic herbicide, S-metolachlor. The no adsorption ($K_f = 0$) or slight adsorption ($K_f = 0.09$) of foramsulfuron on unamended S1 and S2 soils, respectively, was increased up to 13 times in S2 and more than 22 times in S1 by the addition of MM1 to the soils (Table 4). The K_f values determined for S1 and S2 were lower than the range of values (0.31 - 2.61) registered for unamended soils in the PPDB (2021). No adsorption-desorption studies have been found in the literature for foramsulfuron although there are studies reporting the adsorption-desorption behavior of other sulfonylurea herbicides on unamended and amended soils. (Delgado-Moreno and Peña 2008) found a low or very low herbicide adsorption, slightly promoted by the addition of fresh and composted olive cake to soil.

The effect of mulch decomposition degree and the particle size on foramsulfuron K_f values was more significant than that previously indicated for S-metolachlor. Among the mulches, fresh mulch (M1) showed the lowest K_f value and it increased by 1.3 (M2) and 3.5 (M3) times as result of its decomposition, and up to 6.3 times when M1 was milled to obtain MM1.

According to the shape of the isotherms, foramsulfuron showed K_d values lower than the corresponding K_f values for MM1, S1+MM1, and S2+MM1, and vice versa for the adsorbents M1, M2, M3, and S2 following the order $S1 < S2 = S1+MM1 < S2+MM1 \ll MM1 < M1 < M2 < M3$ (Table 4). These K_d values ranged from 0 to 104.8 and they were in the same order of magnitude as the corresponding K_f values for MM1, S1, S2, S1+MM1 and S2+MM1. In contrast, a significant increasing was observed in the K_f values compared to K_d values for M1, M2 and M3 (up to 9.2, 14.7, and 5.4 times, respectively).

These results are supported by a very significant positive correlation ($p < 0.01$) observed between the adsorption of foramsulfuron at high concentrations of herbicide in solution (K_d) and the mulch and soils' OC content (Table 7) while non-significant relationship was determined at low herbicide concentrations (K_f). Compared to S-metolachlor, the OC content would account for a lower percentage of variance in the adsorption (K_d) of foramsulfuron by mulches and soils (71.1%). This suggests that other mulch and soil parameters may influence the adsorption of this non-hydrophobic herbicide. It is in agreement with a greater variability in the K_{foc} and K_{doc} values determined for foramsulfuron (CV = 125.4% and 118.3%, respectively) than for S-metolachlor (CV = 31.1% and 62.7%) (Table 4). A significant positive correlation was also determined between foramsulfuron K_d values and the DOC content of the adsorbents whereas a lack of relationship was observed for K_f vs. DOC content (Table 6). However, a significant ($p = 0.011$) joint effect of OC (positive) and DOC (negative) contents of mulches and soils explained 77.3% of the variability in foramsulfuron K_f adsorption constant (Table 7). The combination of these two variables did not improve, however, the explanation of the K_d variance (60.2%) respect to that explained by the OC content as single variable (71.1%). No relationship was observed between foramsulfuron adsorption constants (K_f and K_d) and adsorbents' pH (Agbaogun and Fischer 2020). in accordance with PPDB (2021). Opposite effects has been observed for other sulfonylurea herbicides. (Delgado-Moreno and Peña 2008) reported that the adsorption of bensulfuron-methyl, chlorsulfuron and

profluroxifen on unamended and amended soils was mainly affected by pH of the soil solution, with the OC content having no significant effect on herbicide retention.

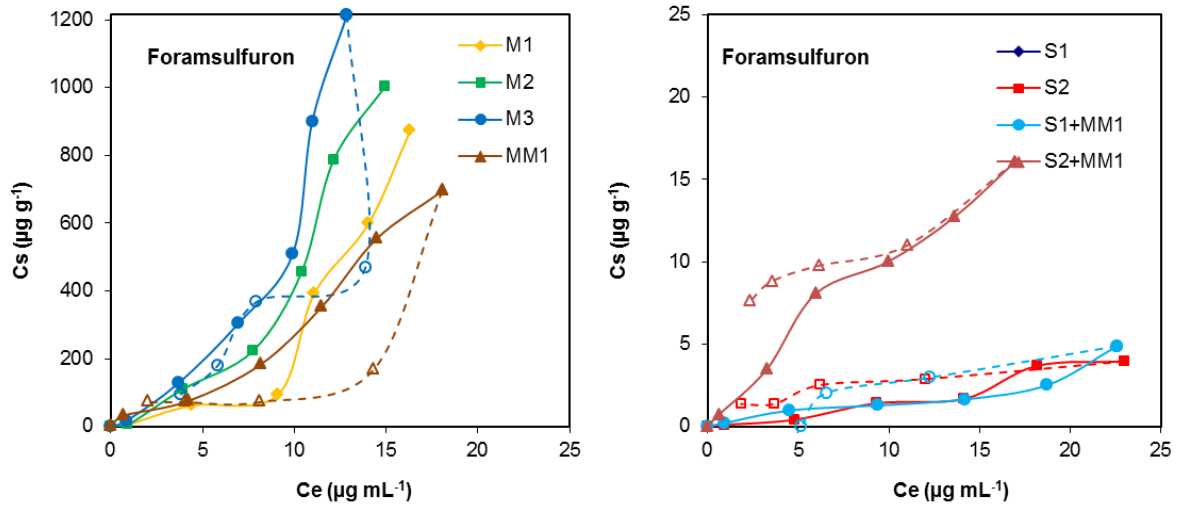


Figure 22. Adsorption-desorption isotherms of foramsulfuron by mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1+MM1 and S2+MM1). Closed symbols and continuous line correspond to adsorption and open symbols and dashed line correspond to desorption.

Table 4. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of foramsulfuron by mulches, unamended and MM1-amended soils, distribution coefficients (K_d), K_f or K_d normalized to 100% OC (K_{foc} , K_{doc}), and hysteresis coefficients (H).

Sample	$K_f \pm SD^a$	K_{foc}	$K_d \pm SD^a$	K_{doc}	$n_f \pm SD$	r^2	$K_{fd} \pm SD$	$n_{fd} \pm SD$	r^2	H^b
M1^c	5.48 ± 0.05	12.3	50.28 ± 0.10	112.8	1.69 ± 0.03	0.938	11.01 ± 12.92	1.63 ± 0.43	0.848	0.93 ± 0.20
M2^c	6.89 ± 0.21	15.6	101.2 ± 24.25	229.4	1.83 ± 0.07	0.990	0	-	-	-
M3^c	19.37 ± 2.14	43.5	104.8 ± 6.76	235.4	1.52 ± 0.05	0.983	0	-	-	-
MM1^d	34.31 ± 0.49	82.3	28.54 ± 1.20	68.5	0.94 ± 0.02	0.909	26.27 ± 35.74	0.84 ± 0.47	0.661	1.13 ± 0.50
S1^e	0	0	0	0	-	-	-	-	-	-
S2^f	0.09 ± 0.01	8.9	0.16 ± 0.01	15.8	1.18 ± 0.01	0.970	0.94 ± 0.03	0.46 ± 0.01	0.909	2.58 ± 0.07
S1+MM1^g	0.22 ± 0.01	3.5	0.14 ± 0.01	2.2	0.87 ± 0.02	0.945	-	3.22 ± 0.25	0.613	0.27 ± 0.03
S2+MM1^h	1.19 ± 0.01	10.4	0.97 ± 0.10	8.5	0.94 ± 0.03	0.989	5.60 ± 0.01	0.33 ± 0.01	0.901	2.81 ± 0.07
CV (%)	145.8	125.4	126.6	118.3						

^a SD = standard deviation of replicates. ^b $H = n_f/n_{fd}$. ^c M1, M2 and M3 = mulches at different decomposition degree. ^d MM1 = milled M1.

^e S1 = unamended soil 1. ^f S2 = unamended soil 2. ^g S1+MM1 = soil 1 amended with 10% of MM1. ^h S2+MM1 = soil 2 amended with 10% of MM1.

ⁱ CV= coefficients of variation. Note – No adsorption or desorption isotherms were obtained where “ - ” is reported.

Thiencarbazone-methyl

The adsorption-desorption isotherms of thiencarbazone-methyl by mulches, unamended and MM1-amended soils are shown in Figure 23. Thiencarbazone-methyl adsorption on mulches and soils was well described by the Freundlich equation with r^2 values ≥ 0.91 (Table 5). In contrast to S-metolachlor and foramsulfuron, thiencarbazone-methyl showed a more homogeneous adsorption mechanism by the different adsorbents since the adsorption isotherms of this herbicide on all the adsorbents assayed in this study were S-type ($n_f > 1$).

Compared to S-metolachlor and foramsulfuron, thiencarbazone-methyl was the herbicide that showed the lowest K_f values ($K_f \leq 1.10$) for all the adsorbents except in the case of foramsulfuron adsorbed on S2 (Table 5). It is in accordance with the lowest hydrophobicity of thiencarbazone-methyl among the three herbicides studied. The adsorption of this herbicide increased in the order: S1 \sim S1+MM1 < S2 < S2 + MM1 = M3 < M2 \sim M1 < MM1. The K_f values determined for S1 and S2 were lower than the range of values (0.40 – 7.0) found in the literature for thiencarbazone-methyl on unamended soils (Gul, Ahmad, and Gul 2020) (PPDB 2021). From a numerical point of view, the increase in surface area from M1 to MM1 after its milling as well as the application of MM1 to soils increased the herbicide adsorption on MM1 and on amended soils compared to M1 (1.3 times) and unamended soils (1.5-4 times), respectively, whereas the opposite effect was observed with the increasing decomposition degree of mulch. However, the low K_f values make difficult to indicate objectively a significant effect of these variables on thiencarbazone-methyl adsorption. This non-hydrophobic herbicide showed the highest K_f adsorption value on MM1, similar to that observed for another non-hydrophobic herbicide, foramsulfuron.

According to S-type isotherms describing the adsorption of thiencarbazone-methyl on all adsorbents, the adsorption of this herbicide was favored by the increase in the solute concentration in solution. This is revealed by K_d values (0.26 – 49.2) that increased from 1.3 (S2+MM1) to 80.7 (M3) times the corresponding adsorption coefficients determined at low herbicide concentrations (K_f). The high n_f values resulting from thiencarbazone-methyl adsorption isotherms, higher than those obtained for S-metolachlor and foramsulfuron, explain the highest variation between the K_f and K_d values for this herbicide. The values of K_d increasing in a more defined order than K_f values: S1 < S2 = S1+MM1 < S2 + MM1 \ll M1 < M2 < MM1 < M3. In an adsorption study involving 10 unamended soils with a predominant sandy

loam texture, an OC content varying from 0.17% to 0.58%, and pH between 7.02 and 7.72, (Gul et al. 2020) determined higher K_d values (4.3 – 26.4) for thien carbazone-methyl than those obtained in this study for S1 and S2 which have similar characteristics to their soils. Gul et al. obtained C-type adsorption isotherms for thien carbazone-methyl on all soils.

Despite the low hydrophobicity of thien carbazone-methyl, a significant ($p < 0.05$) and a very significant positive correlation ($p < 0.01$) was observed between the adsorption of this herbicide at low (K_f) and high concentrations of compound (K_d) in solution, and the adsorbents' OC content, respectively (Table 7). However, similar to foramsulfuron, the OC content would account for a lower percentage of variance in the adsorption of thien carbazone-methyl by mulches and soils (68.3% (K_f) and 71.6% (K_d)) compared to that observed for S-metolachlor. This suggests, as previously indicated for foramsulfuron, that other mulch and soil parameters may influence the adsorption of this another non-hydrophobic herbicide as indicated by higher CV found for its K_{foc} and K_{doc} values compared to those determined for S-metolachlor (Tables 3 and Table 4). Now, contrary to observed for foramsulfuron, a significant positive correlation ($p < 0.05$) was also determined between thien carbazone-methyl K_f values and the DOC content of the adsorbents whereas a lack of relationship was observed for K_d vs. DOC content (Table 7). In this case, the combination of the variables OC and DOC content of mulches and soils allowed explaining a higher percentage (78.9%) of the variance of the adsorption of thien carbazone-methyl only at high concentrations of herbicide in solution (K_d) respect to that explained by the OC content as single variable (71.1%) (Table 6 and table 7). Again, no correlation was established between thien carbazone-methyl adsorption constants (K_f and K_d) and adsorbents' pH as indicated in PPDB (2021).

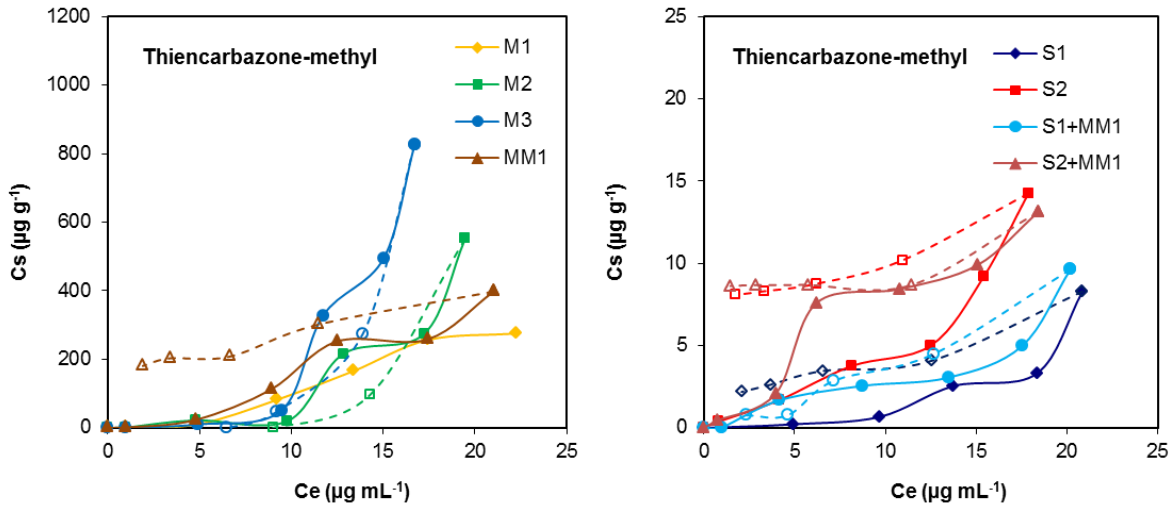


Figure 23. Adsorption-desorption isotherms of thienicarbazone-methyl by mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1+MM1 and S2+MM1). Closed symbols and continuous line correspond to adsorption and open symbols and dashed line correspond to desorption.

Table 5. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of thiencazuron-methyl by mulches, unamended and MM1-amended soils, distribution coefficients (K_d), K_f or K_d normalized to 100% OC (K_{foc} , K_{doc}), and hysteresis coefficients (H).

Sample	$K_f \pm SD^a$	K_{foc}	$K_d \pm SD^a$	K_{doc}	$n_f \pm SD$	r^2	$K_{fd} \pm SD$	$n_{fd} \pm SD$	r^2	H^b
M1^c	0.86 ± 0.10	1.9	17.37 ± 6.77	39.0	1.93 ± 0.17	0.975	0	11.17 ± 1.20	0.872	0.21 ± 0.01
M2^c	0.84 ± 0.26	1.9	21.17 ± 1.30	48.0	2.00 ± 0.08	0.909	0	14.6 ± 0.45	0.934	0.14 ± 0.01
M3^c	0.61 ± 0.02	1.4	49.22 ± 27.61	110.6	2.37 ± 0.19	0.925	0	-	0.907	-
MM1^d	1.10 ± 0.07	2.6	27.61 ± 2.24	66.2	2.00 ± 0.04	0.987	135 ± 11	0.33 ± 0.08	0.907	6.15 ± 1.52
S1^e	0.01 ± 0.00	1.4	0.26 ± 0.04	37.7	1.89 ± 0.06	0.963	1.34 ± 0.27	0.53 ± 0.02	0.907	3.58 ± 0.01
S2^f	0.40 ± 0.17	39.6	0.58 ± 0.09	57.4	1.11 ± 0.18	0.968	6.50 ± 1.34	0.22 ± 0.05	0.906	4.96 ± 0.25
S1+MM1^g	0.04 ± 0.00	0.6	0.57 ± 0.00	9.1	1.85 ± 0.02	0.914	0.19 ± 0.19	1.26 ± 0.35	0.904	1.47 ± 0.37
S2+MM1^h	0.61 ± 0.08	5.3	0.80 ± 0.13	7.0	1.09 ± 0.09	0.952	7.65 ± 0.79	0.12 ± 0.02	0.470	8.89 ± 2.28
CV (%)	69.76	194.0	120.8	70.8						

^a SD = standard deviation of replicates. ^b $H = n_f / n_{fd}$. ^c M1, M2 and M3 = mulches at different decomposition degree. ^d MM1 = milled M1.

^e S1 = unamended soil 1. ^f S2 = unamended soil 2. ^g S1+MM1 = soil 1 amended with 10% of MM1. ^h S2+MM1 = soil 2 amended with 10% of MM1.

ⁱ CV= coefficients of variation. Note – No adsorption or desorption isotherms were obtained where “ - ” is reported.

Table 6. Simple correlation coefficients (r) between Freundlich adsorption constants (K_f), distribution coefficients (K_d) and Freundlich desorption constants (K_{fd}) of herbicides and mulches and soil properties.

Constant/Herbicide	pH	OC	DOC
K_f /S-metolachlor (n=8)	-0.584	0.971 ^a	0.830 ^c
K_d /S-metolachlor (n=8)	-0.670 ^d	0.934 ^a	0.988 ^a
K_{fd} /S-metolachlor (n=8)	0.606	0.994 ^a	0.875 ^b
K_f /foramsulfuron (n=8)	-0.070	0.670 ^d	0.341
K_d /foramsulfuron (n=8)	-0.551	0.843 ^b	0.792 ^c
K_{fd} /foramsulfuron (n=4)	-0.258	0.793	0.433
K_f /thiencarbazone-methyl (n=8)	-0.422	0.826 ^c	0.711 ^c
K_d /thiencarbazone-methyl (n=8)	-0.332	0.843 ^b	0.606
K_{fd} /thiencarbazone-methyl (n=5)	0.076	0.970 ^a	0.991 ^a

^a $p < 0.001$, highly significant. ^b $p < 0.01$, very significant. ^c $p < 0.05$, significant.

^d $p < 0.1$, non-significant.

Table 7. Multiple regression equations between Freundlich adsorption constants (K_f), distribution coefficients (K_d) and Freundlich desorption constants (K_{fd}) of herbicides and mulches and soil properties.

Constant/Herbicide	Regression equation	p	r ²
K _f /S-metolachlor (n=8)	-1.144 ± 3.662 + (1.471 ± 0.269) %OC - (1.330 ± 1.090) %DOC	0.0000	0.938
K _d /S-metolachlor (n=8)	-1.488 ± 2.468 + (0.309 ± 0.181) %OC + (4.430 ± 0.569) %DOC	0.0000	0.978
K _{fd} /S-metolachlor (n=8)	0.998 ± 1.908 + (1.530 ± 0.140) %CO - (0.747 ± 0.569) %DOC	0.0000	0.987
K _f /foramsulfuron (n=8)	-3.668 ± 3.378 + (1.169 ± 0.248) %CO - (3.490 ± 1.010) %DOC	0.0011	0.773
K _d /foramsulfuron (n=8)	-7.170 ± 16.445 + (1.496 ± 1.207) %CO + (1.420 ± 4.910) %DOC	0.0043	0.602
K _{fd} /foramsulfuron (n=4)	-1.741 ± 2.654 + (0.975 ± 0.178) %CO - (2.433 ± 0.669) %DOC	0.1595	0.922
K _f /thiencarbazone-methyl (n=8)	0.176 ± 0.148 + (0.019 ± 0.011) %CO - (0.020 ± 0.040) %DOC	0.0053	0.566
K _d /thiencarbazone-methyl (n=8)	-4.808 ± 4.701 + (1.378 ± 0.345) %CO - (3.00 ± 1.400) %DOC	0.0090	0.789
K _{fd} /thiencarbazone-methyl (n=5)	0.323 ± 7.031 - (1.307 ± 1.827) %CO + (33.76 ± 13.10) %DOC	0.0138	0.972

5.2 Desorption of the herbicides by mulches and soils

S-metolachlor

Desorption isotherms were obtained after herbicide adsorption at initial concentrations of 25 mg L⁻¹ (Figure 21). *S*-metolachlor desorption was also well described by Freundlich equation with r^2 values ranging from 0.88 to 0.99. The K_{fd} and n_{fd} parameters determined from this equation are shown in Table 3. The K_{fd} values represent the amount that remains sorbed after desorption for an equilibrium concentration equal to unity. The K_{fd} values varied between 3.39 and 65.1 and were higher for mulches than for soils (unamended and amended). These values varied in the same sense as K_f adsorption constants for unamended and amended soils although not apparently for mulches ($S1 < S2 < S1+MM1 < S2+MM1 \ll M1 < MM1 < M3 \approx M2$). It should be noted that average K_{fd} values for mulches showed high standard deviation responsible for a non-significant difference between their K_{fd} values (Table 3). Other authors, however, did observe a clear decrease in desorption of *S*-metolachlor with mulch (maize) decomposition (Aslam et al. 2013). There was a very significant ($p < 0.01$) or highly significant ($p < 0.001$) positive correlation between DOC and OC content of the adsorbents and K_{fd} of *S*-metolachlor, respectively (Table 7) being, therefore, these two variables involved in the desorption of this herbicide as well as they were in its adsorption although the multiple lineal regression model obtained by combining OC and DOC content explained a slightly lower variance of K_{fd} (98.7%) than the OC content (98.8%) by itself as previously indicated for K_f .

In all cases, the isotherms exhibited hysteresis to a greater or lesser extent, because desorption data did not coincide with those of the adsorption isotherms. The hysteresis coefficients (H) of the desorption isotherms were >1 in all cases and indicated a greater irreversibility (higher H values, lower desorption) of the adsorption of *S*-metolachlor from soils, especially from unamended ones, than from mulches (Table 3).

Foramsulfuron

Freundlich equation showed a worse ability to fit foramsulfuron desorption from all adsorbents than that of *S*-metolachlor with r^2 values ranging from 0.61 to 0.91 (Table 4). The poorest fit was observed for MM1 and S1+MM1. In MM1 ($r^2 = 0.61$), it is explained by a very fast desorption in the two first desorption points (Figure 22) and no desorption of herbicide

in the other two desorption points. A very fast and complete desorption from the second to the third desorption point explain the low r^2 value in the case of S1+MM1 ($r^2 = 0.66$). A total desorption took place for M2 and M3 in the first desorption point what explains the absence of the desorption isotherms of both adsorbents in Figure 22 and the corresponding desorption parameters in Table 4. In addition, no foramsulfuron desorption data were obtained for S1 as result of the non-adsorption of the herbicide on this soil. Compared to S-metolachlor, foramsulfuron showed lower K_{fd} values (Table 4) that could be explained by the low hydrophobicity and/or high solubility of this herbicide in contrast to those of S-metolachlor. These K_{fd} values ranged from 0 - 26.3 unidades and were also higher for mulches (excluding M1 and M2 due to the absence of desorption isotherms) than for soils as previously indicated for S-metolachlor although it should be noted again that average K_{fd} values for mulches showed high standard deviation responsible for a non-significant difference between their K_{fd} values (Table 7). No correlation simple or combined was observed between K_{fd} values, OC and/DOC contents (Tables 6 and table 7). In all cases, the isotherms exhibited hysteresis. It was positive hysteresis ($H > 1$) for MM1, S2 and S2+MM1, and negative hysteresis ($H < 1$) for M1 and S1+MM1. The treatments S2 and S2+MM1 showed the greatest irreversibility (higher H values) of the adsorption of foramsulfuron (Table 4).

Thiencarbazone-methyl

According to the high r^2 values (0.87 – 0.93), thiencarbazone-methyl desorption from all adsorbents was well fitted to Freundlich equation except for S2+MM1 that showed a poorer fit ($r^2 = 0.47$). The K_{fd} and n_{fd} parameters determined from this equation are shown in Table 5. Thiencarbazone-methyl showed intermediate K_{fd} values (0.19 - 7.65) to those determined for S-metolachlor and foramsulfuron when the herbicides were desorbed from unamended and MM1-amended soils. For mulches, MM1 showed a very high K_{fd} value (= 135) while it was 0 for the other three mulches corresponding to a total desorption of the amount of herbicide initially adsorbed (Table 5). However, it should be noticed that thiencarbazone-methyl desorption process was different for these non-milled mulches. The total desorption of the herbicide was reached for M1, M2 and M3 after the first, second and third desorption point, respectively (Figure 23). It was in accordance with the decrease in DOC of the mulches with their decomposition degree (Table 6). The highly significant ($p < 0.001$) positive correlation

found between K_{fd} desorption constants and the OC and DOC content for the desorption of thien carbazole-methyl from mulches, unamended and MM1-amended soils support these results (Table 6). However, it should be noted that DOC content explained a higher variance of K_{fd} values ($r^2 = 98.2\%$) than CO (94.1%) or even than the combination of both variables (97.2%) (Table 7) Therefore, DOC content of adsorbents was the main variable controlling thien carbazole-methyl desorption whereas their OC content did it for S-metolachlor and foramsulfuron. The isotherms exhibited hysteresis in all cases (Figure 23) and the H values increased in the order: M2 < M1 < S1+MM1 < S1 < S2 < MM1 < S2+MM1 (Table 5). (Gul et al. 2020) also observed hysteresis for thien carbazole-methyl in the adsorption-desorption experiment carried out on unamended soils.

5.3 Influence of herbicides' properties on its adsorption-desorption by mulches, unamended and MM1-amended soils

The adsorption (K_f and K_d) and desorption (K_{fd}) constants were also subjected to multiple linear regression analysis by combining the two most significant variables of the adsorbents involved in the adsorption-desorption processes of the three studied herbicides (OC and DOC), and the solubility in water and hydrophobicity (K_{ow}) of the compounds to determine the relative importance of mulches, soils (unamended and amended) and herbicides parameters when they vary simultaneously.

A highly significant ($p = 0.0000$) multiple linear regression was obtained among the K_f adsorption constants, the K_{ow} of the herbicides and the OC content of adsorbents when we jointly considered all the herbicides and all the types of adsorbents ($n = 22$). The r^2 statistic of the equation obtained:

$$K_f (n=22) = (-1.424 \pm 4.195) + (5.494 \pm 1.171) K_{ow} + (0.541 \pm 0.131) \%CO \quad [\text{eq. 8}]$$

revealed that 62.2 % of the variability in the K_f could be explained by the combination of both variables for a confidence level of 99%.

When we work at high concentrations of herbicides in solution, a highly significant multiple linear regression ($p = 0.0000$) was found among the K_d adsorption constants, the solubility of the herbicides in water and once more the OC content of adsorbents according to the equation obtained:

$$K_d (n=22) = (-12.43 \pm 7.79) + (0.006 \pm 0.003) \text{Solubility} + (1.254 \pm 0.214) \%CO \quad [\text{eq. 9}]$$

The r^2 statistic showed that 63% of the variability in the K_d could be explained by the herbicide solubility and the OC content of adsorbents for a confidence level of 90%.

For the desorption process, the equation:

$$K_{fd} (n=16) = (9.387 \pm 9.341) - (0.010 \pm 0.005) \text{ Solubility} + (1.447 \pm 0.291) \%CO \quad [\text{eq. 10}]$$

points to a highly significant ($p = 0.0005$) relationship between the K_{fd} desorption constants, the solubility of the herbicides in water and the OC content of adsorbents for a confidence level of 95%. The r^2 obtained for this equation shows that it allows explaining 61.5% of the variability in the K_{fd} of the herbicides.

Therefore, based on these results, OC content of mulches and soil was a key factor to explain the variability in K_f , K_d and K_{fd} . About the herbicides' properties, their hydrophobicity expressed as K_{ow} was involved in the variability of the K_f adsorption constant being it replaced by the solubility of the herbicides when K_d and K_{fd} are the constants analyzed.

5.4 Impact of agricultural practices on herbicide's adsorption-desorption: cover crop residues vs. organic amendments

The most direct impact of mulches from cover crop residues and the application of organic amendments to agricultural soils on the environmental fate of herbicides and their effects as potential environmental contaminants of the soil and surface or ground waters, as well as on their efficiency against the weeds is controlled by the equilibrium adsorption-desorption of the compounds in each one of these receptor matrixes. Therefore, from a sustainable point of view, the ideal situation would be represented by the application in agriculture of an amount of herbicide enough high to be available in the soil to deal with weeds but not in excess to avoid their persistence in the soil and/or their transport to water bodies by runoff or leaching.

The amount of herbicide remaining adsorbed by the mulches, unamended and MM1-amended soils after desorption was calculated to evaluate the efficiency of these matrix as adsorbents and to estimate the real impact of using cover crop residues and organic amendments in agriculture. Figure 24 includes adsorbed amounts expressed as percentages of herbicide (S-metolachlor, foramsulfuron or thien carbazono-methyl) in the aqueous

solution for an initial concentration of $25 \mu\text{g mL}^{-1}$, and remaining adsorbed amounts after desorption expressed as percentages of the herbicide adsorbed by the mulches, unamended and MM1-amended soils. Remaining adsorbed amounts $<10\%$ were obtained for the hydrophobic herbicide, S-metolachlor after desorption from mulches M1, M2 and M3. However, no remaining adsorbed amounts of the non-hydrophobic herbicides, foramsulfuron or thien carbazono-methyl, were determined after desorption from the three mulches except for foramsulfuron from M3 that showed a low percentage (3.8%) after four successive desorption stages. These results indicate that, at field scale, the impact of mulching on the adsorption-desorption of the herbicides assayed in this study and consequently on their fate would be negligible in presence of precipitations or under irrigation practices since the wash off of the compounds intercepted by the mulch during their application towards the soil would be total or almost total for the non-hydrophobic herbicides independently of the decomposition degree of the mulch. However, the choice of S-metolachlor application time, it means do it on M1, M2 or M3, involved a loss of herbicide by no desorption ranging between 6.45% and 9.1% of the amount initially applied.

In the case of using MM1 as adsorbent, for example as component of bio beds addressed to control the point pollution of soils and waters caused by an inappropriate handling of pesticides during their storage and use, or during the equipment cleaning process after application, its efficiency is not very high since a percentage $\leq 7.2\%$ remained adsorbed on this organic material. Other organic adsorbents have showed higher adsorption efficiency for different pesticides than the obtained for the herbicides of the present study (García-Delgado et al. 2020) (Karanasios et al. 2010) (Marín-Benito, Rodríguez-Cruz, et al. 2012)

On the other hand, the application of MM1 as organic amendments to the soils S1 and S2 only involved an increasing in the amount of herbicide remaining adsorbed after desorption in the case of S2 + MM1 for the three herbicides (up to 3.4 times for S-metolachlor, 5.6 times for foramsulfuron, and 1.1 times for thien carbazono-methyl) and also for the most

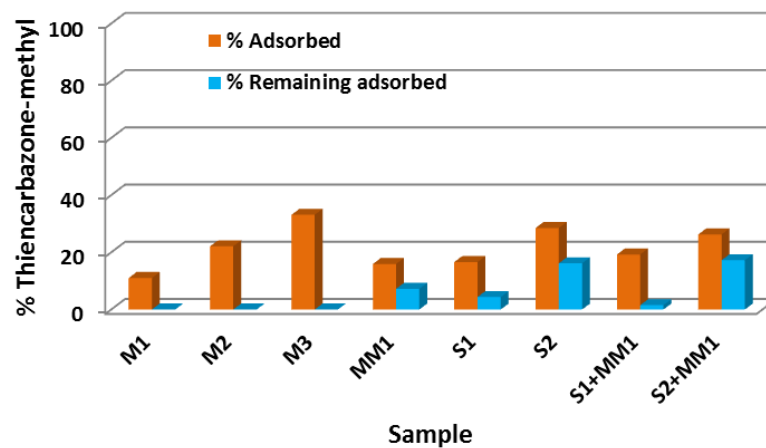
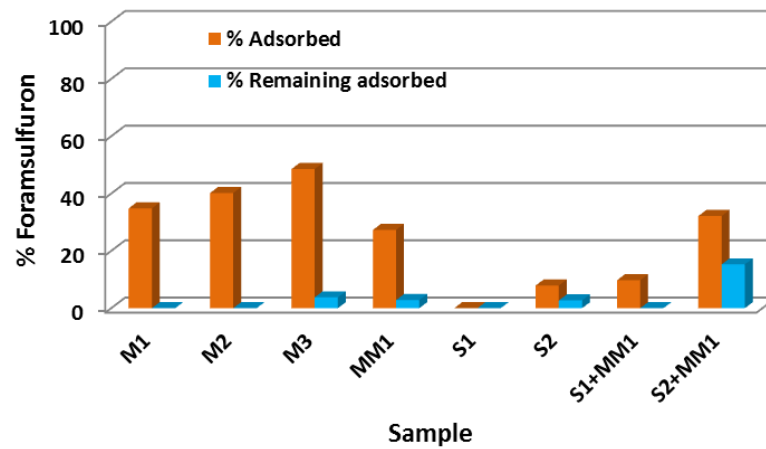
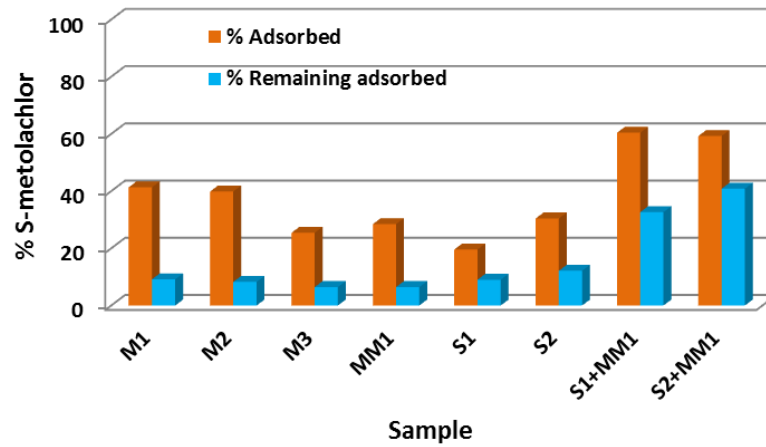


Figure 24. Adsorbed amounts expressed as percentages of herbicide (S-metolachlor, foramsulfuron or thien carbazone-methyl) in the aqueous solution for an initial concentration of $25 \mu\text{g mL}^{-1}$, and remaining adsorbed amounts after desorption expressed as percentages of the herbicide adsorbed by the mulches, unamended and MM1-amended soils.

hydrophobic herbicide, S-metolachlor, in S1 + MM1 (up to 3.6 times). This effect has been frequently cited in the literature and indicated as potential strategy to prevent point pollution of soils and waters by pesticides (Álvarez-Martín et al. 2016)(Marín-Benito et al. 2009)(Marín-Benito, Sánchez-Martín, and Rodríguez-Cruz 2016)(García-Delgado et al. 2020). The impact of organic amendments in the amount of herbicide remaining adsorbed after desorption was higher than that observed for mulches whose main effect could be defined as a delay in the time that the herbicides would need to reach the soil surface as long as rainfall and/or irrigation took place after the application and interception of the herbicides by the mulches.

6. CONCLUSIONS

The adsorption behavior of the three herbicides depended on the adsorbent, however, thien carbazole-methyl showed a more homogenous mechanism of adsorption by the different adsorbents. According to K_f values, the general order of adsorption of the herbicides on all adsorbents was S-metolachlor > foramsulfuron > thien carbazole-methyl. For S-metolachlor and foramsulfuron, mulch decomposition degree held a positive impact in adsorption process, whereas it showed the opposite effect for thien carbazole-methyl. These results indicate that the hydrophobic herbicide S-metolachlor obtained < 10 % remaining adsorbed amount, after desorption from mulches M1, M2, M3. However, for non-hydrophobic herbicides, foramsulfuron and thien carbazole-methyl, there is no remaining adsorbed amount after desorption from three mulches except for foramsulfuron from M3 that showed a low percentage after four successive desorption stage. The main reason for the impact of organic amendments in the amount of herbicide remaining adsorbed after desorption was higher than the observed for mulches could be explained as a slowdown in time that the herbicide would need to get to the soil surface as long as rainfall and /or irrigation took place after the application and interception of the herbicides by the mulches. Results shows that CO and COD play an important role in adsorption-desorption of the three compounds. However, CO was the most important variable controlling the K_f , K_{fd} , of S-metolachlor, K_d of foramsulfuron and K_f of thien carbazole-methyl, while DOC was the one that controlled the desorption K_{fd} of the thien carbazole-methyl. A combined effect of these variable CO, DOC explained better and in significant way the variability of K_d of S-metolachlor, K_f of foramsulfuron and K_d of thien carbazole-methyl. By the results we concluded that the adsorbent OC content has been positively correlated to desorption of S-metolachlor and foramsulfuron in soils, while for thien carbazole-methyl DOC shows positive relation to desorption process.

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8. REFERENCES

- Agbaogun, Babatunde Kazeem, and Klaus Fischer. 2020. 'Adsorption of Phenylurea Herbicides by Tropical Soils'. *Environmental Monitoring and Assessment* 192(4). doi: 10.1007/s10661-020-8160-2.
- Alletto, Lionel, Pierre Benoit, Benoit Bolognesi, Matthieu Couffignal, Valérie Bergheaud, Valérie Dumény, Christian Longueval, and Enrique Barriuso. 2013. 'Sorption and Mineralisation of S-metolachlor in Soils from Fields Cultivated with Different Conservation Tillage Systems'. *Soil and Tillage Research* 128:97–103. doi: 10.1016/j.still.2012.11.005.
- Alletto, Lionel, Yves Coquet, Pierre Benoit, Djilali Heddadj, and Enrique Barriuso. 2010. 'Tillage Management Effects on Pesticide Fate in Soils. A Review'. *Agronomy for Sustainable Development* 30(2):367–400. doi: 10.1051/agro/2009018.
- Álvarez-Martín, Alba, M. Sonia Rodríguez-Cruz, M. Soledad Andrades, and María J. Sánchez-Martín. 2016. 'Application of a Biosorbent to Soil: A Potential Method for Controlling Water Pollution by Pesticides'. *Environmental Science and Pollution Research* 23(9):9192–9203. doi: 10.1007/s11356-016-6132-4.
- Amami, Roua, Khaled Ibrahim, Farooq Sher, Paul Milham, Hiba Ghazouani, Sayed Chehaibi, Zahra Hussain, and Hafiz M. N. Iqbal. 2021. 'Impacts of Different Tillage Practices on Soil Water Infiltration for Sustainable Agriculture'. *Sustainability (Switzerland)* 13(6). doi: 10.3390/su13063155.
- Aslam, Sohaib, Patricia Garnier, Cornelia Rumpel, Serge E. Parent, and Pierre Benoit. 2013. 'Adsorption and Desorption Behavior of Selected Pesticides as Influenced by Decomposition of Maize Mulch'. *Chemosphere* 91(11):1447–55. doi: 10.1016/j.chemosphere.2012.12.005.
- Ayawei, Nimibofa, Augustus Newton Ebelegi, and Donbebe Wankasi. 2017. 'Modelling and Interpretation of Adsorption Isotherms' edited by W. Guo. *Journal of Chemistry* 2017:3039817. doi: 10.1155/2017/3039817.
- Barizon, Robson R M, Ricardo de Oliveira Figueiredo, Débora Renata Cassoli de Souza Dutra, Jussara Borges Regitano, and Vera Lúcia Ferracini. 2020. 'Pesticides in the Surface

- Waters of the Camanducaia River Watershed, Brazil.’ *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes* 55(3):283–92. doi: 10.1080/03601234.2019.1693835.
- Barizon, Robson R.M., Ricardo de Oliveira Figueiredo, Débora Renata Cassoli de Souza Dutra, Jussara Borges Regitano, and Vera Lúcia Ferracini. 2020. ‘Pesticides in the Surface Waters of the Camanducaia River Watershed, Brazil’. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes* 55(3):283–92. doi: 10.1080/03601234.2019.1693835.
- Barriuso, E., D. A. Laird, W. C. Koskinen, and R. H. Dowdy. 1994. ‘Atrazine Desorption from Smectites’. *Soil Science Society of America Journal* 58(6):1632. doi: 10.2136/sssaj1994.03615995005800060008x.
- Busari, Mutiu Abolanle, Surinder Singh Kukal, Amanpreet Kaur, Rajan Bhatt, and Ashura Ally Dulazi. 2015. ‘Conservation Tillage Impacts on Soil, Crop and the Environment’. *International Soil and Water Conservation Research* 3(2):119–29. doi: 10.1016/j.iswcr.2015.05.002.
- Calvet, R. 1989. ‘Adsorption of Organic Chemicals in Soils’. *Environmental Health Perspectives* 83:145–77. doi: 10.1289/ehp.8983145.
- Carpio, María J., M. Sonia Rodríguez-Cruz, Carlos García-Delgado, María J. Sánchez-Martín, and Jesús M. Marín-Benito. 2020. ‘Mobility Monitoring of Two Herbicides in Amended Soils: A Field Study for Modeling Applications’. *Journal of Environmental Management* 260(January). doi: 10.1016/j.jenvman.2020.110161.
- Carpio, María J., María J. Sánchez-Martín, M. Sonia Rodríguez-Cruz, and Jesús M. Marín-Benito. 2021. ‘Effect of Organic Residues on Pesticide Behavior in Soils: A Review of Laboratory Research’. *Environments* 8(4):32. doi: 10.3390/environments8040032.
- Cassigneul, A., L. Alletto, P. Benoit, V. Bergheaud, V. Etiévant, V. Dumény, A. L. Le Gac, D. Chuette, C. Rumpel, and E. Justes. 2015. ‘Nature and Decomposition Degree of Cover Crops Influence Pesticide Sorption: Quantification and Modelling’. *Chemosphere* 119:1007–14. doi: 10.1016/j.chemosphere.2014.08.082.
- Cassigneul, A., P. Benoit, V. Bergheaud, V. Dumény, V. Etiévant, Y. Goubard, A. Maylin, E.

- Justes, and L. Alletto. 2016. 'Fate of Glyphosate and Degradates in Cover Crop Residues and Underlying Soil: A Laboratory Study'. *Science of the Total Environment* 545–546:582–90. doi: 10.1016/j.scitotenv.2015.12.052.
- Cassigneul, A., P. Benoit, C. Nobile, V. Bergheaud, V. Dumény, V. Etiévant, A. Maylin, E. Justes, and L. Alletto. 2018. 'Behaviour of S-metolachlor and Its Oxanilic and Ethanesulfonic Acids Metabolites under Fresh vs. Partially Decomposed Cover Crop Mulches: A Laboratory Study'. *Science of the Total Environment* 631–632:1515–24. doi: 10.1016/j.scitotenv.2018.03.143.
- Delgado-Moreno, L., and A. Peña. 2008. 'Sorptions/Desorption Behaviour of Sulfonylurea Herbicides as Affected by the Addition of Fresh and Composted Olive Cake to Soil'. *Weed Research* 48(5):461–69. doi: 10.1111/j.1365-3180.2008.00645.x.
- Djurovic, Rada, Jelena Gajic-Umiljendic, and Tijana Djordjevic. 2009. 'Effects of Organic Matter and Clay Content in Soil on Pesticide Adsorption Processes'. *Pesticidi i Fitomedicina* 24(1):51–57. doi: 10.2298/pif0901051d.
- FAO. 2016. *Save and Grow in Practice: Maize, Rice and Wheat. A Guide to Sustainable*.
- Gabriel, Jose Luis, Miguel Quemada, Diana Martín-Lammerding, and Marnik Vanclooster. 2019. 'Assessing the Cover Crop Effect on Soil Hydraulic Properties by Inverse Modelling in a 10-Year Field Trial'. *Agricultural Water Management* 222(July):62–71. doi: 10.1016/j.agwat.2019.05.034.
- García-Delgado, Carlos, Jesús M. Marín-Benito, María J. Sánchez-Martín, and M. Sonia Rodríguez-Cruz. 2020. 'Organic Carbon Nature Determines the Capacity of Organic Amendments to Adsorb Pesticides in Soil'. *Journal of Hazardous Materials* 390(January):122162. doi: 10.1016/j.jhazmat.2020.122162.
- Gavrilescu, M. 2005. 'Fate of Pesticides in the Environment and Its Bioremediation'. *Engineering in Life Sciences* 5(6):497–526. doi: 10.1002/elsc.200520098.
- Ghezzi, Jessique, Anastasios Karathanasis, Chris Matocha, Jason Unrine, and Yvonne Thompson. 2014. 'Competitive Sorption Behavior of Arsenic, Selenium, Copper and Lead by Soil and Biosolid Nano- and Macro-Colloid Particles'. *Open Journal of Soil Science* 04(09):293–304. doi: 10.4236/ojss.2014.49031.

- Ghouse, Pedda. 2020. 'Mulching: Materials, Advantages and Crop Production'. *Protected Cultivation and Smart Agriculture* (December). doi: 10.30954/ndp-pcsa.2020.6.
- Gil-Ribes, Jesús A., R. Ordóñez Fernández, E. González Sánchez, F. Sánchez Ruiz, O. Veroz González, M. Gómez, F. Márquez García, and R. Carbonell Bojollo. 2017. *Beneficios de La Agricultura de Conservación En Un Entorno de Cambio Climático*. Vol. 254.
- González-Sánchez, E. J., M. Moreno-García, A. Kassam, A. Holgado-Cabrera, P. Triviño-Tarradas, R. Carbonell-Bojollo, M. Pisante, O. Veroz-González, and G. Basch. 2017. *Conservation Agriculture: Making Climate Change Mitigation and Adaptation Real in Europe*.
- Gul, Palwasha, Khuram Shahzad Ahmad, and Mahwash Mahar Gul. 2020. 'Herbicide Thiencarbazone-Methyl Pedospheric Disposition through Sorption and Degradation Mechanisms in Heterogenous Soils'. *Environmental Earth Sciences* 79(20):1–19. doi: 10.1007/s12665-020-09179-w.
- Herrero-Hernández, Eliseo, M. Sonia Rodríguez-Cruz, Eva Pose-Juan, Sara Sánchez-González, M. Soledad Andrades, and Maria J. Sánchez-Martín. 2017. 'Seasonal Distribution of Herbicide and Insecticide Residues in the Water Resources of the Vineyard Region of La Rioja (Spain)'. *Science of the Total Environment* 609:161–71. doi: 10.1016/j.scitotenv.2017.07.113.
- Hinz, Christoph. 2001. 'Description of Sorption Data with Isotherm Equations'. *Geoderma* 99(3–4):225–43. doi: 10.1016/S0016-7061(00)00071-9.
- Ivanova, Nadezhda, Viliana Gugleva, Mirena Dobрева, Ivaylo Pehlivanov, Stefan Stefanov, and Velichka Andonova. 2016. 'We Are IntechOpen , the World ' s Leading Publisher of Open Access Books Built by Scientists , for Scientists TOP 1 %'. *Intech i(tourism)*:13.
- Kah, Mélanie, and Colin D. Brown. 2007. 'Behaviour of Ionisable Pesticides in Soils To Cite This Version : Mélanie Kah Supervisor : Professor Colin D . Brown University of York'. 1–229.
- Kan, A. T., G. Fu, and M. B. Tomson. 1994. 'Adsorption/Desorption Hysteresis in Organic Pollutant and Soil/Sediment Interaction.' *Environmental Science & Technology* 28(5):859–67. doi: 10.1021/es00054a017.

- Karanasios, Evangelos, Nikolaos G. Tsiropoulos, Dimitrios G. Karpouzas, and Urania Menkissoglu-Spiroudi. 2010. 'Novel Biomixtures Based on Local Mediterranean Lignocellulosic Materials: Evaluation for Use in Biobed Systems'. *Chemosphere* 80(8):914–21. doi: 10.1016/j.chemosphere.2010.06.003.
- Kaur, Rajveer, Gurjot Kaur Mavi, Shweta Raghav, and Injeela Khan. 2019. 'Pesticides Classification and Its Impact on Environment'. *International Journal of Current Microbiology and Applied Sciences* 8(03):1889–97. doi: 10.20546/ijcmas.2019.803.224.
- Kaye, Jason P., and Miguel Quemada. 2017. 'Using Cover Crops to Mitigate and Adapt to Climate Change. A Review'. *Agronomy for Sustainable Development* 37(1). doi: 10.1007/s13593-016-0410-x.
- Kranz, Christina N., Richard A. McLaughlin, Amy Johnson, Grady Miller, and Joshua L. Heitman. 2020. 'The Effects of Compost Incorporation on Soil Physical Properties in Urban Soils – A Concise Review'. *Journal of Environmental Management* 261. doi: 10.1016/j.jenvman.2020.110209.
- Li, Yangyang, Junfeng Niu, Zhenyao Shen, Chi Zhang, Zhengzao Wang, and Tiande He. 2014. 'Spatial and Seasonal Distribution of Organochlorine Pesticides in the Sediments of the Yangtze Estuary'. *Chemosphere* 114:233–40. doi: 10.1016/j.chemosphere.2014.04.112.
- Lionel, A., C. Yves, B. Pierre, H. Djilali, and B. Enrique. 2010. 'Tillage Management Effects on Pesticide Fate in Soils. A Review'. *Agronomy for Sustainable Development* 30:367–400.
- Luo, Gongwen, Ling Li, Ville Petri Friman, Junjie Guo, Shiwei Guo, Qirong Shen, and Ning Ling. 2018. 'Organic Amendments Increase Crop Yields by Improving Microbe-Mediated Soil Functioning of Agroecosystems: A Meta-Analysis'. *Soil Biology and Biochemistry* 124(June):105–15. doi: 10.1016/j.soilbio.2018.06.002.
- Maqueda, C., T. Undabeytia, J. Villaverde, and E. Morillo. 2017. 'Behaviour of Glyphosate in a Reservoir and the Surrounding Agricultural Soils'. *Science of the Total Environment* 593–594:787–95. doi: 10.1016/j.scitotenv.2017.03.202.
- Marín-Benito, Jesús M., M. Soledad Andrades, M. Sonia Rodríguez-Cruz, and María J. Sánchez-Martín. 2012. 'Changes in the Sorption-Desorption of Fungicides over Time in

- an Amended Sandy Clay Loam Soil under Laboratory Conditions'. *Journal of Soils and Sediments* 12(7):1111–23. doi: 10.1007/s11368-012-0525-x.
- Marín-Benito, Jesús M., Eliseo Herrero-Hernández, José M. Ordax, M. Jesús Sánchez-Martín, and M. Sonia Rodríguez-Cruz. 2021. 'The Role of Two Organic Amendments to Modify the Environmental Fate of S-metolachlor in Agricultural Soils'. *Environmental Research* 195(November 2020). doi: 10.1016/j.envres.2021.110871.
- Marín-Benito, Jesús M., M. Sonia Rodríguez-Cruz, M. Soledad Andrades, and María J. Sánchez-Martín. 2012. 'Assessment of Spent Mushroom Substrate as Sorbent of Fungicides: Influence of Sorbent and Sorbate Properties'. *Journal of Environmental Quality* 41(3):814–22. doi: 10.2134/jeq2011.0437.
- Marín-Benito, Jesús M., María J. Sánchez-Martín, and M. Sonia Rodríguez-Cruz. 2016. 'Impact of Spent Mushroom Substrates on the Fate of Pesticides in Soil, and Their Use for Preventing and/or Controlling Soil and Water Contamination: A Review'. *Toxics* 4(3). doi: 10.3390/toxics4030017.
- Marín-Benito, Jesús M., María J. Sánchez-Martín, M. Soledad Andrades, Margarita Pérez-Clavito, and M. Sonia Rodríguez-Cruz. 2009. 'Effect of Spent Mushroom Substrate Amendment of Vineyard Soils on the Behavior of Fungicides: 1. Adsorption-Desorption of Penconazole and Metalaxyl by Soils and Subsoils'. *Journal of Agricultural and Food Chemistry* 57(20):9634–42. doi: 10.1021/jf902108n.
- Marín Benito, J. 2011. 'Dinámica de Fungicidas En Suelos de Viñedo Enmendados Con Sustratos Postcultivo de Hongos'.
- Peña, David, Ángel Albarrán, Antonio López-Piñero, José Manuel Rato-Nunes, Javier Sánchez-Llerena, and Daniel Becerra. 2013. 'Impact of Oiled and De-Oiled Olive Mill Waste Amendments on the Sorption, Leaching, and Persistence of S-metolachlor in a Calcareous Clay Soil'. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes* 48(9):767–75. doi: 10.1080/03601234.2013.780884.
- Pierzynski, Gary M., George F. Vance, and Thomas J. Sims. 2020. 'Organic Chemicals in the Environment'. *Soils and Environmental Quality* 377–426. doi: 10.1201/b12786-18.

- Sabur, S. A., and A. R. Molla. 2001. 'Pesticide Use, Its Impact on Crop Production and Evaluation of Ipm Technologies in Bangladesh'. *Bangladesh J. Agric. Econs.* XXIV 1(2):21–38.
- Sánchez, Lourdes, Esperanza Romero, Francisco Sánchez-Rasero, Gonzalo Dios, and Aránzazu Peña. 2003. 'Enhanced Soil Sorption of Methidathion Using Sewage Sludge and Surfactants'. *Pest Management Science* 59(8):857–64. doi: 10.1002/ps.686.
- Santel, Hans-joachim. 2012. 'Thiencarbazone-Methyl (TCM) and Cyprosulfamide (CSA) – a New Herbicide and a New Safener for Use in Corn'. *Julius-Kühn-Archiv* 2(434):499–505. doi: 10.5073/jka.2012.434.062.
- Sciences, Crop. n.d. 'Environmental Soil Chemistry SOCR 567'.
- Sharma, Anket, Vinod Kumar, Babar Shahzad, Mohsin Tanveer, Gagan Preet Singh Sidhu, Neha Handa, Sukhmeen Kaur Kohli, Poonam Yadav, Aditi Shreeya Bali, Ripu Daman Parihar, Owias Iqbal Dar, Kirpal Singh, Shivam Jasrotia, Palak Bakshi, M. Ramakrishnan, Sandeep Kumar, Renu Bhardwaj, and Ashwani Kumar Thukral. 2019. 'Worldwide Pesticide Usage and Its Impacts on Ecosystem'. *SN Applied Sciences* 1(11):1–16. doi: 10.1007/s42452-019-1485-1.
- Silburn, D. Mark. 2020. 'Pesticide Retention, Degradation, and Transport Off-Farm'. *No-till Farming Systems for Sustainable Agriculture* (September):281–97. doi: 10.1007/978-3-030-46409-7_17.
- Silva, Vera, Hans G. J. Mol, Paul Zomer, Marc Tienstra, Coen J. Ritsema, and Violette Geissen. 2019. 'Pesticide Residues in European Agricultural Soils – A Hidden Reality Unfolded'. *Science of the Total Environment* 653:1532–45. doi: 10.1016/j.scitotenv.2018.10.441.
- Singh, Dileep. 2012. 'Pesticide Chemistry and Toxicology'. *Environmental Pollution* 61(3):261.
- Singh, Neera. 2003. 'Organic Manure and Urea Effect on Metolachlor Transport through Packed Soil Columns'. *Journal of Environmental Quality* 32(5):1743–49. doi: 10.2134/jeq2003.1743.
- Sousa, João C. G., Ana R. Ribeiro, Marta O. Barbosa, M. Fernando R. Pereira, and Adrián M.

- T. Silva. 2018. 'A Review on Environmental Monitoring of Water Organic Pollutants Identified by EU Guidelines'. *Journal of Hazardous Materials* 344:146–62. doi: 10.1016/j.jhazmat.2017.09.058.
- Spokas, K. A., W. C. Koskinen, J. M. Baker, and D. C. Reicosky. 2009. 'Impacts of Woodchip Biochar Additions on Greenhouse Gas Production and Sorption/Degradation of Two Herbicides in a Minnesota Soil'. *Chemosphere* 77(4):574–81. doi: 10.1016/j.chemosphere.2009.06.053.
- Thierfelder, Christian, Rumbidzai Matemba-Mutasa, and Leonard Rusinamhodzi. 2015. 'Yield Response of Maize (*Zea Mays* L.) to Conservation Agriculture Cropping System in Southern Africa'. *Soil and Tillage Research* 146(PB):230–42. doi: 10.1016/j.still.2014.10.015.
- Trail, Patrick, Ozzie Abaye, Wade E. Thomason, Thomas L. Thompson, Fatou Gueye, Ibrahima Diedhiou, Michel B. Diatta, and Abdoulaye Faye. 2016. 'Evaluating Intercropping (Living Cover) and Mulching (Desiccated Cover) Practices for Increasing Millet Yields in Senegal'. *Agronomy Journal* 108(4):1742–52. doi: 10.2134/agronj2015.0422.
- Tudi, Muyesaier, Huada Daniel Ruan, Li Wang, Jia Lyu, Ross Sadler, Des Connell, Cordia Chu, and Dung Tri Phung. 2021. 'Agriculture Development, Pesticide Application and Its Impact on the Environment'. *International Journal of Environmental Research and Public Health* 18(3):1–24. doi: 10.3390/ijerph18031112.
- Zhang, Wenju, Minggang Xu, Xiujun Wang, Qin Hai Huang, Jun Nie, Zuzhang Li, Shuanglai Li, Seon Woong Hwang, and Kyeong Bo Lee. 2012. 'Effects of Organic Amendments on Soil Carbon Sequestration in Paddy Fields of Subtropical China'. *Journal of Soils and Sediments* 12(4):457–70. doi: 10.1007/s11368-011-0467-8.
- Zolgharnein, Javad, Ali Shahmoradi, and Jahanbakhsh Ghasemi. 2011. 'Pesticides Removal Using Conventional and Low-Cost Adsorbents: A Review'. *Clean - Soil, Air, Water* 39(12):1105–19. doi: 10.1002/clen.201000306.