COUPLING PESTICIDES FATE MODELLING AND CONSERVATION CROPPING SYSTEMS TO REDUCE THE AGRICULTURE FOOTPRINTS ON ECOSYSTEMS

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DOCTORAL THESIS, 2023

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A report presented by the Environmental Biotechnology Engineer Marwa Douibi for the degree of Doctor in Agrobiotechnology within the PhD programme in Agrobiotechnology of the University of Salamanca.

Salamanca, 6 November 2023

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CERTIFIES:

That the present report entitled "**Coupling pesticides fate modelling and conservation cropping systems to reduce the agriculture footprints on ecosystems**" has been carried out within the Doctorate Programme in Agrobiotechnology of the University of Salamanca by the engineer Marwa Douibi, under the supervision of Dr. MARÍA SONIA RODRÍGUEZ CRUZ and Dr. JESÚS MARÍA MARÍN BENITO.

And for the record, I sign this certificate in Salamanca on the 6th of November 2023

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CERTIFY:

That the Biotechnology Engineer Marwa Douibi has carried out in the Department of Environmental Degradation Processes and their Recovery of the Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), under their direction, the work to qualify for the degree of Doctor in Agrobiotechnology presented by the title:

"Coupling pesticides fate modelling and conservation cropping systems to reduce the agriculture footprints on ecosystems"

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And for the record, they have signed this certificate in Salamanca on 6th of November 2023.

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And in loving memory of my father, Mohammed. His unwavering love, guidance, and the values he instilled in me continue to be a source of inspiration and strength, and without him, I would not have been here. This is for you.

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Conventional agriculture is an intensive farming practice that involves the use of excessive soil tillage, intensive land use, continuous inputs of synthetic chemical fertilizers and pesticides, heavy irrigation, and concentrated monoculture production. This type of agriculture is widely used as it has been successful in increasing food production and meeting the demands of a growing global population. However, it has also been associated with several environmental and sustainability issues, including soil degradation, erosion and runoff, loss of microbial diversity, chemical pollution, groundwater contamination, and emission of greenhouse gases. In response to these challenges, new soil management practices and cropping systems have been developed and implemented in the last decades to ensure alternative and more sustainable farming systems. These new practices address some of these issues while promoting long-term sustainable and environmentally friendly agricultural practices. These new approaches are represented by **conservation agriculture**.

These practices include **non-tillage**, the presence of **cover crops** during the fallow period, and the accumulation of harvested crop residues as mulch on the soil surface (**mulching**). Non-tillage and the presence of crop residues on the soil surface improve soil structure, fertility, and organic matter content, protect the soil from wind and water erosion, and maintain soil moisture while reducing the need for irrigation and increase soil microbial biodiversity.

Accordingly, all these agricultural practices and soil management have important social and agricultural benefits. However, the use of pesticides remains, to a greater or lesser extent, necessary even in this type of conservation agriculture from a productive point of view. Farmers consider pesticides (mainly herbicides) essential chemicals for increasing crop yields by controlling pests and diseases that threaten the food supply. In this regard, it is necessary to take into account that the application of these **conservation management practices** results in changes in soil physicochemical properties, which **could modify** the processes that govern the dynamics of herbicides in natural soils (adsorption, desorption, degradation/dissipation, mobility via leaching or runoff, and volatilization). Changes in these processes are highly relevant to predict **the current and future environmental fate of herbicides in soils under conservation agricultural practices**.

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Therefore, the knowledge of the fate of applied herbicides under conservation practices is particularly important and needs to be carefully studied in order to assess and minimize their potential environmental risk to soil and water quality. In this sense, the use of **mathematical models,** which evaluate the environmental fate of these compounds is of great interest, especially if they are parameterized and tested with data and results obtained under field conditions. These models, after a correct validation, can be used as a **tool to predict pesticide concentrations** in the different environmental compartments (soil, air, plant and water) **in the long-term** without carrying out further experimental tests.

In accordance with the above, and considering that there is only a few studies that combine intermediate cover crops, mulching and pesticide fate models, the **main objective of this thesis was to study under real field conditions (experimental plots) the effect of conservation agricultural practices including intermediate cover crops, the accumulation of crop residues on the soil surface (mulching), non-tillage, and direct seeding, on the environmental fate of three herbicides, S-metolachlor (SMOC), foramsulfuron (FORAM) and thiencarbazone-methyl (TCM)**. The study was carried out through: 1) the evaluation of the **dissipation, persistence, distribution and/or mobility** of the herbicides in the soil profiles under conventional and conservation cropping systems, 2) the changes in soil **microbial communities** influenced by these agronomic practices as indicators of soil quality and conservation, and 3) the modelling of the herbicides' environmental fate using **PRZM** (Pesticide Root Zone Model) and **MACRO** (Water and solute transport in macroporous soils) models, that were parameterised and validated with data measured under real field conditions to **predict the impact and viability of these agronomic practices** on soil sustainability and surface and groundwater quality in the long-term.

In order to achieve the main objective of the work, the following **secondary objectives** were addressed:

1.   Evaluation of the **adsorption-desorption behaviour of the herbicides SMOC, FORAM, and TCM** by soils and mulch involving two different agricultural practices, winter wheat mulch alone and soil amended with mulch as an organic amendment, considering this process is an indicator of their potential environmental fate. The adsorption-desorption behaviour of these compounds was compared for (a) winter

wheat mulch residues at different stages of decomposition and particle size, (b) unamended soils and (c) soils amended with milled wheat mulch in order to assess the real **impact of using cover crop residues as mulches or as soil organic amendment on the retention of herbicides** and conclude about the best strategy to avoid groundwater contamination.

2. Determination of the **degradation kinetics of SMOC, FORAM and TCM, and the formation of their metabolites** in milled wheat mulch, unamended and milled wheat mulch amended agricultural soils **under laboratory conditions at two different temperatures**, 14ºC and 24ºC, to obtain the respective Q_{10} factor for the subsequent simulation of the environmental behaviour of herbicides with PRZM and MACRO models.

3. Evaluation of the **dissipation kinetics of the herbicides SMOC, FORAM and TCM and the formation of their degradation metabolites** in agricultural soils under conventional tillage (soils) and non-tillage practices (soils+mulch) after two applications (once per year) **in a two year field experiment.** Adjustment of the herbicides' dissipation to the simplest and most acceptable kinetic model for their description through statistical indexes.

4. Evaluation of the **changes in soil microbial communities after the second application of SMOC, FORAM and TCM herbicides** in soils under conventional and non-tillage treatments under field conditions. Determination of the evolution of the respiration, enzymatic activity, total microbial biomass and structure of the soil microbial communities over the second dissipation period of these herbicides in experimental plots.

5. Evaluation of the **distribution of SMOC, FORAM and TCM herbicides through the soil profile** (0-50 cm) after their application (once per year) **in experimental plots** cultivated with maize under conventional (soils) and non-tillage (soils+mulch) practices **over a two-year field experiment**. Determination of the effect of non-tillage practices on the environmental behaviour of the herbicides based on the relationship of herbicide concentrations with the characteristics of the soil profile with and without tillage, and irrigation/precipitation events.

6. **Simulation of the volumetric soil water content and the mobility of the herbicides SMOC, FORAM, and TCM through the soil profile** under conventional and conservation agriculture practices using the **PRZM and MACRO** models. Evaluation and comparison of the performance of both models for their potential use as tools to predict the environmental fate of these herbicides under conservation agricultural practices.

INTRODUCTION

1. INTRODUCTION

1.1 PESTICIDES

Pesticides are chemical compounds or a mixture of chemical substances predominantly used in agriculture, intended to prevent, inhibit, destroy or kill living organisms known as pests to increase agronomic yields and food production (Dar et al., 2020; Siddiqui et al., 2022).

The term pesticide is usually connected to insecticides only; however, pesticides are not exclusive to insecticides. In fact, pesticides include a variety of subclasses, sorted based on their target pests. Pests are described by World Health Organization (WHO) as "any plant, animal or pathogenic agent, strain or plant biotype harmful to plants and their products, ecosystems and include vectors of human and animal disease parasites or pathogens causing harm to people's health". Pesticides targeting insects are called insecticides, weeds are herbicides, fungi and moulds are fungicides, rodents are rodenticides and so on (Richardson et al., 2019).

Despite their crucial benefits for agricultural production, pesticides can be destructive and toxic to ecosystem biodiversity (soil, water and air contamination) and human health since these chemicals can affect non-target organisms as much as target organisms (Sabzevari and Hofman, 2022). In fact, less than 1% of the total amount of pesticides applied for weed and pest control reach the target pests (Bernardes et al., 2015). However, farmers regard pesticides as a necessary tool to fight and control pests and diseases that threaten the food supply.

1.2 CURRENT PRODUCTION AND USE

The significant increase in the world's population, which is now more than three times larger than it was in the mid-twentieth century and reaching 8.0 billion in mid-November 2022, with an annual variation of 5.9% from an estimated 2.5 billion people in 1950, 1 billion people have been added since 2010 and 2 billion since 1998 (Worldometer, 2023). World's population is expected to increase by almost 2 billion over the next 30 years, reaching 10 billion, but it is only possible with a parallel increase in food production. To meet this demand, the food supply factors of increased yields,

expansion of agricultural area and increase in crop and livestock farming productivity are necessary. This would not be possible without the use of pesticides, as about a third of crop production is dependent on these chemicals (Tudi et al., 2021).

Business Association for the Protection of Plants (AEPLA) reported an estimated loss of 40% of crop production worldwide due to pests and diseases. The FAO has estimated that 50% of the cotton grown in the developing world would be destroyed if it was not treated with insecticides, as bollworms can almost destroy it; they can reduce yields to just 21.3% and 59.7%, respectively (Lalah et al., 2022). However, in maize, yield increases of 24.4%, 38.4% and 10.7% were achieved by insecticide control of corn borers, leaf hoppers and corn rootworms, respectively. In wheat, yield increases of 79%, 47% and 29.5% were achieved by insecticide control of brown wheat mites, cutworms and white grubs, respectively (Yu, 2008). Pesticides not only reduce losses from pests and weeds but also increase farmers profits by reducing the need for workloads, especially when using herbicides.

Worldwide use of pesticides has increased steadily over the last few decades and now stands at approximately 3 million tonnes, 80% higher than in 1990 when it was 1.7 million tonnes (**Figure 1**) (FAOSTAT, 2020). The top pesticide-consuming countries in 2020 were the United States at 407.8 thousand tonnes, Brazil at 377.2 thousand tonnes, and China at 263 thousand tonnes (**Figure 2**) (FAO, 2022).
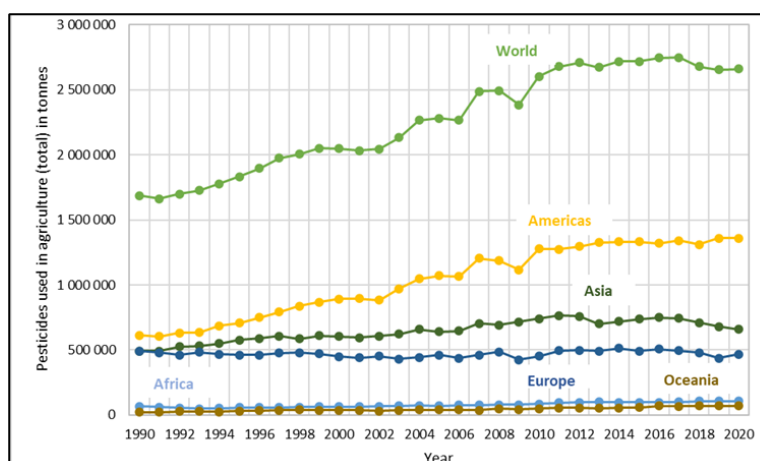
Figure 1. Pesticides use worldwide and in different world regions between 1990 and 2020. The graph is drawn based on data from FAOSTAT (2020).
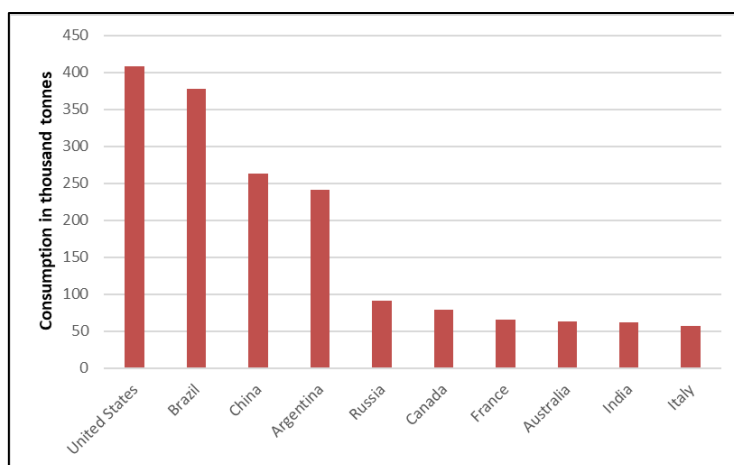
Figure 2. Top ten leading countries in agricultural consumption of pesticides worldwide in 2020 (FAO, 2022).

The global pesticide market size reached nearly $84.5 billion in 2019, with an annual growth rate of more than 4% since 2015. Over the next few years, the growth rate will likely increase even further (Pesticide Atlas, 2022). By 2023, the total value of all pesticides in use will be nearly $130.7 billion, an increase of 11.5% per year. Syngenta Group, Bayer, Corteva and BASF are the four top agrochemical companies dominating the global market of pesticide production by 75% (Böll-Stiftung, 2019). In 2020, global herbicides consumption reached 52% of total pesticide consumption, followed by fungicides and bactericides by 23%, then insecticides by 18% (**Figure 3**) (FAO, 2022).
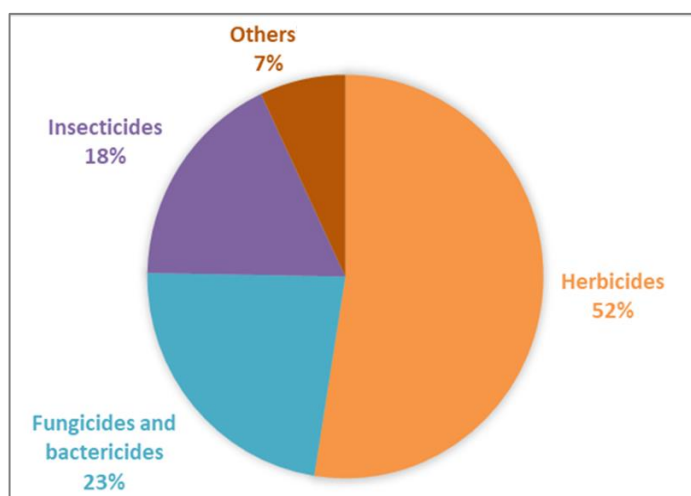
Figure 3. Agricultural consumption by type of pesticides worldwide in 2020, (FAO, 2022).

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The consumption of pesticides in the countries of the European Union (EU) remained relatively stable, with total annual consumption of 34600 tonnes in 2020, compared to 304031 tonnes in 2019 (FAOSTAT, 2023). As shown in **Figure 4**, the most pesticide consuming countries in the EU are France (65216 tonnes), Italy (56556 tonnes), Germany (48002 tonnes) and Spain (43337 tonnes) (FAOSTAT, 2023).
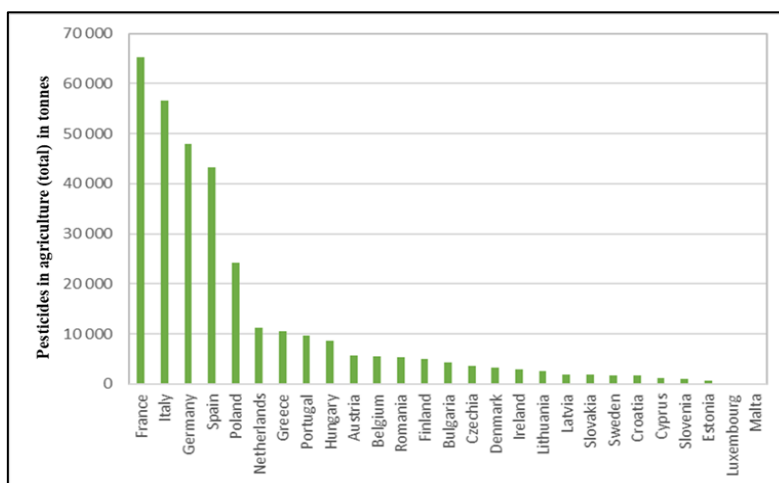
Figure 4. Pesticides use (tonnes) in the European Union countries for the year 2020. The graph is drawn based on data from FAOSTAT (2023).

Despite this, there has been a significant decrease in the consumption of pesticides in Spain compared to 2017, when it was estimated at 60896 tonnes (FAOSTAT, 2023). The most used pesticides in Spain in the year 2020 were: fungicides and bactericides with 32123 tonnes (74%), herbicides with 6093 tonnes (14%), insecticides with 4461 tonnes (10%) and other pesticides forming the last 2% with 658 tonnes (FAOSTAT, 2023) (**Figures 5** and **6**).

In recent years, multiple countries of the EU and the European Free Trade Association (EFTA) have established a series of regulations intended to decrease the use of pesticides within these countries. Some countries have banned some types of pesticides that were classified hazardous like the herbicide glyphosate, that was banned permanently by Luxembourg since the first of January 2021, as it was considered carcinogenic by the EFTA.
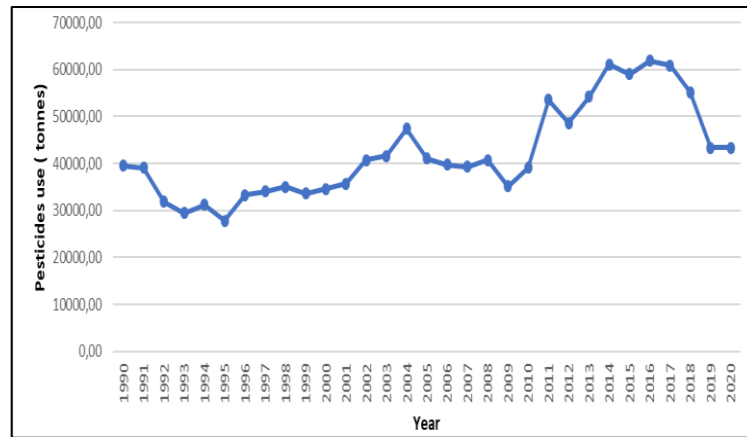
Figure 5. Total pesticides use between 1990 and 2020 measured in tonnes in Spain (FAOSTAT, 2023).
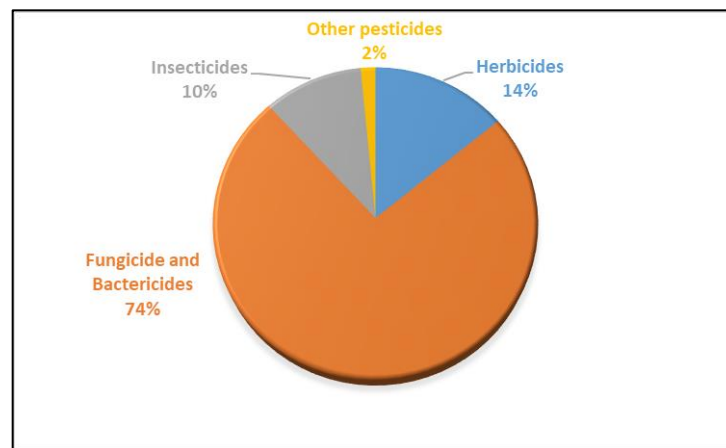
Figure 6. The most used pesticides in Spain in the year 2020. Chart drawn based on the data from FAOSTAT (2023).

1.2.1 Pesticide characteristics

Each pesticide contains at least one active ingredient coupled with compatible inert ingredients of chemicals (EPA, 2014). Active ingredients are the chemicals in a pesticide that influence pests. These substances are not suited for direct field application in a pure form, therefore, the use of inert ingredients is indispensable for proper pesticide formation (Lalah et al., 2022). Inert ingredients, which are adjuvants, help the active ingredients to be delivered to the target pests, they are essential to the performance and usefulness of

the commercial product. Adjuvants are grouped into three general types: activators, spray modifiers and utility modifiers (Sherwani et al., 2015). They are either added directly to the pesticide formulation, or used in the spray tank to modify their activity or application characteristics, improving the pesticide's efficiency since the concentration applied against pests in the field is considerably low. Moreover, they contribute to minimising their drift off-site movement at the time of application, enhancing the mixing with active ingredients, reducing foam formation in the spray tank, and increasing droplet coverage (Chow, 2017; Sherwani et al., 2015).

New strategies are now in place for the manufacture of commercial pesticides because for a pesticide to be ready for use, it should be: 1) less persistent in the environment with high degradation rates, 2) particular to target pests with no chance of affecting non-target organisms and, 3) the effective application dose is extremely low (Umetsu and Shirai, 2020). Introducing these new strategies is essential to reduce the hazardous effect of these compounds on the environmental bodies (soils, water, and air) and human health, as the agricultural community is still highly dependent on these substances to protect crop yields and prevent their loss to pests.

1.2.2   Types of pesticides

Pesticides are chemicals man-made and cannot be found naturally. These compounds belong to different classes depending on their physical and chemical properties that differ from one class to another. There are three popular methods to classify pesticides depending on their: i) mode of action, ii) pesticide function and the pest target, iii) chemical composition of the pesticides (**Figure 7**) (Kearney et al., 2000).

The **mode of action** is known as the ways in which pesticides come into contact with or enter the target organism. In this category, pesticides are classified as systemic and non-systemic (contact), stomach poisoning, stomach toxicants and fumigants. Systemic pesticides can enter and move within the animal or plant to kill target pests (Parween and Jan 2019). Non-systemic (contact) pesticides are toxic when they encounter the target organism but do not penetrate the plant or animal, and the contact is superficial. Stomach poisoning and stomach toxicants enter the target pests through the mouth and digestive system, whereas fumigant pesticides are toxic to organisms via the vapour that

produces toxic gases, killing pests by inhalation (Parween and Jan, 2019; Tsao et al., 2002).
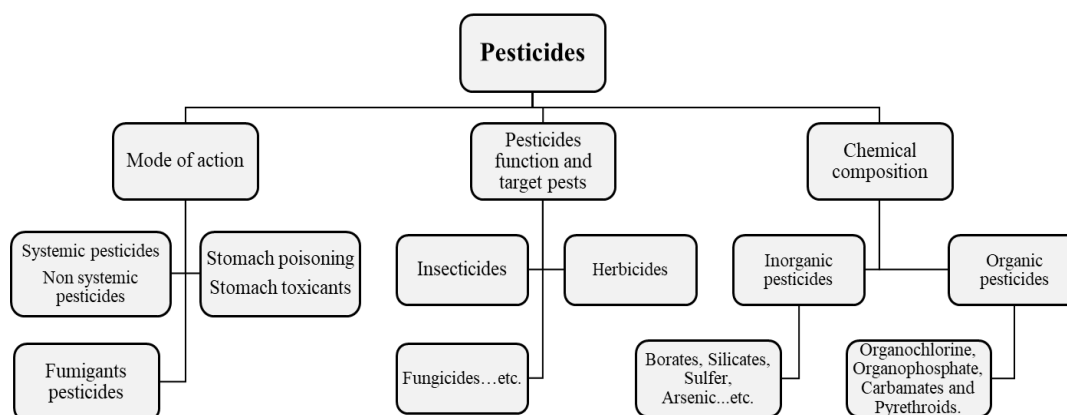
Figure 7. Classification of pesticides

The second classification is based on the **pesticides function and the pest organisms they kill.** Under this category, the pesticides are given a special nomenclature based on the targeted pests they destroy, the names finish with the suffix *-cide,* which means to kill in *latin*. For example, the pesticides that kill or control insects are called insecticides, pesticides killing weeds are called herbicides, fungicides kill fungi, rodents like rats and mice, are killed by rodenticides, bacteria are with bactericides and so on (Parween and Jan, 2019).

The third classification is based on the **chemical composition of the pesticide**. This method is the most effective way of categorising pesticides, as it provides the necessary information on how the pesticide is used and the application rate. The pesticides are classified into organic and inorganic pesticides. The inorganic pesticides consist of borates, silicates, sulphates, arsenic, copper, lead, etc. Moreover, organic pesticides are classified into four major classes: organochlorine (OCs), organophosphate (OPs), carbamates and pyrethroids (Lalah et al., 2022; Parween and Jan, 2019).

There are also another class of pesticides called **biological pesticides** or **biopesticides**. Biopesticides are naturally made pesticides, where their active ingredients are natural materials such as plants, animals and microorganisms (bacteria, fungi, viruses

and nematodes) (Neal et al., 2018). This class falls into three categories: microbial pesticides, plant-incorporated protectants (PIPs), and biochemical pesticides. Biopesticides tend to be more environmentally friendly because they are less toxic, break down easily, and are needed in small quantities, contrary to the currently used pesticides.

1.2.3 Herbicides

Herbicides are agrochemical compounds that belong to a class of pesticides used to control, destroy or kill the development of undesirable plants that grow in a crop field, called weeds (Mesnage et al., 2021; Sherwani et al., 2015). Herbicides are the largest pesticides type consumed globally, accounting for 52% of global pesticides use in the year 2020, followed by fungicides, bactericides and insecticides (**Figure 3**), being China the leading country in herbicides consumption with 226844 tonnes (FAOSTAT, 2023). Spain's herbicide consumption was estimated at 6093 tonnes in 2020 (FAOSTAT, 2023). Glyphosate and atrazine have been the most widely used herbicides globally in recent years (Böll-Stiftung, 2019; Chang et al., 2022; Sabzevari and Hofman, 2022).

Weeds are unwanted plants that grow in an agricultural field and compete with the main crop for nutrients, light and water, causing yield destruction and losses (Zimdahl, 1991). The growth of weeds in agricultural fields leads to excessive use of herbicides and increasing manual labour (Mesnage et al., 2021). The global loss of crop yields due to weeds is estimated at 10% (Chauhan, 2020).

A study of 11 years was conducted by Gharde et al. (2018) to estimate the loss of different crops to weeds. It showed a 50% − 76 % loss for soybean, 15% − 60 % for rice, and 18% − 65 % for maize. Another study estimated that a loss ranged from 2.9 % to 34.4 % in Canada and the United States of America (USA) (Flessner et al., 2021). Therefore, the use of herbicides is essential for the protection of agricultural crops and for securing food production.

Herbicides mode of action in weeds encompasses a variety of processes which occur from the point of contact between herbicides and the plant, through the droplet's persistence on the surface or inside the plant, its translocation and metabolism activity within the plant, as well as the physiological response of the plant due to the biochemical mechanism of the active ingredients at the target site. Depending on the biochemical activity of the active ingredients at the target site, herbicides have common cytotoxic

agents, such as compounds inhibiting the photosynthesis reaction, modulators of cell division and growth (inhibition of cell proliferation, DNA replication, RNA, and protein synthesis) and cellular metabolism disruptors. Plant's cell nucleus, cell wall, chloroplast and mitochondria are the common cellular targets where herbicide's biochemical activity takes place (Székács, et al,. 2021).

Herbicides can be classified based on different categories, based upon their application time, toxicity mode or specificity, or mode of exposure (Sherwani et al., 2015; Vats, 2015). **Figure 8** resumes all the different classification of herbicides.
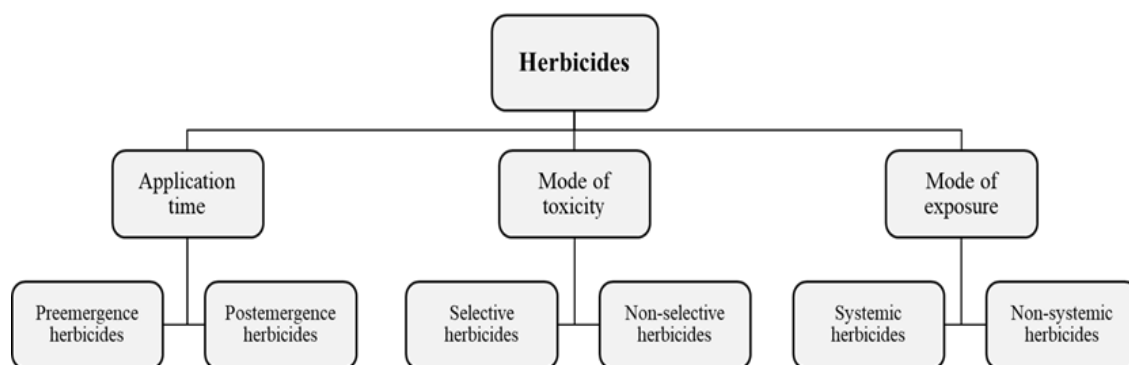
Figure 8. Classification of herbicides.

In terms of **application timing**, there are pre-emergence herbicides, which are applied before the weeds emerge as seedlings and post-emergence herbicides are applied after weed seedling has emerged (Lalah et al., 2022; Vats, 2015).

Based on **their mode of toxicity**, herbicides are divided into two categories: selective herbicides, which are toxic to specific plant species without affecting other plants (specific target), and non-selective herbicides, which are capable of killing all plant species (broad target) (Sherwani et al., 2015).

Based on **the mode of exposure**, there are systemic herbicides, which act by getting translocated within the plant through its vascular system, and non-systemic herbicides, which only kill the part of the plant´s tissue they come into contact with (Vats, 2015).

The use of herbicides to control weeds is an essential agricultural practice to mitigate the loss of crops. Herbicides can be applied through the foliage or the soil; however, it does not matter the method of application because a portion of the amount applied will always end up in the soil.

Once herbicides are in the soil, their fate is governed by the interaction between a variety of processes such as; adsorption-desorption, degradation, leaching, volatilization and absorption by plants (Acharya et al., 2020; Gao et al., 2021; Gul et al., 2020; Mendes et al., 2022; Temgoua et al., 2020). These processes, in turn, are controlled by the soil's physicochemical and biological characteristics, the herbicide's properties and the environmental conditions in which the interaction occurs (Guimarães et al., 2022; Willkommen et al., 2021).

Long persistent herbicides in soils can lead to the contamination of both soil and water as herbicides move through the soil profile to reach groundwater or surface waters such as rivers, reservoirs and lakes through runoff (Nogueira Bandeira et al., 2022). Also, their presence in the soil can affect its microbiota and cause toxic alteration (Allagui et al., 2018). Therefore, the use of these products should be monitored in a way to avoid the contamination of these systems.

1.2.4 Contamination of soil and water by herbicides

The use of herbicides in agriculture is indispensable to secure food production and enhance crop yields to cover the rising demand for food due to the increasing world population. Nevertheless, these compounds are considered hazardous to human health and the environmental compartments and can cause severe alterations in these systems leading to their contamination (Allagui et al., 2018). The contamination of soils and water by herbicides is produced by the leaching and runoff of these compounds or by drifting while spraying or wind erosion from agricultural fields (Sherwani et al., 2015; Yang et al., 2016). The concentration of herbicide residues found in soils and waters differs from one site to another, depending on their chemical properties, application method, soil type and agricultural management in the field (Graymore et al., 2001). Last years, herbicide residues have been detected in soils and waters from different agricultural areas in the world (Herrero-Hernández et al., 2017; Kosubová et al., 2020; Silva et al., 2019; Zambito et al., 2020).

The extensive use of herbicides in agricultural fields is the leading cause of soil contamination. This occurs in conventional agriculture, where excessive soil tillage leads to frequent use of herbicides to control weeds. Consequently, this type of agricultural practice led to soil degradation, erosion and depletion of organic carbon OC, which ultimately increases herbicide leaching into groundwater (Thiour-Mauprivez et al., 2019).

High herbicides residues in soils have been shown to reduce the abundance and biomass of microorganisms, along with their enzymatic activity, such as the inhibition of dehydrogenases, catalase, urease, acid phosphatase, alkaline phosphatase, arylsulfatase and β-glucosidase enzymes (Baćmaga et al., 2014; Thiour-Mauprivez et al., 2019; Wang et al., 2023). These enzymes play a crucial role in breaking down herbicides into non-toxic and more stable compounds in soils. Their inhibition means that herbicides remain in the ecosystem for longer periods. High doses of herbicides in soil could also have a negative effect on denitrifying bacteria causing alteration in nitrogen cycling in the soil, as well as inhibiting the activity of zinc-solubilizing bacteria (Ghani et al., 2022; Sathya et al., 2018).

Herbicides interaction with soils also depends on their physicochemical properties. High water solubility and low adsorption onto soil particles governed by rainfall will lead at the end to their vertical movement from soil to groundwater (Islam et al., 2018). Phenylurea herbicides have been reported to be water body pollutants because of their high solubility in water (Hussain et al., 2015).

Herbicides are frequently found in soils, but their ultimate fate will be in aquatic systems. After their application in fields, they can reach surface waters such as rivers, lakes, oceans, and groundwater through leaching or soil runoff (Ribeiro et al., 2022). The contamination of water bodies by herbicides poses a serious threat to aquatic ecosystems. It has been shown that high concentrations of atrazine in water streams led to the destruction of macrophyte communities and decreased water pH due to decreased bicarbonate uptake for photosynthesis (Graymore et al., 2001; Solomon et al., 2013). It also affects the algae community by reducing its biomass and abundance through inhibition of photosynthesis, the same as zooplankton, macrophytes, gastropods, crustacea and aquatic insects (Graymore et al., 2001).

The toxic effect of herbicide residues can also affect the fish population, as exposure to high herbicide concentration results in changes in their immune, respiratory, reproductive, nervous and gastrointestinal systems (Ribeiro et al., 2022). In addition,

changes related to inhibiting vital enzymes of the vertebrate metabolism, fatty acid degeneration in the liver and neuronal degeneration in the brain have been reported (Singh et al., 2020a). Also, herbicides may contaminate drinking water sources, causing severe health effects like cancer, liver failure, anaemia and eye infection (Ghani et al., 2022).

1.3 HERBICIDES DYNAMICS IN SOILS

The distribution of herbicides after their application to agricultural soils is affected by three major processes: 1) **Accumulation**, mainly determined by their adsorption-desorption; 2) **Elimination**, determined by their degradation; and 3) **Movement**, determined by processes including leaching, runoff, volatilization and absorption by plants (**Figure 9**) (Sandanayake et al., 2022; Vagi and Petsas, 2022).
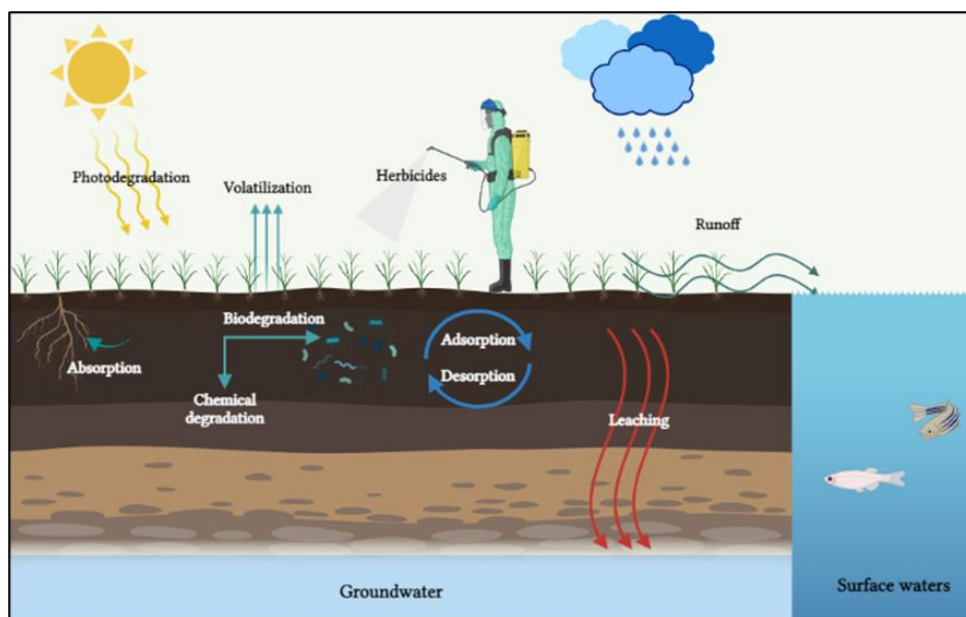
Figure 9. Processes governing herbicides dynamics in soils (Created with BioRender).

1.3.1   Accumulation process: Adsorption-desorption of herbicides in soils

The accumulation process of herbicides involves their transfer from one compartment to another without the interference of any chemical transformation and the

maintenance of the herbicidal function. It is mainly determined by an adsorption and desorption process.

Adsorption of herbicides by soils is the prominent phenomenon that governs the environmental fate of herbicides, it is a fundamental process that influences other processes, such as degradation, leaching, volatilization and runoff of herbicides in soils (Gul et al., 2020). Soil adsorption is the physical-chemical process by which a molecule, ion or other particle adheres to the soil surface as a result of the interaction between the dissolved substances (e.g. herbicides) and the interface of the adsorbent (soil) by Van der Waals forces, charge transfer, ion exchange, hydrogen bonding or hydrophobic interactions (Blanco et al., 2013; Essington, 2003; Sadegh-Zadeh, 2017). Soil adsorption is generally a reversed phenomenon being the **desorption** a process where the adsorbate is released from the adsorbent surface, making it negatively related to the adsorption energy (Peña et al., 2022). The desorption process is equally essential as it moderates the release rate at which herbicides become mobile in the soil (Kumari et al., 2020; Yue et al., 2017).

The adsorption-desorption processes are strongly influenced by the physicochemical properties of the soil, including organic matter (OM), dissolved organic matter (DOM), type and amount of clay minerals, ion exchange capacity and pH (Acharya et al., 2020; Carpio et al., 2021; Sadegh-Zadeh, 2017). It is also influenced by the physicochemical characteristics of herbicides, such as water solubility, octanol-water partition coefficient and pK_a value (Wu et al., 2011). Herbicides' water solubility is the most critical factor controlling their adsorption by soil. James et al. (2019) reported that herbicides with high solubility in water have less tendency to be adsorbed.

The soil OM is one of the soil's most relevant constituents affecting herbicides' adsorption, followed by clay fraction. OM has a complex surface activity due to the presence of different chemical functional groups such as carboxyl, carbonyl and phenolic groups (Spohn et al., 2022). Most of herbicides are adsorbed by the soil, acting these functional groups as binding sites for herbicides through ion-dipole, hydrogen and hydrophobic interactions or Van der Waals forces (Takeshita et al., 2019; Yue et al., 2017). The increase in these functional groups correlated positively with the increase in OM, leading to enhance the adsorption capacity of herbicides by soils (Chang et al., 2022). Several studies showed that the increase in OM led to increased herbicide adsorption by soils (James et al., 2019; Kumari et al., 2020; Liu et al., 2001; Tomić et al.,

2015). Also, the desorption of herbicides from soils is governed by OM, showing a reduction of 30-57% desorption of diuron with the increase in OM of soils (Petter et al., 2016). Meanwhile, high desorption of flucetosulfuron was observed in sandy loam soils with relatively low content in OM (Kumari et al., 2020).

The adsorption of herbicides is also affected by the presence of DOM in the soil solution (Sadegh-Zadeh, 2017). It has been widely reported that DOM alters the adsorption behaviour of herbicides depending not only on the physicochemical properties of the chemicals but also on the source, properties, composition and concentration of the DOM (Ben-Hur et al., 2003; Peña et al., 2022; Tian et al., 2019).

Clay minerals also affect the adsorption of herbicides by soils. Guimarães et al. (2022) reported that the adsorption of tebuthiuron herbicide was 30% and 35% higher in clay soil than in loamy-sandy soil. These values corresponded with the desorbed amount (19% higher) in loamy-sandy soils. Soil moisture also has a significant effect on the process, the higher the moisture, the lower the adsorption. This is because H^+ ions, whose concentration depends on soil moisture, compete with herbicide molecules for adsorption sites on the surface of soil colloids and this results in increased adsorption under water deficit conditions (Garcia Blanco et al., 2013).

The adsorption of some herbicides is also pH dependent when the fluctuation of soil pH can affect herbicides with acidic or weak basic properties (Gámiz et al., 2019). However, the effect of pH is not highly consistent, it depends mainly on the herbicide's physicochemical properties (Maheswari and Ramesh, 2007; Sunulahpašić et al., 2020) since non-ionic herbicides have shown a high tendency to be adsorbed by soil colloids than acidic herbicides (Jamshidi et al., 2022). Lower adsorption of herbicides by soils when the pH is high has been reported, although other authors showed high adsorption in low pH levels (Kumar and Singh, 2020; Kumari et al., 2020; Palma et al., 2016; Pandey et al., 2021). For phenylurea herbicides, pH is considered the second most influential factor for their adsorption after soil OM content (Agbaogun Fischer, 2020; Dan et al., 2021; El-Nahhal and Elabadsa, 2013; Hussain et al., 2015).

1.3.2 Elimination processes: Degradation of herbicides in soils

The elimination process of herbicides in soils is related to the removal of these substances through chemical, photochemical or biological transformation, resulting in

smaller compounds with different properties than the initial substances. This process is mainly known as **degradation**.

Degradation is the process by which the herbicides are broken down into more environmentally stable and non-toxic smaller molecular substances and is considered, alongside adsorption, to be a major process influencing the fate of herbicides in soils (Huang et al., 2018). It is important to understand the mechanism of herbicides' degradation/dissipation to evaluate their behaviour and fate in the natural environments.

The degradation of herbicides in soils occurs through two main paths: abiotic degradation, such as photodecomposition (Huang et al., 2019), oxidation (Jiang et al., 2020) and hydrolysis (Temgoua et al., 2020), and biotic degradation, mainly represented by the microbial degradation (Pang et al., 2020).

Abiotic degradation is the process of chemically degrading herbicides into more stable molecules. The major abiotic transformation of herbicides occurs by photodegradation and chemical reduction (hydrolysis, oxidation, hydroxylation….. etc.) (Chand et al., 2022; Chen et al., 2018; Jiang et al., 2020; Pang et al., 2020). **Photodegradation** is the decomposition of herbicides under the influence of sunlight. After application, herbicides are present on the soil or plant surface and are exposed to sunlight, where they absorb light energy causing molecular excitation and oxidation of functional groups in the herbicide molecules as a result of various organic reactions (Katagi, 2004). Photodegradation of herbicides in soils is a complex process because of the heterogeneity of soil compounds, their characteristics, and the climatic conditions, which can affect herbicide degradation (Coleman et al., 2020). Nevertheless, photodegradation and hydrolysis are the most dominant reactions that herbicides undergo under abiotic degradation (Chand et al., 2022; Ghani et al., 2022; Gul and Ahmad, 2020; Liu et al., 2021; Noshadi and Homaee, 2018).

Biotic degradation or biodegradation of herbicides is the process by which soil microbes (bacteria, fungi and yeast) use herbicides as a source of nutrients and energy through a series of physiological and biochemical reactions due to their enzymatic activity. These chemical compounds are entirely broken down into smaller substances, usually inorganic compounds, carbon dioxide, and water (Carpio et al., 2021; Sadegh-Zadeh, 2017; Wołejko et al., 2017). The process where these organic compounds are degraded into more stable and non-toxic inorganic molecules is called mineralization (Huang et al., 2018). In the environment where microorganisms coexist, bacteria are

responsible for the majority of herbicides degradation in soils, where a variety of bacteria species proved to be efficient in degrading these compounds (Khatoon and Rai, 2020; Łozowicka et al., 2021; Singh et al., 2020b). Biodegradation is considered the most important process controlling the mineralization of herbicides in the environment, thereby reducing their persistence and mobility in soils (Carpio et al., 2020; James et al., 2021).

Several factors control herbicides dissipation in soils, varying from soil´s physicochemical parameters such as OM and clay content, pH and texture, alongside its biological properties including density, variation and activity of the microbial population, as well as the climatic factors such as water content and temperature (Hussain et al., 2015; Marín-Benito et al., 2019). On the other hand, the physicochemical properties of herbicides such as their structure, composition, water solubility and application method are also important (Huang et al., 2018; Pandey and Choudhury, 2021).

The presence of high amounts of OM has been proven to have a significant decrease in herbicides dissipation in soils and increasing their persistence (Carpio et al., 2021; Dollinger et al., 2022; Fernandez et al., 2020; James et al., 2021; Marín-Benito et al., 2019). On the contrary, the degradation of herbicides was significantly faster in soils with low content of OM (Takeshita et al., 2019). This is because the OM promotes the adsorption of herbicides by soil, reducing their bioavailability to be degraded (Carpio et al., 2021). However, it has been cited that the DOM could reduce the adsorption of herbicides by increasing their solubility, thereby increasing their availability for degradation (Yang et al., 2021). Nevertheless, DOM's influence on pesticide biodegradation depends on its source, nature and concentration, and therefore on soil type and pesticide characteristics (Artigas et al., 2020; Rodríguez-Liébana et al., 2017).

Soil pH can often alter the degradation of herbicides because it could interfere with herbicides oxidation and biodegradation, as has been shown (Hussain et al., 2015). For herbicides mainly degraded by microorganisms, their degradation rate tends to be faster under alkaline pH because of their high biological activity under these conditions (Hussain et al., 2013; Villaverde et al., 2008). Also, herbicide characteristics have been shown to alter their degradation under different pH levels (Chand et al., 2022; James et al., 2021; Rao, 2019).

Another important factor in controlling herbicide degradation in soils is the temperature since high temperature can enhance microbial biomass and microorganism activity, increasing herbicide degradation rates (James et al., 2021; Marín-Benito et al.,

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2019). Overall, herbicides bioavailability in soils mostly depends on moderate soil OM content, lower clay content, higher pH and temperature or moisture content (Gehrke et al., 2021).

1.3.3 Movement processes: Leaching, runoff, volatilization and plant uptake of herbicides in soils.

Movement of herbicides in soils is the process by which herbicides are transported through the soil profile or to the air, being different phenomena involved in their transport into deeper soil layers such as leaching, runoff, and plant absorption, as well as their volatilization from the soil or plant surface to the air.

Leaching process of herbicides involves their horizontal and vertical movement downward through the soil profile along with water flow (Braschi et al., 2011; Guimarães et al., 2019). Leaching phenomena are affected by soils physicochemical properties such as OM, clay type and content, soil pH, and the physicochemical characteristics of herbicides and climatic conditions (Willkommen et al., 2021). Rainfall intensity and irrigation patterns are important factors affecting herbicides leaching into groundwater and the adsorption process (Islam et al., 2018; Nogueira Bandeira et al., 2022). To some extent, herbicides move with the rainwater as it moves down the soil profile from the surface (Meite et al., 2018, 2018). Adsorption is the major phenomenon influencing herbicide movement, as it controls herbicide availability in soils (Gul et al., 2020). Herbicides with low adsorption to soil particles are easily transported with the water flow under high rainfall intensity. Therefore, the rate of movement of herbicides alternates between being dissolved in water and moving with it or being adsorbed to soil particles resulting in its immobilisation (Nogueira Bandeira et al., 2022). Another factor contributing to herbicide leaching is the existence of preferential flows, which refers to the uneven and often rapid movement of water and solutes through porous soils due to the presence of macropores created by root zones, fractures or the action of soil fauna such as earthworms (Cueff et al., 2020; Lupi et al., 2019).

The **runoff** process is the transport of dissolved herbicides from agricultural land by water to surface water bodies such as reservoirs, lakes, streams and rivers, causing contamination (Krutz et al., 2005). The surface transport of herbicides is controlled by soil properties, soil type, rainfall intensity and herbicides properties (Lerch et al., 2017).

The type of agricultural practice can also increase herbicide runoff. For example, in conventional agriculture, extensive tillage and high soil disturbance with frequent applications of herbicides in bare soils to control weeds lead to soil degradation and reduced water-holding capacity, resulting in herbicide runoff (Baffaut et al., 2020). Therefore, to mitigate herbicide runoff, new conservation practices have been developed. Among these new practices is the adoption of permanent soil cover using crop residues or mulch (Thierfelder et al., 2018). The presence of crop residues on the soil surface protects the soil from raindrop impacts, increases soil infiltration, and enhances water-holding capacity (Elias et al., 2018; Silburn, 2020; Vaz et al., 2021). Another important practice that proved to be efficient in reducing herbicides surface transport is the vegetative buffer strips (VBS). They are areas planted with grass or other vegetation, usually placed between an agricultural field and a watercourse that traps herbicide transport and reduces off-site movement (Carretta et al., 2017; Krutz et al., 2005). It has been proven to be an efficient practice by increasing dissolved herbicides adsorption to vegetation or soil, increasing water infiltration and enhancing soil-solute interaction (Lerch et al., 2017).

In recent years, a new approach has been also investigated and proved to be useful in mitigating herbicide runoff: adding adjuvants to spray tanks with specific properties that promote herbicides binding to soil and reducing their runoff while maintaining herbicides efficiency (Fillols and Davis, 2020).

Volatilization is herbicide loss due to evaporation from its liquid to gaseous phase by transforming from the spray droplets or soil and plant surface to the atmosphere (Schreiber et al., 2015). Volatilization is a highly unwanted process for several reasons: i) the loss of an amount of herbicides in the air results in a lower amount of applied dose to reach the target weed, and more herbicide has to be applied, and ii) once in the atmosphere, the herbicide is transported and deposited in soil and water surfaces causing their contamination via dry deposition (wind) or wet deposition (rain and fog) (Schneider et al., 2013).

Volatilization rates from agricultural fields soils are influenced by a variety of complex interactions ranging from herbicides physicochemical characteristics (compound-saturated vapour pressure, Henry constant, K_{oc}), climatic conditions (wind, solar radiation and temperature) as well as soil properties (water content, OM, temperature) and farming practices (tillage, non-tillage, presence of cover crop residues)

(Bedos et al., 2002; Reichman et al., 2013). The degree of herbicide volatilization is highly dependent on its volatility which is influenced by temperature and the force of attraction of the volatile substance with other non-volatile compounds present in the solution (Mueller and Steckel, 2019). Vapour pressure is perceived as the most factor controlling herbicide volatilization, as an increase in vapour pressure makes the active ingredient more susceptible to volatilization (Gao et al., 2021). This phenomenon is also affected by surface soil moisture, it has been proved that herbicide vapour losses were doubled in wet conditions compared to dry conditions (Gish et al., 2009; Prueger et al., 2017). Dry conditions usually happen in bare soils under the direct influence of solar radiation, where the adsorption process plays an important role by governing the active ingredient concentration in the air of soil pores to be adsorbed from the gaseous state to the soil matrix resulting in decreasing their volatilization (Garcia et al., 2014; Schneider et al., 2013). Nevertheless, the volatilization process is difficult to predict and understand due to the complexity of the interaction between herbicides characteristics, soil properties and local meteorological conditions, all these factors make understanding this process a challenge.

Absorption of herbicides by plants or plant uptake is the process of taking up a percentage of applied herbicide from the soil by plants through leaves and roots (Nandula and Vencill, 2015). Herbicides can penetrate the plants through the aerial part, such as leaves, stems, flowers and fruits or through the underground area, such as roots, rhizomes, stolons etc. The leaves are the main penetration route for post-emergence herbicides applied to the plant surface, and roots, the young structure of seedlings (radicle and stem) and seeds are the most important absorption route for preemergence herbicides applied to soil (Mendes et al., 2022). The absorption of herbicides is controlled by various factors such as their availability in the absorption sites, their physicochemical properties, and the environmental factors (soil type, temperature, light, soil moisture and pH).

The passage of herbicide molecules through leaves is influenced mainly by the particle size and concentration of herbicide, cuticle thickness, use of surfactants and environmental factors like temperature, light and relative humidity (Mendes et al., 2022).

Herbicides present in the soil solution are primarily taken by plant roots. Mass flow of the soil solution and diffusion are the most important processes governing herbicides absorption at the area behind the root tip, where most water and nutrients are absorbed (Mendes et al., 2022; Reis et al., 2021).

The absorption of herbicides by roots is mainly affected by their physicochemical properties such as lipophilicity and pK_a, as well as the pH of the soil solution. Among these factors, pH is the most significant one that affects herbicide absorption. The water solubility of certain herbicides varies with soil solution pH due to changes in their functional groups, causing them to shift from neutral to negatively charged forms. As a result, herbicides that are more water-soluble tend to be more present in the soil solution and available for absorption (Nissen et al., 2003).

1.4 SOIL MANAGEMENT PRACTICES

1.4.1 Soil conventional management

Conventional agriculture is a mechanical operation mainly represented by excessive tillage of soil using mouldboard ploughing and disk harrow to invert and break the soil to help conceal weeds and establish a suitable seedbed for sowing crop seeds, resulting in high soil disturbance which ultimately leads to negative impacts on soil environment (Alletto et al., 2010; Keshavarz Afshar et al., 2022). Typically, plant residues from the previous crop are removed by burning or grazing to facilitate tillage and sowing for the next crop (Dang et al., 2020).

Although widely practiced, conventional farming is detrimental to soil health, leading to the loss of soil structure and aggregate stability, OM depletion, decreased soil fertility, reduced soil organisms and microbial diversity, water loss, increased soil erosion and runoff, and increased emission of greenhouse gases (Elias et al., 2018; Hassan et al., 2022; Peigné et al., 2018). The conventional tillage methods used in farming have been found to be unsustainable and damaging to the soil and crop production in the long-term. As a response to these negative effects, new soil management practices and cropping systems have been developed and implemented to ensure the longevity and sustainability of both the soil and crop production. These new approaches are represented by conservation agriculture (Jayaraman et al., 2021; Obia et al., 2020; Ravichandran et al., 2022).

1.4.2 Soil conservation management

Conservation agriculture is a set of agronomic practices and techniques that involve minimal or zero tillage, maintaining permanent soil cover through crop residues (mulching) and diversified crop rotations. This approach aims to optimize agroecosystems managements by preserving and improving the resource base and environment, which ultimately leads to production sustainability and improved food security (Jayaraman et al., 2021; Kassam et al., 2019; Perego et al., 2019). It is also defined as any tillage and planting practice that maintains soil coverage of at least 30% by crop residues after planting (Alletto et al., 2010). These modern agricultural managements have shown a significant effect in decreasing topsoil erosion and runoff, enhancing the OM and the fertility of soils, decreasing soil physical degradation and water loss, as well as improving water infiltration and enhancing microbial diversity (Chatterjee and Acharya, 2021; Silva et al., 2019).

The adoption of conservation agriculture was first introduced in the 1960s when non-tillage entered farming practices (Derpsch, 2004). However, it took several years for farmers and researchers to develop and improve farm equipment and agronomic practices to create well-performed technologies in non-tillage systems to shape what is called today conservation practices (Kassam et al., 2019). The use of conservation agriculture in cropping land has significantly increased and has been widely practised in the world. Between the years 2008 and 2009, the cultivated cropland under conservation agriculture was reported to be 106 M ha worldwide. Since then, it has increased by 69%, reaching 180 M ha in 2015/2016, according to the latest global estimation (Derpsch and Friedrich, 2009; Kassam et al., 2019). Non-tillage is applicable in all agricultural field sizes and soils that vary from 90% sand to 80% clay, where all types of crops can be produced adequately according to the literature (Derpsch et al., 2009; Farooq and Siddique, 2015).

Conservation agriculture is a set of interlinked practices since the application of non-tillage individually does not qualify the agronomic land as conservation agriculture. It must be linked with the other two practices, cover mulch and crop rotation, to ensure better soil preservation and yield production (**Figure 10**) (Kassam et al., 2019). These practices collectively mitigate physical soil degradation and enhance soil aggregation stability. As a result, an increase in the soil OM content and a decrease in soil erosion occurs by increasing water infiltration due to minimal soil disturbance, the presence of

cover mulch at the soil surface and the adoption of cover crops in the fallow period (Jakab et al., 2019; Madarász et al., 2021). Enhancing soil moisture content by mitigating drought stress is due to the reduction of evaporation and preservation of low temperatures at the top soil layer, as crop residues protect the soil surface from solar radiation (Obia et al., 2020; Thierfelder et al., 2013). Enhancing microbial biomass and activity is also produced, thus improving and restoring soil fertility and long-term productivity (Thierfelder et al., 2018; Yu et al., 2020; Zhang et al., 2022). Reducing manual labour required for land preparation and weeding if herbicides are used (Thierfelder et al., 2013).

Figure 10. The main practices in conservation agriculture.

The changes produced by conservation practices in soil physicochemical and biological properties can affect the behaviour of herbicides applied in cultivated soils under these systems. The increase in OM in the topsoil layer will influence herbicides' adsorption-desorption processes, consequently affecting their bioavailability in the soil (Prado et al., 2014). Also, increasing soil OM and moisture content under these practices favours microbial activity, thus influencing herbicides degradation and altering their transport and fate (Cueff et al., 2021). In addition, the presence of mulch residues on the soil surface may intercept herbicides, reducing the amount of the initial applied dose that

reaches the soil surface and increasing the possibility of herbicides volatilization (Mendes et al., 2017).

Non-tillage and direct seeding

One of the main practices of conservation agriculture is non-tillage or zero tillage and consequently performing direct seeding. This method involves planting and growing seeds without disturbing the soil during the process (Dang et al., 2020). Direct seeding involves sowing seeds directly into undisturbed soils through mulch left on the soil surface (Khan, 2019). To plant the seeds, a direct seeding is used to create narrow strips of soil below the mulch layer. The seeds are then placed in the soil and covered again with a thin layer of soil and crop residues, ensuring that no bare soil is visible on the surface (Choudhary et al., 2016; Thierfelder et al., 2013). The disturbed area must not exceed 15 cm, it must be less than this limit for which the soil surface is kept undisturbed to a large extent, and the only disturbance that the soil undergoes is at a seeding time to make a small planting opening for placing seeds (Kassam et al., 2015; Thierfelder et al., 2016).

Minimum soil disturbance is an important agronomic practice that prompts increasing soil surface OC and enhancing soil structure and its stability, substantial nutrients supply, and improving biological diversity, which leads to boosting soil macropores for water movement and infiltration and creating a suited environment for seed germination (Dang et al., 2020; González-Chávez et al., 2010).

Permanent soil cover (mulching and cover crops)

Mulching is an agricultural conservation practice of covering the soil surface with materials (plant residues or plastic film), which operate as a physical shield to protect soil health management and increase crop yield (Ravichandran et al., 2022). Depending on the nature of the materials used, two types of mulch are found: organic and inorganic mulch. **Organic mulch** involves natural or biodegradable materials, mainly plant residues, whereas inorganic mulch includes synthetic materials such as polyethylene plastic film (Kader et al., 2017). Adopting suitable mulching depends on climatic conditions, crop type and crop management practices (Kader et al., 2017). Organic mulching is the more commonly used in conservation agriculture by farmers than plastic

mulching as it is considered inexpensive and environmentally friendly (Ravichandran et al., 2022).

Inorganic mulch is witnessing a significant increase in use worldwide in conservation agriculture, especially in strawberry cultivation farms. It has been proven to reduce water use in dryland farming, enhance soil microclimate, and increase crop yield and food productivity (Meyer et al., 2021; Ravichandran et al., 2022). However, due to its composition, mainly plastics, concerns have raised about this type of mulching that it can induce soil contamination by plastic residues and consequently affect the sustainability of the soil system (Meyer et al., 2021).

Organic mulch is a layer of plant residues of the previous cover crop or specifically grown crop left on the soil surface to protect it from erosion (Rusinamhodzi, 2015). The amount of mulch covering the soil surface range between $30\% - 60\%$, $> 60\% - 90\%$, or $> 90\%$, as the soil must be at least 30% covered by mulch, or it is not considered a conservation practice (Kassam et al., 2015). **Cover crops** are grown in the fallow period, after which they are cut mechanically or killed chemically (e.g. glyphosate) and left on the topsoil during soil preparation for the following cash crop (Cassigneul et al., 2015). A period of one or two weeks is required for the decomposition of crop residues before seeding the following crop to minimise the allelopathic effect of the residues (Farooq and Siddique, 2015). Due to the presence of mulch and the adoption of cover crops, the soil is consistently covered during the fallow period and during cash crop growth (Farooq and Siddique, 2015).

Mulch provides several advantages for soil health and conservation (Choudhary et al., 2016): 1) Reduce runoff and soil erosion and protects the soil surface against chemical and physical weathering (**Figure 11**); 2) Function as a shield against rainfall energy and strong winds, which causes soil crusting; 3) Ameliorate soil moisture retention during severe conditions by mitigating evaporation and facilitate infiltration in the soil thus increases nutrients available for plants; 4) Boost soil regeneration by increasing soil OM and enhancing the diversity of soil microorganisms by providing energy, habitat and substrate for their activity; 5) Enhance carbon sequestration; and 6) Moderate soil temperature for better roots development and optimal seed germination.

Figure 11. Soil physical weathering without (left) and with mulch (right).

As mentioned earlier, mulch is typically found on the soil surface. However, in intensive farming, crop residues can also be incorporated into the soil as organic amendments. The practice of using **crop residues as organic amendments** to improve soil OM content and reduce soil degradation and erosion is a commonly adopted agricultural technique (Bonanomi et al., 2020). This practice has been shown to produce a positive impact on soil health and facilitate an increase in soil OC content across various climates, soils, and cropping systems (Nicholson et al., 2014; Siedt et al., 2021). The incorporation of crop residues as soil amendments can also enhance the soil's capacity to retain and hold water, resulting in a significant increase in soil water content (Ampofo, 2018). Additionally, this practice has a beneficial effect on soil microbiota, promoting their biomass and activity while also reducing nitrate leaching and enhancing the immobilization of mineral N (Yang et al., 2018).

Crop rotation

Crop rotation is also an important principle of conservation agriculture. It is a consecutive system of growing different types of crops in a specific order on the same agricultural land over time. It permits boosting the residual nutrients in the soil, which continue to be accessible for the following rotational crop, with the maintenance of land fertility (Carpio et al., 2022; Tanveer et al., 2019). The rotation should require at least three different types of crops (Kassam et al., 2015). Continually cultivation of the same

crop in a particular field leads to frequent and excessive nutrient extraction from the same soil depth as well as the heavy consumption of certain crop nutrients and leaving extra amounts of other nutrients unused, resulting in rhizosphere exhaustion, alteration of nutrient balance in the soil profile and reducing crop yield (Tanveer et al., 2019). The crops used in this practice are classified based on their residual effect on the soil into two categories: exhaustive rotation, which contains exhaustive crops that consume nutrients and leave the soil penurious in fertility and restorative rotation, which includes leguminous and oilseed species that help to enhance soil fertility (Tanveer et al., 2019).

The growing of diversified crops leads to an increase in root penetration and formation, porosity, and moisture and assure the equivalent distribution of nutrients in the soil profile. Moreover, it improves the activity of soil biota, as the roots produce different organic substances that captivate a variety of microorganisms (bacteria and fungi), which in turn transform these substances into plant nutrients. Legume crops have also shown to enhance biological nitrogen fixation to the soil and mitigate the risk of nitrate leaching (Choudhary et al., 2016; Plaza-Bonilla et al., 2015).

1.5 EFFECT OF SOIL CONSERVATION MANAGEMENT PRACTICES ON HERBICIDES BEHAVIOUR

The implementation of conservation agricultural practices may lead to significant alterations in the biological, physicochemical, and microclimate aspects of soils. As a result, the behaviour of herbicides in the soil under these conservation systems may be affected, either directly or indirectly (Cassigneul et al., 2016; Cueff et al., 2021; Jing et al., 2022; Maznah et al., 2018; Saha et al., 2019).

1.5.1   Effect on adsorption-desorption of herbicides

The accumulation of crop residues as mulch on the topsoil in conservation agriculture primarily affects the adsorption-desorption processes, as it prompts an increase in the interception of applied herbicides as well as enhancing the soil OC in the topsoil layer, which in turn increases herbicides adsorption (Cueff et al., 2021).

The interception of herbicides by mulch layer is highly controlled by the chemical and physical composition of plant residues as well as by herbicides properties, (Saha et

al., 2019). The adsorption capacity of the crop residues or mulch is influenced by their development stage and the particle size or surface area, and it may be 10 to 60 times higher than that of the soils. Mulch is considered a lignocellulosic biomass, and it is mainly consistent of cellulose, hemicellulose, and lignin. These materials could be biologically decomposed in soils over time depending on microorganisms, temperature and precipitation and consequently the bioavailability of herbicides in soils could be modified (Alletto et al., 2010; Jing et al., 2022). The chemical composition of crop residues undergoes significant changes during the decomposition process, leading to the formation of aromatic and aliphatic compounds. As a result, the hydrophobicity, aromaticity, or polarity of these materials may be modified and in consequence changes in the interception and adsorption of herbicides may occur. This is particularly relevant for herbicides with low polarity or non-polar characteristics (Aslam et al., 2013) being crucial to understand this evolution in order to effectively manage the use of herbicides in agriculture.

Results reported on adsorption of herbicides by crop residues are contradictory in the literature (Alletto et al., 2010; Aslam et al., 2013; Jing et al., 2022; Oliveira et al., 2020). However several studies indicated that herbicides adsorption to mulch increased with further stages of decomposition, taking into account always the type and properties of herbicides together with the amount, type and the biochemical characteristics of the crop residues (Cassigneul et al., 2015, 2018; Khalil et al., 2018; Marín-Benito et al., 2017).

A study conducted by Cassigneul et al. (2018) explored the adsorption of S-metolachlor in four different types of cover crop residues: hybrid ryegrass (Lolium hybridum, Rg), white mustard (Sinapsis alba), common vetch (Vicia sativa) and a mixture of common vetch + oat. Their findings revealed that the degree of decomposition and the specific type of cover crop residue had a significant impact on the adsorption of S-metolachlor. It was determined that as the degree of decomposition of the cover crop residue increased, so did the adsorption of S-metolachlor. Similar results were found in Aslam et al. (2013) study on the adsorption and desorption of S-metolachlor in maize residues, where the adsorption of S-metolachlor increased with the degree of decomposition of maize residues, while its desorption decreased. Also, Alletto et al. (2013) has determined the behaviour of S-metolachlor under conservation agriculture

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management, and the results showed that the presence of cover crop during the fallow period improved S-metolachlor adsorption.

Herbicides desorption is also highly influenced by herbicides characteristics, as herbicides with high solubility in water tend to leach easily into the soil after the first rainfall event. This factor, as well as the decomposition stage, is an important factor that controls their desorption (Aslam et al., 2013; Khalil et al., 2019; Marín-Benito et al., 2017).

Another key factor that influences adsorption-desorption processes under conservation tillage is soil OC. Due to the presence of dead decomposed crop residues that enriches the topsoil layer in OC, which gradually decreases with depth, leads to greater herbicides adsorption at this soil level (Cueff et al., 2021). For several herbicides, adsorption is positively correlated with soil OC content and it is usually considered the most important factor affecting herbicides adsorption to soil (James et al., 2019; Kumari et al., 2020; Liu et al., 2001; Tomić et al., 2015). A study was conducted by Prado et al. (2014) to evaluate the adsorption of atrazine in soil after a period of 20 years since its application, under varying agronomic management practices such as tillage practice (conventional and zero tillage), residue management (with and without residue retention), and crop rotation (wheat, maize rotation, and maize monoculture), using batch and column experiments. The results indicated that the highest distribution coefficient K_d (1.1 L kg^{-1}) was observed at 0–10 cm soil depth in the batch experiment for the practices of zero tillage, crop rotation, and residue retention (conservation agriculture). The study identified soil OM content and type as the key factors influencing adsorption, and this was further confirmed in the column experiment. The highest K_d values were observed in treatments with residue retention, either under zero or conventional tillage (0.81 and 0.68 L kg^{-1}, respectively). The absence of soil movement in zero tillage contributed to the increase in K_d. Overall, the results of the study indicated that conservation agriculture exhibited a higher potential for atrazine retention than conventional tillage. A research conducted by Carretta et al. (2021) delved into the impact of soil tillage systems on the adsorption and dissipation of glyphosate and the formation/dissipation of its metabolite aminomethylphosphonic acid (AMPA). The study analysed two soil tillage systems, non-tilled (NT) and conventionally tilled (CT) soil, at two sampling depths, 0-5 and 5-20 cm. The findings showed that the K_f value was significantly higher in the NT soil (41.1 and 54.5 $\mu g^{1-1/n}$ (mL)$^{1/n}$ g^{-1} for $0 - 5$ and $5 - 20$ cm, respectively) compared to the CT soil

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(22.4 and 29.8 $\mu g^{1-1/n}$ (mL)$^{1/n}$ g^{-1} for 0 - 5 and 5 - 20 cm, respectively) at both sampling depths. The difference in the adsorption behaviour of glyphosate in the two soil types was attributed to the intrinsic soil properties of NT and CT soil.

Due to the accumulation of OM at the soil surface under conservation tillage, soil pH can be significantly modified, leading to its increase, no change, or frequent decrease (Alletto et al., 2010). For various herbicides, adsorption is controlled mainly by decreased soil pH, as more acidic conditions favour herbicides' adsorption under conservation tillage (Cueff et al., 2021).

Modelling of the adsorption-desorption of herbicides in soils

The modelling of the adsorption of organic molecules by soils is often carried out by obtaining adsorption isotherms. Adsorption isotherms are constructed by measuring the residual concentrations of the herbicides in an aqueous solution at the equilibrium point after adsorption to the soil of different initial concentrations at a constant temperature. The concentrations of adsorbed molecules are determined by the difference between the initial and equilibrium concentrations at each concentration point (Braschi et al., 2011). The adsorption isotherms are classified into four classes according to the shape of the initial slope (Giles et al., 1960). These four classes are H (high affinity), L (Langmuir type), C (constant partition), and S (sigmoidal or with an "s" form) isotherms (**Figure 12**). The L-isotherm is the most common type, it shows that as more the number of sites in the substance (soil) are occupied, it becomes progressively challenging for the solute (herbicide) to find an available adsorption site.
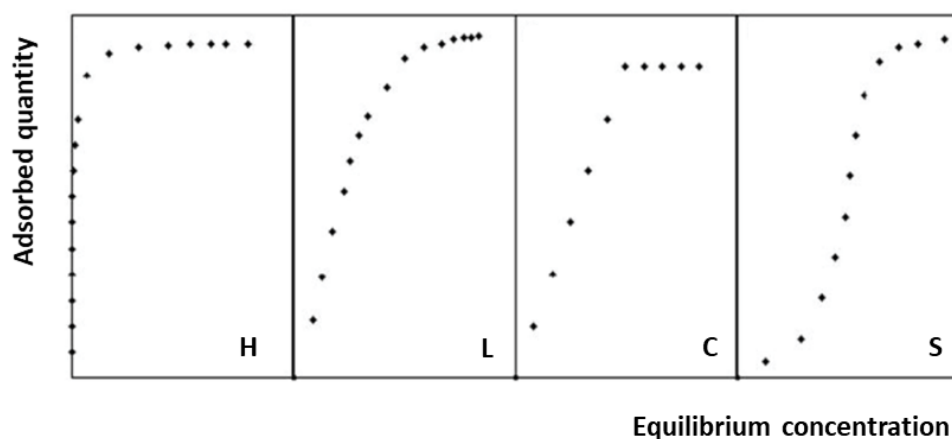
Figure 12. Main classes of isotherms (Braschi et al., 2011).

The experimental results of herbicide isotherms could be fitted to several models, the most frequently used is the Freundlich (1909) equation. It is used mainly to describe the adsorption of herbicides by heterogeneous surfaces with non-uniform energy distribution (Yue et al., 2017). The Freundlich empirical equation is generally applied to express the adsorption of herbicides by soils, clay minerals or OM (Nelson et al., 2000), and it is expressed as:

$$C_s = K_f \, C_e^{\,nf} \qquad \text{[eq.1]}$$

where C_s ($\mu g \, g^{-1}$) is the amount of herbicides adsorbed per unit mass of adsorbent, C_e ($\mu g \, mL^{-1}$) is the equilibrium concentration of herbicides in the solution, K_f ($\mu g^{1-nf} \, mL^{nf} \, g^{-1}$) is the Freundlich adsorption coefficient which indicates the amount of herbicide adsorbed for an equilibrium concentration equal to the unit ($C_e = 1 \, \mu g \, mL^{-1}$) that is at low equilibrium concentration in solution and n_f is the exponent of Freundlich equation used as an indicator of adsorption isotherm non-linearity (C. Wu et al., 2011). These two parameters, K_f and n_f, are considered important parameters to characterise the soil capacity to adsorb herbicides (Sharipov et al., 2021), and they are calculated from the linear form of the Freundlich equation expressed as:

$$\text{Log } C_s = \log K_f + n_f \log C_e \qquad \text{[eq.2]}$$

Distribution coefficient K_d (mLg^{-1}) is another adsorption parameter used to determine the adsorption of herbicides at high concentration levels, mainly when the isotherm is non-linear. It is determined by the ratio between the concentration of herbicides in soil and in solution under equilibrium conditions for a given equilibrium concentration, and it is calculated by the equation (Aslam et al., 2013):

$$K_d = \frac{C_s}{C_e} \qquad \text{[eq.3]}$$

K_d describes the degree and favourability of the adsorption between herbicides and soil, as high Kd values mean strong herbicides adsorption on soil and low K_d values indicate low adsorption (Doretto et al., 2014). The extent of herbicides adsorption on soil is frequently described as a coefficient normalised by OC content, K_{oc} ($cm^3 g^{-1}$), which is calculated as a function of K_d and the percentage of OC content in the soil (Petter et al., 2016):

$$K_{OC} = \frac{K_d}{\% \, OC} \times 100 \qquad \text{[eq.4]}$$

The desorption of herbicides from the soil after adsorption is determined by consecutive washings of soil with water and measuring the herbicide concentration in the equilibrium solution. The experimental results of herbicides desorption can also be described by Freundlich equation (Aslam et al., 2013):

$$\mathbf{C_s = K_{fd}\ C_e^{\ nfd}} \qquad\qquad \textbf{[eq.5]}$$

where C_s (µg g^{-1}) is the amount of herbicides remaining adsorbed per unit mass of adsorbent after each desorption, C_e (µg mL^{-1}) is the equilibrium concentration of herbicides in the solution, K_{fd} (µg^{1-nfd} mL^{nfd} g^{-1}) and n_{fd} are two constants characteristics of desorption process on soil, which are determined using the linear form of equation 5, expressed as follow (Pandey et al., 2021):

$$\textbf{Log }\boldsymbol{C_s} = \textbf{log}\boldsymbol{K_{fd}} + \boldsymbol{n_{fd}}\textbf{ log }\boldsymbol{C_e} \qquad\qquad \textbf{[eq.6]}$$

The desorption process of herbicides is governed by the interaction between herbicides and soil via weak or reversible bonds. However, these interactions are not always in this form because herbicides can be retained on soil via strong and irreversible bonds. This prevents their complete desorption, eventually obtaining desorption data different from adsorption data, resulting in desorption hysteresis to a greater or lesser extent (Essington, 2003). The hysteresis coefficient (H) is calculated using the Freundlich n_f coefficients for adsorption and desorption as follows (Yue et al., 2017):

$$\boldsymbol{H = \frac{n_f}{n_{fd}}} \qquad\qquad \textbf{[eq.7]}$$

Theoretically, if H = 1, hysteresis is absent and if H > 1, it means positive hysteresis where the Freundlich slope for desorption is lower than the Freundlich slope of adsorption, which indicates that herbicides are resisting desorption from the soil. If H < 1, it means negative hysteresis where the Freundlich slope for desorption is higher than the Freundlich slope for adsorption, which indicates that desorption is improved (Doretto et al., 2014).

1.5.2   Effect on herbicides degradation/ dissipation and persistence

Herbicides degradation processes under conservation tillage are highly influenced by the adsorption process. As aforementioned, herbicides adsorption is higher under conservation agriculture, which consequently leads to low herbicides bioavailability for

degradation. However, herbicides degradation remains a complex process mainly influenced by various factors such as soil microflora, OM, moisture content, temperature and pH, where these parameters are significantly altered under conservation agriculture management.

The presence of mulch at the soil surface is a significant factor that influences herbicides persistence in conservation tillage systems. Depending on herbicides properties as well as the nature of crop residues and their interaction, herbicides intercepted by mulch residues can be either susceptible to photodegradation or degraded by the microorganisms in mulch, as it contains high microbial activity compared to soil (Alletto et al., 2010; Cassigneul et al., 2016). The changes in the biochemical composition of crop residues and associated microbial activity during decomposition could significantly alter herbicide degradation (Aslam et al., 2014; Rampoldi et al., 2011). For that, herbicides dissipation in mulch residues remains a contradictory process, as some studies have indicated that herbicides degradation is higher in mulch than in soils (Aslam et al., 2014; Cassigneul et al., 2018; Rampoldi et al., 2011), while other studies reported lower or slow degradation (Aslam et al., 2018; Cassigneul et al., 2016; Cueff et al., 2021).

Cassigneul et al. (2018) compared the degradation of S-metolachlor in bare soils versus soils covered with ryegrass and vetch + oat mixture cover crop residues. The study found that in bare soil, the half-live time (DT_{50}) lasted for 23 days, while in cover crop residues, the DT_{50} was 9, 15, 39, and 25 days, in order of increasing decomposition state (0, 6, 28, or 56 incubation days) at the time of application. These findings suggest that the proportion of herbicide intercepted by the cover crop residues, as well as higher levels of OM and microbial activity in less decomposed cover crop residues, could be factors contributing to these results. In addition, Aslam et al. (2015) provided further insight into the degradation of S-metolachlor in soil columns manually packed and covered with a mulch composed of maize and lablab residues. They conducted simulations of both frequent light rainfall and less frequent but intense rainfall on the columns. The findings revealed that the decomposing mulch on the surface of the soil retained over 50% of the applied S-metolachlor under these conditions. Moreover, it was observed that high levels of humidity resulted in accelerated mulch decomposition, leading to faster dissipation of S-metolachlor in mulch residues under frequent light rainfall. Consequently, this increased the formation of S-metolachlor metabolites, namely S-metolachlor-ESA and S-metolachlor-OA.

Herbicides are not retained permanently in the mulch since they are washed-off from plant residues under the action of irrigation or rainfall. When they reach the soil, their degradation is governed by a combination of factors, mainly microbial activity (Aslam et al., 2018). Minimum soil disturbance or non-tillage and the accumulation of organic residues at the soil surface provide an appropriate soil microclimate and an increase in OM which create suitable conditions for the development of soil microflora (Cueff et al., 2021). Generally, high microbial activity and biomass generate high degradation rates, as most pesticides are broken-down through biotic degradation (James et al., 2021; Carpio et al., 2020).In this sense, Yousefi et al. (2016) investigated the degradation of sulfosulfuron in various wheat cultivation systems. These systems included conservation tillage by Combinate, non-tillage by Baldan grain drill, conservation tillage by Chizelpacker, conservation tillage by Delta Model, surface tillage by heavy disk, and conventional tillage by mouldboard plough and twice disk. The study also analysed the impact of soil microbial respiration and pH levels on sulfosulfuron degradation. Results revealed that the non-tillage system by Baldan grain drill displayed the shortest half-life of 4.62 days for sulfosulfuron persistence. Furthermore, the study highlighted the significant impact of different tillage systems on soil microbial respiration, mainly in the first 5 hours and 7 days after sulfosulfuron application. The research concluded that soil microorganisms were the primary factor affecting sulfosulfuron degradation.

Nevertheless, herbicides degradation in soils under conservation tillage could be low compared to conventional tillage, as the microbial activity can be limited due to the reduction in herbicides bioavailability because of their high retention.

Soil pH has also a great influence on herbicides degradation. Under conservation tillage, pH fluctuates from acidic to alkaline or no change, however, due to the accumulation of OM in soil surface, pH tends to decrease (Alletto et al., 2013). The acidification of the topsoil will promote to adsorption of weakly basic herbicides rather than their degradation, and even if herbicides are not affected by the change of pH values, like non-ionizable herbicides, the activity of microbial communities responsible for their degradation will be highly altered to a greater or lesser extent (Bedmar et al., 2017; James et al., 2021).

In addition, water content and temperature are highly altered in conservation tillage, as the soil water content is generally enhanced, promoting herbicides availability in soil

solution, thus increasing their bioavailability for biodegradation (Alletto et al., 2008). Temperature is generally regulated due to crop residues at the soil surface, creating an optimum condition for microbial activity (Alletto et al., 2012). Alletto et al. (2012) examined the impact of temperature and water pressure head into the degradation of diketonitrile (DKN) in loamy soil under two different tillage practices, conventional and conservation, over the course of 84 days. The results showed that the DT_{50} of DKN varied significantly between the two tillage practices. In samples obtained from conventional tillage, the DT_{50} ranged between 19 to 239 days, while in samples from conservation tillage, the DT_{50} ranged between 8 to 92 days. The shortest half-lives were observed in seedbed samples under conservation tillage at a temperature of 25ºC and a water pressure head of -33 cm. As a result, it was concluded that soil temperature played a significant role in regulating DKN degradation in both tillage systems.

Modelling herbicides degradation in soils

To determine herbicides persistence in soils, it is necessary to know herbicides degradation kinetics and the interlinked factors that affect this process. The evaluation of herbicides degradation kinetics is carried out by measuring the remaining concentrations of herbicides in the soil, usually expressed as a percentage of the amount of herbicides initially applied to the soil versus time. It is performed either at field scale, under real temperature and humidity conditions, or at laboratory scale after an incubation process at controlled temperature and humidity conditions. The experimental results of herbicides degradation kinetics are fitted to an appropriate mathematical model to determine the kinetic parameters. These parameters are the degradation rate constant (k) and DT_{50}. DT_{50} refers to the time (expressed in days) for 50% of the initially applied amount of herbicides to be degraded, and DT_{90} refers to the time by which only 10% of the initially applied dose of herbicides remains in the soil under certain incubation conditions.

Degradation kinetics parameters are determined using the FOCUS (Forum for the Co-ordination of pesticide fate models and their USe) guidelines (FOCUS, 2006). It is a workgroup of experts that have been established to outline models able to mathematically describe experimental data for calculating degradation kinetics for compounds (e.g. herbicides) and their metabolites in soil and water sediment systems. These models are the single first-order model (SFO), several models that are able to describe bi-phasic

degradation kinetics (FOMC, DFOP and HS) and two models that are suitable to describe degradation patterns with a lag-phase.

The **Single First Order kinetic model (SFO)** considers that the number of herbicide molecules is low relative to the number of degrading microorganisms and their enzymes or number of water molecules in the case of hydrolysis. Therefore, the speed of the variation in herbicide concentration (dC/dt) is any time directly proportional to the actual concentration remaining in the system. The time for the concentration to decrease by a certain rate is constant throughout the experiment and independent of the initial herbicide concentration, which means that degradation is independent of time and initial concentration. This kinetic model is given in the absence of microbial growth as it assumes that there is no limitation in the degrading micro-organisms and assumes that mineralization is limited to a maximum amount that will depend on the type of herbicide and soil.

The SFO model is expressed by a simple exponential equation with two parameters:

$$\frac{dC}{dt} = -KC \qquad\qquad \textbf{[eq.8]}$$

whose integrated form is:

$$C = Co\ e^{-kt} \qquad\qquad \textbf{[eq.9]}$$

where C is the herbicide concentration at time t, C_0 is the initial herbicide concentration at t = 0, and k is the dissipation rate constant.

DT_{50} and DT_{90} are calculated by equations 10 and 11, respectively:

$$\textbf{DT}_{50} = \frac{\ln 2}{K} \qquad\qquad \textbf{[eq.10]}$$

$$\textbf{DT}_{90} = \frac{\ln 10}{K} \qquad\qquad \textbf{[eq.11]}$$

Although SFO is often used to simulate herbicide degradation in soil and water, it may not accurately describe degradation that follows a **bi-phasic** pattern. In such instances, a rapid initial decline in herbicide concentration is followed by a slower, substantial decline, which suggests that the herbicide is becoming more tightly bound to the soil and persisting for longer periods of time. **Biphasic degradation** is characterized by the partition of herbicide between the solid and liquid phase, where only a small fraction of herbicide is available for degradation. This behaviour is due to aged adsorption, non-linear adsorption, slow diffusion process and decrease in microbial

activity with time under laboratory conditions where the samples are exposed to limited resources of carbon sources and nutrients availability. However, at field conditions, biphasic degradation could occur because of climatic changes from temperature and moisture. Soil is also a spatially variable medium, where small changes in pH, OC and microorganism biomass across the experimental plot will impact in the degradation process in a microscale, resulting in biphasic degradation. According to the European kinetics guidance, in order to consider a biphasic degradation and to reject SFO fit for herbicide, three criteria must be considered; 1) χ^2 – test error > 15 %, 2) the degradation rate (k) t-test fails, and 3) visual assessment is unacceptable.

A variety of biphasic kinetic model exist, among them (Gustafson and Holden (1990) model also known as **First Order Multi Compartment model (FOMC)**. This model considers the soil as a heterogeneous medium with spatial variability, where degradation rate is variable across the different soil horizons. For that, Gustafson and Holden divided the soil into a substantial number of sub-compartments each with a different rate of first order degradation constant. They developed a differential equation with three parameters to describe the FOMC kinetic model:

$$\frac{dC}{dt} = -\frac{\alpha}{\beta} \, C \left(\frac{t}{\beta} + 1\right)^{-1} \qquad \text{[eq.12]}$$

whose integrated form is as follow:

$$C = \frac{Co}{(\frac{t}{\beta}+1)^{\alpha}} \qquad \text{[eq.13]}$$

where C is the herbicide concentration at time t, C_0 is the initial herbicide concentration at time 0, α is a shape parameter determined by the coefficient of variation of the values of the first order constants and β is a location parameter, and the DT_{50} is calculated by the following equation:

$$\mathbf{DT_{50}} = \boldsymbol{\beta} \left(2^{\frac{1}{\alpha}} - 1\right) \qquad \text{[eq.14]}$$

The parameters α and β are indicators of degradation rate, as degradation is faster with larger α values and smaller β values as shown in **Figure 13**. Although simple, FOMC has drawbacks which limit its implementation in FOCUS leaching models, because the degradation is time dependent.
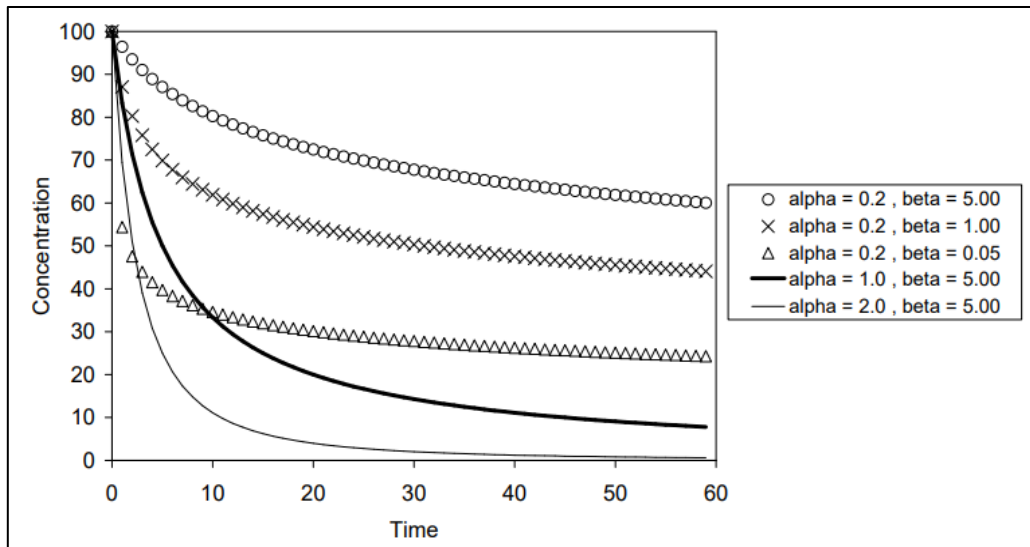
Figure 13. Patterns of degradation calculated with the Gustafson and Holden (1990) model for different values of α and β.

There are also other biphasic kinetic models used, such as the **Double First Order in Parallel model** (**DFOP**) and the **Hockey Stick model** (**HS**). However, because of their high number of parameters compared to FOMC kinetic model, their use is limited.

The last kinetic models used to describe herbicide degradation are **lag-phase models**. Lag-phase is the period that microorganisms take to adapt to the new environmental conditions. Because of this adaptation period, the herbicide concentration is constant for a period of time, after which is followed by a first order or biphasic model. Under laboratory conditions, this phase could occur as a result of a decrease in the active biomass of degrading microorganism due to the poor storage or incubation conditions (e.g. excessive drying of the soil). Also, high herbicide concentration at the initial may induce a negative effect on the microflora leading to the inhibition of their degrading activity. In tests under real field conditions, it may be due to losses by leaching, volatilization, loss by photolysis at the soil surface, or an adaptation of the microorganisms to the soil surface.

1.5.3   Effect on herbicides leaching

Herbicides ability to leach in soils and contaminate groundwater is highly dependent on their mobility and their persistence (Alletto et al., 2010). Under conservation tillage managements, adsorption plays a key role in determining herbicides

mobility (Aslam et al., 2013). Due to the presence of mulch, OC at the top soil layer is increased, in turn promote to high herbicides retention which significantly limit their migration within the soil (Cueff et al., 2021). Along with adsorption, herbicides degradation is also an important factor that control herbicides leaching in these systems, as their dissipation is generally enhanced which in turn mitigate herbicides persistence in soils and hence their downward movement to groundwater (Cassigneul et al., 2018). Even though these processes are considered main factors that control herbicides leaching risk under conservation tillage management, there are other factors that control their movement and transfer within the soil profile.

Herbicides leaching is also dependent on soil physical properties, such as the hydraulic conductivity that is directly influenced by the soil structure generated by conservation tillage (CT) practices (Alletto et al., 2010; Strudley et al., 2008). Under non-tillage (NT), soil is not disturbed which leads to the formation of a continuous macropore network due to earthworm burrows, root channels and cracks, which create a preferential flow pathway that promotes the downward movement of water flow and herbicides transfer through the soil (Alletto et al., 2010; Larsbo et al., 2009). Preferential flow is generally activated under saturated conditions that occur at low initial water content and water entry restriction into soil matrix caused by the hydrophobicity of mulch, ultimately creating saturation conditions and favouring the movement of water and herbicides through macropores fluxes (Alletto et al., 2011; Maznah et al., 2018; Weber et al., 2006).

Soracco et al. (2018) examined the differences in physical and hydraulic soil characteristics between CT and NT practices and analysed the movement of glyphosate within the soil under both practices during a soybean cycle. The findings indicated that both CT and NT practices retained the herbicide in the top 20 cm of soil. However, CT practices exhibited higher values for saturated hydraulic conductivity, total macroporosity, and effective macroporosity, leading to greater temporal variation in herbicide leaching. On the other hand, NT practices showed lower values for these characteristics, which restricted the vertical mobility of glyphosate. Overall, the study emphasized the significance of changes in physical and hydraulic soil properties in the temporal variation of glyphosate transport. In another recent study conducted by Villarreal et al. (2020), the accumulation and mobility of glyphosate in soil profiles were investigated during a crop cycle in two different textured soils, silty loam and sandy loam, under NT and CT systems. The results showed that soils under NT had higher available

water content and lower saturated hydraulic conductivity compared to CT, which had an impact on the behaviour of glyphosate. Glyphosate persistence and leaching were found to be correlated with soil water retention and hydraulic conductivity, respectively. The researchers concluded that fine-textured soils, particularly under NT, with high water retention, low hydraulic conductivity, and low pore connectivity, were more susceptible to glyphosate accumulation. However, the study also observed that high hydraulic conductivity under CT in silty loam soil could enhance glyphosate leaching.

After their application, herbicides are retained primarily by mulch residues present at the soil surface and due to irrigation or precipitation events, herbicides are washed-off from crop residues to the soil. The amount of herbicides leached is variable depending on the intensity and timing of irrigation/rainfalls, mulch decomposition and herbicides properties (Aslam et al., 2015; Khalil et al., 2019).

To determine the effect of rainfalls on herbicides leaching, trials are often conducted at the laboratory using soil columns and simulated rainfalls regimes. In the experiments where light-intensity and frequent rainfalls are applied, herbicides are slowly washed-off from mulch which permits their penetration to soil matrix and reduces their leaching by the adsorption process (Alletto et al., 2011; Khalil et al., 2019). Aslam et al. (2015) studied the degradation and leaching behaviour of S-metolachlor and glyphosate in soil columns covered with maize and lablab residues and subjected to two simulated rainfall regimes, one with frequent but light rain (LF) and the other with less frequent but more intense rain (HI). Results shown that mulch decomposition under light rainfall regime was higher due to the increase in humid conditions on surface and this could lead to an increase in herbicides dissipation in plant residues, hence reducing their leaching. Though both regimes received the same amount of rainwater, the results revealed that S-metolachlor and its metabolites penetrated deeper into the soil under the HI rainfall regime. Conversely, glyphosate remained in the surface layer due to its strong adsorption capacity, while its metabolite AMPA showed little difference in leaching between the two rainfall regimes. The study concludes that the impact of crop residues on pollution through wash-off and leaching depends on the herbicide type and rainfall regime. Greater transport of S-metolachlor through the soil occurred with more intense and infrequent rainfall, while glyphosate was less mobile.

In the studies where high-intensity rainfalls are applied, water and solute fluxes are increased and herbicides intercepted by mulch residues are washed-off at higher rate,

resulting in the activation of preferential flow in macropores which leads to greater herbicides leaching to groundwater (Alletto et al., 2011; Aslam et al., 2015, 2018). However, it was also cited that even with high precipitation regimes, the leaching of some herbicides is limited due to their high retention at the soil top layer under these conservation systems (Aslam et al., 2015; Gish et al., 1995). Overall, leaching of herbicides under conservation agriculture practices is highly related to the activation of macropore flow due to no tillage, which is considered the main drawback of these systems (Carpio et al., 2022). Over the course of eight years, a study was conducted by Giuliano et al. (2021) to compare the performance of a conventional maize monoculture (MMConv) with four alternative cropping systems designed to minimize irrigation and herbicide leaching. The four systems were MMLI, which utilized low-input methods such as cover crops and integrated weed management (IWM) techniques; MMStill, which employed strip tillage and cover crops; MMCT, which utilized conservation tillage and cover crops; and maize-MSW, which involved rotating maize with soybean and wheat using IWM. The study also sought to identify the key factors driving herbicide leaching in maize and assess the impact of cropping systems on this issue. Drainage water was collected through lysimeter plates at 1-m depth and analysed for six herbicide molecules (glyphosate, S-metolachlor, bentazone, mesotrione, nicosulfuron and dicamba) and the degradation metabolite of glyphosate AMPA. The results revealed that MMLI had an average annual herbicide loss of 0.5 ± 1.0 g ha^{-1}, while maize-MSW had 0.7 ± 1.2 g ha^{-1}. MMStill had 1.3 ± 2.1 g ha^{-1}, MMConv had 2.0 ± 4.8 g ha^{-1}, and MMCT had 3.0 ± 9.6 g ha^{-1}. High leaching peaks were found for mesotrione and glyphosate, which may indicate preferential flows, especially in MMCT and it was found that herbicide leaching remained variable but was consistently and mostly influenced by drainage volume.

Laboratory assays are usually carried out to study herbicides leaching although the majority of these studies are conducted under controlled conditions, and they only provide an estimation of herbicides leaching. By this, their extrapolation is limited because they are not representative of real conditions. On the contrary, field assays are more realistic, as they take into consideration the interaction between multiple variables that inform a different behaviour than that observed under laboratory studies, which is more realistic and more representative (Gish et al., 1995; Marín-Benito, Alletto, et al., 2018; Weber et al., 2006). Besides, the data collected from field studies will allow the calibration and validation of herbicides leaching models in soils under conservation agriculture

management, which could be subsequently used as a tool for predicting the environmental fate of herbicides under these systems (Marín-Benito et al., 2018).

Modelling herbicides leaching in soils

Various mathematical models have been developed to evaluate the behaviour and environmental fate of herbicides after their application to an agricultural field and their transfer from soil surface to groundwater (Mamy et al., 2008; Marín-Benito et al., 2014). Among these models are the four mathematical models recommended to simulate the herbicides leaching in soils by the scientists and experts of the FOCUS workgroup (FOCUS, 2000): **MACRO** (water and solute transport in MACRO porous soil), **PELMO** (Pesticide Leaching Model), **PEARL** (Pesticides Emission Assessment at Regional and Local scales) and **PRZM** (Pesticides Root Zone Model). Currently, these models are used for risk assessment of the possible movement of active substances and their metabolites to groundwater for pesticides registration in Europe.

These mathematical models are cost-effective, economic, practical and useful tools for predicting the environmental fate of pesticides together with field and laboratory data (Marín-Benito et al., 2014). They take into account the major processes influencing herbicides behaviour in soil (adsorption, degradation, leaching, volatilization, runoff, erosion and absorption by plants), in addition to the different environmental and hydrological conditions, pesticides chemical properties, agricultural practices and cropping systems (Mamy et al., 2008; Marín-Benito et al., 2014; 2020). FOCUS workgroup has determined 125 groundwater scenarios based on 9 pedoclimatic scenarios with 12 to 16 crops each to assess the leaching of pesticides and to simultaneously represent the agricultural conditions in the European Union (Boesten et al., 2009; FOCUS, 2000).

Several studies have shown the ability of these mathematical models to present a reliable simulation of pesticides leaching under spatially and temporally limited conditions (Lammoglia et al., 2017; Mamy et al., 2008; Marín-Benito et al., 2015, 2018, 2020). However, in some cases these models are not capable of providing a sufficiently good simulation of pesticides environmental fate, due to some limitation like the quality and quantity of available experimental data, the incorrect parameterization by the user and the models incapability of describing some processes and agronomic conditions (Garratt et al., 2003; Marín-Benito et al., 2020). For example, pesticides leaching under

conservation agriculture with the presence of mulch residues at the soil surface is poorly simulated by the four FOCUS models, as the models does not consider the mulch layer (FOCUS, 2000). Therefore, the implementation of new strategies has been adopted like the development of new calibration factors for an efficient simulation of pesticides leaching under conservation agricultural management (Dahiya et al., 2007; Marín-Benito et al., 2018; Singh et al., 2011).

FOCUS work group recommends the utilization of at least two models in the study of pesticides leaching and the comparison of their results. In this work, **PRZM** and **MACRO** have been used for modelling herbicides dynamics in soils under conservation agricultural practices.

1.5.4 Effect on soil microbial community

Soil microorganisms are an important bioindicator of soil health, functionality and ecosystems sustainability (Baghel et al., 2018; Belmonte et al., 2018). Soil microbiota governs various functions in the soil. It is responsible for the mineralization and decomposition of soil OM from residues, regulates nutrient cycling, including carbon (C) and nitrogen (N), provides and supports the flow of energy and biochemical cycles and enhance soil aggregation (Arantes et al., 2020). These functions are related to the diversity, biomass, composition and the size of microbial population present in the soil, which in turn could be influenced by the agricultural managements (Legrand et al., 2018).

As previously mentioned, conservation agricultural practices, including non-tillage, mulch residues and crop rotation, could induce changes in the soil's physicochemical, biological and microclimate properties, consequently affecting the soil microbial population. Conservation tillage generally promotes higher microbial activity, as the accumulation of organic residues at the soil surface and minimal soil disturbance results in higher carbon concentration, which correlated positively with microbial communities, as an increase in soil OC under these practices resulted in a stable bacterial network and higher microbial diversity, leading to an increase in enzyme activity levels and microbial metabolic activity (Wang et al., 2020; Zheng et al., 2022).

Microbial communities' diversity and distribution are highly influenced by the type of mulch used. A study conducted by Zhang et al. (2020) on the application of two types of mulch: plastic ethylene film mulch and peanut null mulch, using high-throughput 16S

rRNA and ITS rDNA gene Illumina sequencing, reported an increase in both bacterial and fungal communities under organic mulch compared to plastic mulch. Zhang et al. (2020) also indicated that mulching patterns influence the distribution of microbial communities since organic mulch increases the diversity of fungal community in 0-20 cm soil layer, whereas the diversity of bacterial community was increased in the 20-40 cm soils. It was concluded that the organic mulch had a positive regulatory effect on the soil bacterial and fungal communities. In another experiment conducted by Zhang et al. (2022), the effect of non-tillage on microbial communities was studied and the results reported that non-tillage significantly enhanced microbial communities associated with N cycling processes, especially N fixation, nitrate reduction, nitrification and denitrification. Li et al. (2020) also studied the effect of non-tillage on soil microbial population size and diversity using microbial count and phospholipid fatty acid measurements (PLFAs) Results showed a notable increase in soil microbial count, fungal biomass and bacterial diversity compared to conventional tillage. In addition, Panettieri et al. (2020) showed that non-tillage promoted a greater abundance of soil fungi over bacteria.

Overall, the full implementation of conservation agriculture components could results in the improvement of microbial community growth, diversity, structure and activity with better C and N cycling, that improves soil health and promote to nutrients availability for plant growth and an increase in crop yields (Jayaraman et al., 2021). These changes carried out by conservation agriculture management could also be affected by the application of herbicides whose use could affects the soil microbial population at the same time. The effects of herbicides on microbial communities are studied by experiments generally conducted at the laboratory using field samples, where the parameters indicating their abundance, activity and structure are determined by biochemical techniques such as: microbial biomass, respiration, enzymatic activities, PLFAs measurements, etc. and/or molecular biology techniques like high-throughput mass sequencing and bioinformatics.

Panettieri et al. (2013) reported a contrasted response of microbial community after herbicides application under conservation tillage ranging from negligible, inhibitory to a pronounced simulation of some of their properties. It was showed that herbicides generally increase microbial biomass and enzymatic activity (dehydrogenase activity, DHA), by acting as an easily available carbon source under non-tillage treatments. When

applied at the recommended field dose, herbicides could also have a benign impact on the structure of microbial community. Ratcliff et al. (2006) shown that the addition of glyphosate to forest soils stimulated the functional diversity of total bacteria and bacterial: fungal biomass. Meanwhile, Liphadzi et al. (2005) observed that the application of herbicides had no effect on microbial population, and the variability of microbial biomass was due to the type of tillage practices. However, Gomez et al. (2009) reported that herbicides could have an inhibitory effect on microbial biomass, mainly with increasing doses.

Overall, herbicides could affect some biochemical parameters of microbial population in soils, but the level of the impact strongly depends on soil characteristics, agricultural management practices and climatic conditions together with the type and herbicide concentration (Panettieri et al., 2013; Zabaloy et al., 2008).

MATERIALS AND METHODS

2. MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Herbicides
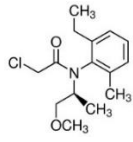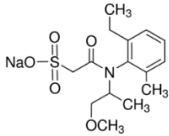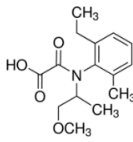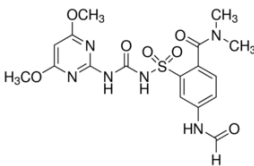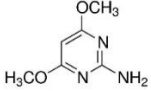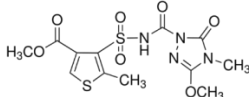
Three herbicides were selected for this work S-metolachlor (SMOC), foramsulfuron (FORAM) and thiencarbazone-methyl (TCM), which have a selective herbicidal activity and control of pre- and post-emergence grasses and broadleaf weeds in maize. Each compound belongs to a different chemical group with different structure and physicochemical properties (water solubility, hydrophobicity, leaching potential, degradation rate. etc.) (**Table 1**).

The three herbicides were used in the field under the commercial formulations Efica 960EC® (SMOC 96% w/v ADAMA Agriculture Spain, S.A., Madrid) and Monsoon Active® (TCM 1% w/v and FORAM 3.15% w/v, Bayer Crop Science S.L., Valencia) (**Figure 14**). The PESTANAL^{TM} analytical standards of herbicides SMOC ($\geq$ 99.1% purity), FORAM ($\geq$ 98.5% purity), and TCM ($\geq$ 99.8% purity) and metabolites metolachlor ethane sulfonic acid (SMOC-ESA) sodium salt ($\geq$ 95.8% purity) and metolachlor oxanilic acid (SMOC-OA) ($\geq$ 99.5% purity) and the Aldrich analytical standard of the FORAM metabolite (FORAM-MET), 2,4-dimethoxypyrimidin-2-amine ($\geq$ 98% purity), were supplied by Merck Life Science S.L. (Madrid, Spain).

Figure 14. Commercial formulations of herbicides, Efica 960EC® and Monsoon Active®.

Table 1. Main physicochemical characteristics of the three studied herbicides and their corresponding metabolites.

Herbicide or Metabolite	Chemical structure	WS[a] (mg L^{-1})	Log K_{ow}[b]	Kf_{oc}/K_{oc}[c] (mL g^{-1})	DT$_{50}$[d] field/ lab (days)	GUS index[e]
S-metolachlor (SMOC) [2-chloro- N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-meth-oxy-1-methylethyl] acetamide]		480	3.05	200.2	23.2//51.8	2.32
Metolachlor ethane sulfonic acid (SMOC-ESA) [2-[2-ethyl-N-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoethanesulfonic acid]		212461	-1.89	9.0	-/235	7.22
Metolachlor oxanilic acid (SMOC-OA) [N-(2-ethyl-6-methyl-phenyl)-N-(2-methoxy-1-methyl-ethyl)-oxalamic acid]		360000	-	18.3	-/325	6.88
Foramsulfuron (FORAM) [2-[[[[(4,6-dimethoxy-2-pyrimidinyl) amino] carbonyl]amino]sulfony]-4-(formylamino)-N,N-dimethylbenzamide]		3293	-0.78	78.4	-/25.3	2.95
2-amino-4,6-dimethoxypyrimidine (FORAM-MET) [4,6-dimethoxypyrimidin-2-amine]		5487	0.92	1237	-/37.2	1.43
Thiencarbazone-methyl (TCM) [methyl 4-[[[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl) carbonyl] amino] sulfonyl]-5-methyl-3-thiophenecarboxylic acid]		436	-1.98	100.0	17/51.5	2.46

[a] Water solubility at 20ºC; [b] Octanol/water partition coefficient at pH 7 and 20ºC; [c] Adsorption coefficient corrected for soil organic carbon content; [d] Time required for the concentration to decline to 50% of the applied amount at field/laboratory; [e] Groundwater Ubiquity Score index for leaching into groundwater (Lewis et al., 2016).

S-metolachlor (SMOC)

SMOC is a selective chloroacetamide herbicide used to control grasses and broadleaf weeds by inhibiting the biosynthesis of very-long-chain fatty acid and impairing cell division and shoot development (Zemolin et al., 2014). It is absorbed by shoot tissues in annual grasses, leading to the malformation of seedlings and by roots in broadleaf weeds (Zemolin et al., 2014). The commercial formulation of SMOC contains a mixture of S-enantiomer (88%) and R-enantiomer (12%) isomers of the herbicide which are chemically and physically similar to metolachlor although the biologically active ingredient is the S-isomer (Wołejko et al., 2017). SMOC is a selective herbicide that effectively controls weeds in various crops, including maize, soybeans, potatoes, sugar beets, carrots, strawberries and peas. In maize, it can be used as a pre- or post-emergence herbicide, with a maximum application rate of 1536 g active ingredient (a.i. ha^{-1}). It has moderate water solubility, high hydrophobicity and an intermediate leaching capacity with a moderate possibility of contaminating the surface and groundwater (Pannacci et al., 2020; Lewis et al., 2016). It is considered to be non-persistent in soils with values of DT$_{50}$ = 23.2 days at field conditions, its degradation is mainly carried out by microbial activity (Kouame et al., 2022). The degradation process leads to the formation of two metabolites, SMOC-OA and SMOC-ESA (Lewis et al., 2016) (**Table 1**).

Foramsulfuron (FORAM)

FORAM is a post-emergence herbicide used selectively to control grasses and a range of broadleaf weeds in maize and turf crops (Lewis et al., 2016). This herbicide works by inhibiting the activity of the acetolactate synthase enzyme and stopping the biosynthesis of branched-chain amino acids (Nurse et al., 2007). The standard dosage of FORAM is 1.5 L ha^{-1}, but one can use up to 2 L ha^{-1} as a rescue treatment when weeds exceed the sizes listed on the label (Bunting et al., 2004). The rate of 2 L ha^{-1}, equivalent to 63 g a.i. ha^{-1}, can be applied twice per cycle of maize (126 g a.i. ha^{-1}). FORAM proves to be an effective herbicide that can be combined with other herbicides to better control important weeds in vegetable crops. FORAM belongs to the sulfonylurea family, which are characterized by high water solubility, low hydrophobicity and high leaching capacity being often detected in surface and groundwater (Ghobadi et al., 2015). It is a weak acid (pKa = 4.6) highly mobile in alkaline soils and in soils with low OM content. It is weakly adsorbed by soils and non-persistent with DT$_{50}$ values of 25.3 days under controlled laboratory conditions (Lewis et al., 2016). It is mainly degraded into two metabolites FORAM-MET and 4-amino-2-(3-(4,6-dimethoxypyrimidin-2-yl)

ureidosulfonyl)-N, N-dimethylbenzamide being commercial only FORAM-MET (**Table 1**) (Lewis et al., 2016).

Thiencarbazone-methyl (TCM)

TCM is a systemic selective triazole herbicide, which offers cross spectrum action against grasses and broadleaf weeds as an inhibitor of the aceto-lactate-synthase enzyme (Santel, 2012). It is applied primarily in maize and can be used at the preemergence or post-emergence timing at a maximum total rate of 2 L ha^{-1} on maize (EFSA, 2013; Lewis et al., 2016). The rate of 2 L ha^{-1}, equivalent to 20 g a.i. ha^{-1}, can be applied twice per cycle of maize (40 g a.i. ha^{-1}). During the manufacturing of commercial formulation, TCM is usually co-formulated with other herbicidal active ingredients. It is mixed with isoxaflutole for pre-emergence application and with FORAM, iodosulfuron or tembotrione for post-emergence application (Santel, 2012). TCM is widely used in the most important maize producing countries since its first registration in 2008 (Santel, 2012). It is a weak acid (pKa = 3.0), characterized by moderate water solubility, low hydrophobicity and intermediate leachability with the tendency to reach groundwater and contaminate water surface (EFSA, 2013; Lewis et al., 2016). It has moderate adsorption and rapid dissipation rate which make it non-persistent in soils with DT$_{50}$ values of 17 days in the field (Gul et al., 2020; Lewis et al., 2016). TCM is degraded in soil to several metabolites whose standards are not commercially available (**Table 1**) (Lewis et al., 2016).

2.1.2   Soil

The field experiment was carried out in experimental plots at Muñovela farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC) (40º 54' 15'' N latitude and 5º 46' 26'' W longitude), for a 2-year period (October 2019 − December 2021). Based on an initial study of the spatial variability of soil properties, an area of the experimental farm was selected to locate and prepare the experimental plots (**Figure 15**).

The selected soil for performing the field and laboratory experiments was an Eutric-chromic Cambisol (WRB et al., 2015) with a predominant sandy loam texture in the 0-90 cm soil layer with 72.9% −80.4% sand, 4.7% − 7.4% silt and 14.9% − 19.7% clay, and clay-sandy loam texture from 90 to 160 cm with: 22% sand, 9.7% silt and 68.3% clay (Carpio et al., 2020; WRB et al., 2015). The soil selection of a sandy soil was based on the low capacity of this type of soils for water retention, their more easily erodible and because they are subject to a greater soil loss making them interesting for testing the environmental benefits of a conservation

agriculture system. The selected soil has been usually dedicated to the cultivation of cereal and for this experiment winter wheat was selected as cover crop.

Figure 15. Experimental plots at the Muñovela experimental farm of IRNASA-CSIC (Salamanca).

2.1.3   Wheat mulches

Winter wheat residues or mulch were sampled immediately after harvest (mulch 1, M1) on experimental plots subjected to conservation tillage at the Muñovela experimental farm on 4 June 2020. Additionally, winter wheat residues left on the soil surface and decomposed under field conditions and irrigation (~ 26 mm per week) were collected one month (mulch 2, M2) and 2.5 months (mulch 3, M3) after harvest, on 8 July 2020 and on 18 August 2020, respectively, to evaluate the influence of its decomposition degree on the adsorption-desorption of herbicides (**Figure 16**). Multiple sub-samples of each mulch type were collected up to a total amount of 500 g and they were mixed, dry cleaned to remove soil particles, and cut into 1- 2 cm pieces. In addition, samples of mulch 1 (M1) were milled (< 1 mm) (MM1) to evaluate its individual adsorbent capacity as a mulch with a different particle size and the impact of using it as an organic amendment on the adsorption-desorption (**Section 2.2.4**) and degradation (**Section 2.2.5**) of herbicides by soils.

Figure 16. Soil and winter wheat mulch samples at different decomposition degree.

2.1.4   Pesticide environmental fate mathematical models: PRZM and MACRO

Two mathematical models have been selected in this work to study the herbicides leaching in the field, **PRZM** (Carsel, 1998) and **MACRO** (Larsbo and Jarvis, 2003). These one-dimensional models include the main processes affecting the behaviour of pesticides in soils (adsorption, degradation, leaching, volatilization, plant uptake and wash-off, erosion and runoff) to simulate their transport in the soil profile. PRZM 3.21 and MACRO 5.2 have been selected for their different description of water and solute transport, each with its features and limitations (**Figure 17**). The summary of the most important processes simulated by both mathematical models are shown in **Table 2**.

PRZM is a one-dimensional, dynamic, compartmental model used to simulate the movement and transformation of field applied pesticides in the crop root zone region and the underneath unsaturated zone. It is able to simulate three pesticides or parent compound and two metabolites simultaneously. It has two main components: hydrology and solute transport. The hydrology component is grounded on the Soil Conservation Service Curve Number technique (SCS-CN) and the Universal Soil Loss Equation (MUSLE) for calculating runoff and erosion.

The soil hydrology is described based on the approach of a 'tipping-bucket' where water will leach to the deeper soil layer only if field capacity is surpassed. Water transport is simulated using generalized soil parameters, including wilting point, field capacity and saturation water content. The evapotranspiration factor is predicted either directly from pan evaporation input or based on an empirical formula. It is divided between evaporation from crop interception, evaporation from soil, and transpiration by the crop. The solute movement component can simulate pesticides application on the soil or on the plant foliage. The solute transport is estimated by convection and numerical dispersion considering the processes of adsorption, plant uptake, degradation, volatilization, leaching and foliar wash-off. The adsorption process is estimated based on the Freundlich isotherm, linear and instantaneous adsorption equilibrium. The degradation of pesticides in soils is calculated by first order kinetic model or bi-phasic equation, together with the effect of soil temperature and moisture. One of the advantages of this model is its ability of simulating the change in pesticides concentration with depth within the soil profile. This model is a useful tool for the estimation of pesticides behaviour in soil system for the aim of performing exposure assessments as it can consider the effects of agricultural management practices as well as the variability in the natural systems and the uncertainty in system properties (Carsel, 2005).
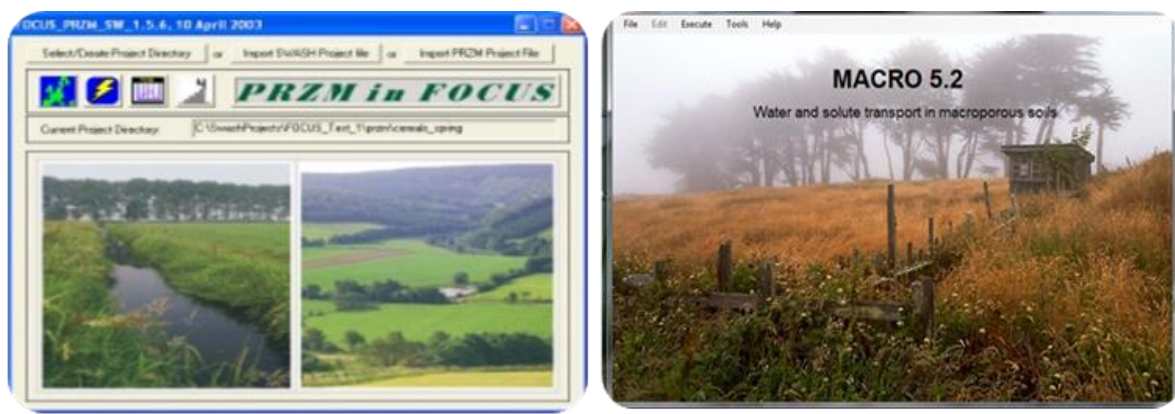
Figure 17. Home page of the mathematical models used to simulate the environmental fate of the herbicides studied: PRZM3.21 (left), and MACRO 5.2 (right).

MACRO is a one-dimensional model that considers the unstable fluxes of water and solute to describe their movement within a variably saturated layered soil profile for a variety of soil types. MACRO is a dual-permeability and physically based preferential flow model, where the total soil porosity is divided into two separate flow domains, micropores and macropores, each characterized by a degree of saturation, conductivity, water flow rate, solute concentration, and solute flux density. The boundary between the two regions is defined by a soil water pressure head close to saturation, and its related water content and hydraulic conductivity.

The partitioning of percolated water at the surface boundary depends on the infiltration capacity of the micropores and the rainfall intensity. The flow of soil water through micropores is simulated using Richards' equation, while gravity drives the flow in the macropore domain. MACRO has the ability to simulate a complete water balance, including precipitation such as rainfall, irrigation, and snow, as well as evapotranspiration, root uptake, deep seepage, and horizontal fluxes to tile drains. The transfer between micropores and macropores is determined by an approximate, physically based expression that uses an effective aggregate half-width. Unlike PRZM, MACRO can account for the upward movement of water and solute, but it cannot account for erosion and surface runoff. The convection-dispersion equation is used to model solute movement in micropores, while in macropores, it is suggested to be only convective. The processes of adsorption, degradation, leaching, plant uptake and canopy interception are also included in MACRO.

Contrary to PRZM, MACRO simulates only one pesticide and its associated metabolites in each simulation. It simulates degradation and adsorption processes in both micro- and macropores regions. Pesticides degradation is determined by the first order kinetic model, while their adsorption is calculated by linear, Freundlich or instantaneous equation. Soil temperatures are calculated from air temperatures using the heat conduction equation. For volatilization process, MACRO does not include a comprehensive description of this process (Larsbo and Jarvis, 2003).

Table 2. Summary of the most important processes simulated by PRZM and MACRO models.

Processes	PRZM	MACRO
Water hydrology	'Tipping-bucket' approach	Micropores: Richards' equation
		Macropores: gravity flow
		Capillarity and preferential flow
Pesticides adsorption	Linear or Freundlich Instantaneous, reversible or fx (time)	Freundlich, instantaneous, Linear, reversible or fx (time) in micro- and macropores
Degradation	1st order or bi-phasic	1st order
Solute transport	Convection + numerical dispersion	Micropores : convection-dispersion
		Macropores : convection
Plant uptake	Fx (transpiration)	Fx (transpiration)
Volatilization	From soil and plant surface	Empirical relationship or global coefficient (leaves)
Erosion	Modified Universal Soil Loss Equation	-
Surface runoff		-
	Curve number approach	
Crop growth	Linear	Bi-linear (height, root depth) and linear + two power-law phases Green Leaf Area Index: annual crop
		Constant: perennial crop
Soil temperature	Heat conduction equation	Heat conduction equation

2.2 EXPERIMENTAL PLOTS

2.2.1 Soil analysis

Samples of the selected agricultural soil were collected at 0-50 cm of depth with a 100 cm (length) × 3 cm (internal diameter, i.d.) probe and sectioned into 5 segments (each with a depth of 10 cm). The soil was sampled from two sites at the same location (Muñovela experimental farm) with different OC content in the top 30 cm of soil. They were labelled as soil S1 (0.69% − 0.73 %OC) and soil S2 (1.01% − 1.26 %OC). This difference in OC content

is due to the treatment of field plots with organic amendments corresponding to spent mushroom substrate in November 2016, in a previous experiment (Carpio et al., 2020). The physicochemical characteristics of the soil samples contained in each segment were determined after drying and sieving (< 2 mm) by standard analytical methods (Carpio et al., 2020; Sparks, 1996).

Soil particle size distribution was determined using the pipette method. The pH was determined in a soil/water suspension (1/2.5 w/v ratio). Inorganic carbon was determined as $CaCO_3$ with a Bernard calcimeter. Total OC and N content were determined using a LECO CN628 (LECO Corporation, Saint Joseph, MI) elemental analyzer. OM was calculated from the OC results multiplied by 1.724. The dissolved organic carbon (DOC) content was determined in soil extracts (1/2 w/v ratio) in deionized water after shaking (24 h at 20 °C), centrifugation (5045 g, 20 min), and filtering (Minisart nylon filters < 0.22 μm, Sartorius Stedim Biotech, Germany). DOC analysis was carried out using a Shimadzu 5050 (Shimadzu, Columbia, MD, USA) organic carbon analyser. The main characteristics of the soils at the beginning of the experiment are shown in **Table 3**.

Table 3. Initial physicochemical characteristics of soils S1 and S2.

Soil	Sand (%)	Silt (%)	Clay (%)	pH	CaCO₃ (%)	OC (%)	OM (%)	N (%)	C/N	DOC (mg g⁻¹)
S1										
0-10 cm	80.4	4.7	14.9	6.81	0	0.69	1.19	0.09	7.93	0.14
10-20 cm	79.7	4.9	15.4	6.77	0	0.69	1.19	0.08	8.27	0.17
20-30 cm	79.7	4.9	15.4	6.82	0	0.73	1.26	0.09	8.21	0.13
30-40 cm	77.4	6.0	16.6	7.13	0.07	0.51	0.88	0.04	13.8	0.09
40-50 cm	77.4	6.0	16.6	7.13	0.07	0.51	0.88	0.04	13.8	0.08
S2										
0-10 cm	76.7	6.8	16.5	7.67	0.14	1.01	1.74	0.12	8.27	0.14
10-20 cm	78.8	5.0	16.2	7.83	0.28	1.24	2.14	0.14	9.11	0.20
20-30 cm	78.8	5.0	16.2	7.67	0.32	1.26	2.17	0.14	8.97	0.18
30-40 cm	77.4	6.0	16.6	7.13	0.07	0.51	0.88	0.04	13.8	0.09
40-50 cm	77.4	6.0	16.6	7.13	0.07	0.51	0.88	0.04	13.8	0.08

2.2.2 Mulch analysis

The physicochemical characteristics of the different mulches, including M1, M2, M3, and milled mulch MM1, were analyzed as previously indicated for soil samples (Carpio et al., 2020; Sparks, 1996). Their OM content was calculated as 100 % ash being ash percentage determined by weight difference after ignition at 540°C for 24 h; and their DOC content was analyzed in a mulch/water suspension with a ratio of 1/100 w/v (Marín−Benito et al., 2012) (**Table 4**). Cross-polarization and magic angle spinning nuclear magnetic resonance (CP-MAS ^{13}C NMR) were used to identify the main functional groups present in the OC and their evolution during mulch decomposition, according to García-Delgado et al. (2020). Chemical shifts were reported relative to tetramethyl silane at 0 ppm, and the spectra were divided into five chemical shift regions: 0-45 ppm alkyl-C, 45-60 ppm N-alkyl-C, 60-110 ppm O-alkyl-C, 110-160 ppm aromatic-C, and 160-220 ppm, which is typically associated with carboxyl and carboxylic-C. The carbon distribution of mulches is shown in **Table 5.**

Table 4. Main characteristics of the mulches at different stages of decomposition (M1, M2, and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1+MM1 and S2+MM1) soils.

Sample	pH	OC (%)	N (%)	C/N	DOC (mg g^{-1})
M1	5.38	44.6	1.21	36.8	125
M2	5.43	44.1	1.56	28.3	114
M3	6.09	44.5	1.53	29.1	66.0
MM1	5.95	41.7	2.22	18.8	55.8
S1	6.81	0.69	0.09	7.93	0.14
S2	7.67	1.01	0.12	8.27	0.14
S1+MM1	5.85	6.26	0.13	47.2	5.81
S2+MM1	6.15	11.4	0.14	79.6	5.96

On the other hand, mulch MM1 was also uniformly mixed with soils S1 and S2 (10% w/w on dry weight basis) in the laboratory (S1+MM1 and S2+MM1) as performed with other organic residues (García-Delgado et al., 2020). The soils S1+MM1 and S2+MM1 were used to study the impact of using MM1 as an organic amendment on the adsorption-desorption (**Section 2.2.4**) and degradation (**Section 2.2.5**) of the herbicides by soils. The physicochemical characteristics of amended soils were determined as indicated in **Section 2.2.1** (**Table 4**).

Table 5. Carbon distribution of mulches calculated by relative areas of the chemical shift regions (ppm) in 13C cross-polarization and magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra.

Mulch	Alkyl-C 0 - 45	N-alkyl-C 45 - 60	O-alkyl-C 60 - 110	Aromatic-C 110 - 160	Carboxyl/carbonyl-C 160 - 220
M1	11.1	0.56	80.4	2.77	5.17
M2	6.23	0.52	87.0	2.35	3.90
M3	9.43	0.46	82.0	2.16	5.95
MM1	7.80	1.15	83.8	4.23	3.02

2.2.3 Preparation of experimental plots, soil management practices and application of herbicides

A design of 12 experimental plots of 81 m^2 (9 m × 9 m) was established including four treatments with a random distribution resulting from the combination of two soil management systems (conventional and conservation system), and two different soils, S1 and S2, each of them with three repetitions (**Figure 18**). The conventional system corresponded to a conventional tillage (CT) with a cultivator up to 25-28 cm (S1+CT and S2+CT), and the conservation system corresponded to non-tillage (S1+NT and S2+NT) during two winter wheat - maize cycles (**Figures 18 − 19**).

For the first year, winter wheat was sown as cover crop in S1+NT and S2+NT plots on 29 October 2019 chemically destroyed by glyphosate on 24 April 2020, cut and deposited on the NT surface plots as mulch, covering 65% − 70% of soil surface prior to maize sown. Soil was kept bared in S1+CT and S2+CT plots during this period. Maize (Buckley variety) was sown by direct seeding in the 12 experimental plots on 8 June 2020. The sowing depth was 7

cm and the seed separation were 19-20 cm in the same furrow. It was harvested on 2 December 2020 (first crop cycle). For the second year, the soil was again kept bare after maize harvest in S1+CT and S2+CT plots while winter wheat was sown as cover crop in S1+NT and S2+NT plots during the fallow period. The winter wheat was sown on 26 of February 2021, and destroyed by glyphosate on 17 of May 2021, to prepare the field for the second crop cycle of maize that took place between 3 of June 2021 and 19 November 2021. It is important to note that in the second year the winter wheat sowing was delayed due to unfavorable weather conditions. Moreover, the winter wheat did not grow adequately, and as a result, external winter wheat straw from nearby plots had to be used as mulch to cover the soil surface.
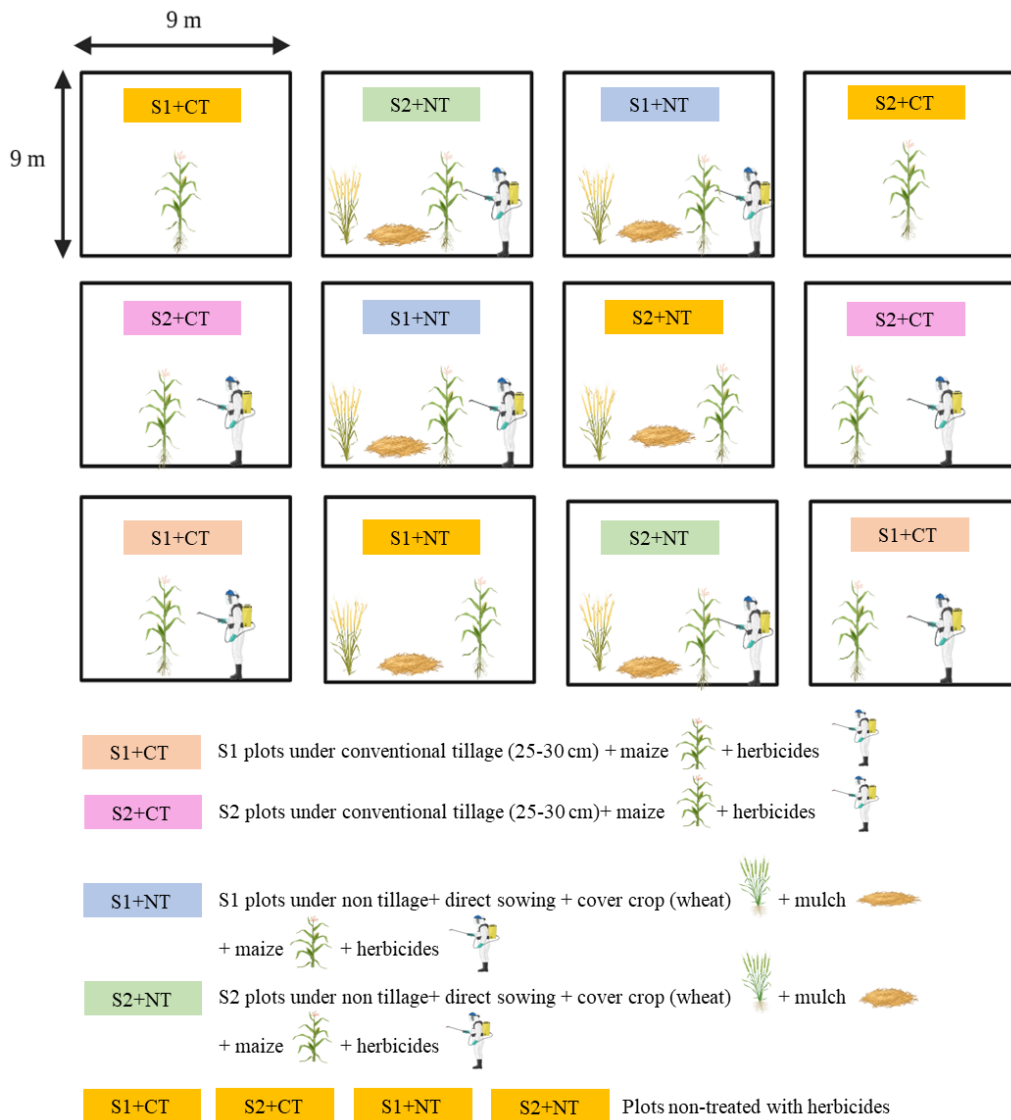
Figure 18. Experimental field design.

Figure 19. Maize at different development stages in plots under conventional (left) and conservation (right) tillage.

Prior to first cover crop sowing (October 2019), the experimental plots were equipped with a 120 cm (length) × 5.2 cm (i.d.) PVC tube to periodically (once every 7-15 days) measure the volumetric soil water content in the soil profile and evaluate its temporal evolution every 20 cm from 20 to 60 cm depth using a Troxler Sentry 200-AP electric probe (Troxler International Ltd., NC, USA) (**Figure 20**). A total of 76 measurements of the volumetric water content of the soil were recorded at 20, 40, and 60 cm per plot from 19 November 2019 to 17 December 2021. The volumetric water content of the soil was also initially measured at 80 and 100 cm depth to parameterize the initial humidity soil conditions in the mathematical models (**Section 2.2.10**).

Figure 20. PVC tube installed in the soil profile (left) and Troxler Sentry 200-AP electric probe (right) for measuring the volumetric soil water content.

The herbicides SMOC, FORAM and TCM were jointly applied using a tractor in pre-emergence of maize on 9 June 2020, at the rates of 0.621, 0.621 and 0.197 kg a.i ha^{-1}, respectively, and on 8 June 2021, they were applied manually with an automatic sprayer attached to a backpack at the rates of 0.975, 0.840 and 0.267 kg a.i ha^{-1}, respectively (**Figure 21**). They were applied under commercial formulations (Efica 960EC®) and Monsoon Active®) in 8 plots (2 replicates per treatment) while one replicate more per treatment was not treated with herbicides to be used as control plot in the microbiological studies. Control plots were divided in two subplots of 45 m^2 to perform the microbiological studies by duplicate. The rate of SMOC applied the first and the second year was 40% / 63% of the maximum agronomic dose , respectively, and those of TCM and FORAM corresponded to 5 (first year) / 6.7 (second year) times the maximum agronomic dose considering that it can be applied twice per maize

cycle. The application was made on bare soil in treatments S1+CT and S2+CT, while the herbicides were partially intercepted by the wheat mulch in treatments S1+NT and S2+NT.

All experimental plots were irrigated weekly (~26 mm week^{-1}) by sprinkler between June and September 2020 (333 mm total irrigation) for the first maize cycle and between July 2021 and August 2021 for the second maize cycle (~26 mm week^{-1}, 234 mm total irrigation). The first irrigation was carried out 7 and 35 days after the first and second herbicide application, respectively.

Figure 21. Application of herbicides using a tractor (first application) (left) and an automatic sprayer attached to a backpack (second application) (right).

2.2.4 Evaluation of herbicides adsorption-desorption by wheat mulches, soils and soils amended with milled wheat mulch at the laboratory

Adsorption-desorption isotherms of herbicides SMOC, FORAM and TCM by mulches at different stages of decomposition (M1, M2, M3) and particle size (MM1), and by unamended soils (S1 and S2) collected from the top layer (0-10 cm) (**Figure 22**) or MM1-amended soils (S1+MM1 and S2+MM1) were obtained using the batch equilibrium technique. Soil samples were taken from the corresponding field experimental plots prior to herbicides application and mulches from plots under NT treatments and non-treated with herbicides (see **Section 2.1.3**). Duplicate samples of dry mulch (0.1 g) or soil (5 g) (**Figure 23**) were equilibrated with 10 mL of an ultrapure water solution of each herbicide at concentrations of 1, 5, 10, 15, 20, and 25 mg L^{-1}. The suspensions were shaken at 24ºC for 24 h in a thermostatted chamber, with intermittent shaking for 2 h at three-hour intervals. Preliminary experiments revealed that contact for 24 h

was long enough for reaching equilibrium. The suspensions were subsequently centrifuged at 5045 g for 30-40 min, and the supernatant was filtered through 0.22-μm nylon filters prior to the determination of the equilibrium concentration of each herbicide in the supernatant by ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS, Agilent Technologies, Avondale, AZ, USA) (**Figure 24**). The amount of herbicide adsorbed was taken to be the difference between that initially present in solution and that remaining after equilibration with the mulch or soil. Calculations assumed that the herbicides did not degrade during the adsorption studies.

Figure 22. Soil sampling at the top layer (0-10 cm).
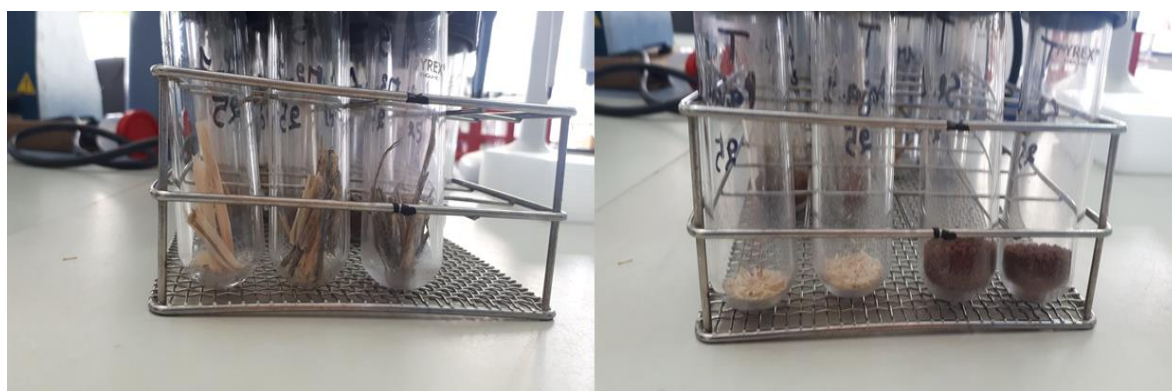
Figure 23. Mulch and soil samples for adsorption-desorption experiment.

The desorption isotherms of the herbicides were obtained from 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, and after adsorption equilibrium had been reached, a 5 mL aliquot was taken from the solution and immediately replaced by 5 mL of ultrapure water. The resuspended samples were shaken as indicated above, after which the suspensions were centrifuged, filtered, and the desorbed herbicide was calculated as the difference between that initially adsorbed and the amounts desorbed measured by UHPLC-QTOF-MS (**Figure 24**). Adsorption and desorption parameters were determined from the adsorbed and desorbed amounts of herbicides as indicated in **Section 2.2.11.**

Figure 24. UHPLC-QTOF-MS for herbicide analysis.

2.2.5   Evaluation of herbicides degradation and the formation of their main metabolites in milled mulch and soils under controlled laboratory conditions

The degradation of herbicides SMOC, FORAM and TCM and the formation of their metabolites (commercially available) was evaluated in fresh, homogenized and sieved (< 2 mm) S1 and S2 soil samples taken from the top layer (0-10 cm) of the corresponding experimental plots prior to herbicides application (**Figure 22**). Degradation of herbicides was also evaluated in MM1 samples and in MM1-amended soils (S1+MM1, S2+MM1)

A total of thirty unamended and MM1-amended soils or MM1 microcosms were set. Treatments corresponded to non-sterile (duplicate) and sterile (single) S1, S2, S1+MM1, S2+MM1 and MM1 incubated at 14°C and 24°C.

For the non-sterile soil treatments, 500 g of unamended soils (S1, S2), 350 g of the MM1-amended soils (S1+MM1, S2+MM1) and 50 g of MM1 were weighed in glass containers and the moisture content was adjusted to 40% of the maximum water holding capacity according to the moisture content of each sample previously determined. For the sterile soil treatments, 300 g of soil (SS1, SS2) and MM1- amended soil (SS1+MM1, SS2+MM1) and 50 g of SMM1 were weighed in Erlenmeyer flasks with a cotton stopper and autoclaved at (120°C, 1 h). The sterilization process was repeated for 5 consecutive days and after each sterilization the samples were left at the laboratory temperature for 24 h to help germinate as many spores as possible to be killed in the next sterilization. Sterile soil treatments were used as controls to check the chemical degradation of the herbicides.

The three herbicides were jointly added to the non-sterile and sterile soils and MM1 at a concentration of 2 mg each herbicide kg^{-1} of MM1, unamended and MM1-amended soils. Soils or MM1 and herbicides were mixed with a spatula to achieve a homogeneous distribution of the herbicides previously to be incubated in darkness at two different temperature 14°C and 24°C (**Figure 25**). These temperatures correspond to average mean temperature during maize crop campaign where the experimental plots were located, and 10°C higher. Moisture losses were periodically refilled by adding sterile water. Soils and MM1 were sampled at different incubation times (0, 1, 4, 7, 11, 14, 18, 25, 32, 41, 49, 60, 81, 102, 130, 158, 193 and 284 days) being the sterile soils sampled in a laminar flow cabinet (**Figure 25**).

At each sampling time, duplicate samples of MM1 (3 g) were mixed with 16 mL of methanol, and duplicate unamended and amended soil samples (5 g) were mixed with 10 mL of methanol: Milli-Q ultrapure water (Millipore) 50:50 to extract the herbicides and the possible metabolites formed. They were subjected to sonication (1h, 20°C), intermittent shaking (24 h, 20°C), centrifugation (5045 g, 30 min) and filtration (< 0.22 µm). In the treatment MM1, the herbicides/metabolites contained in the extracts were concentrated by evaporating 8 mL of supernatant to dryness under nitrogen stream using an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany) (**Figure 27**). The residue was redissolved in 0.6 mL of methanol and the analytical determination of herbicides remaining and/or metabolites formed in the extracts of different samples was carried out by UHPLC-QTOF-MS (**Section 2.2.9 and Figure 24**). The recovery percentages for each herbicide/metabolite and treatment studied are shown in **Table 6.**

Degradation parameters were determined by fitting the experimental data to the corresponding degradation kinetic models (SFO or FOMC model) and the effect of incubation temperature was determined by the factor Q_{10} as indicated in **Section 2.2.11.**

Figure 25. Degradation experiment at the laboratory: Incubation of soil samples at 14°C or 24°C (left), and sterile soil samples in the laminar flow cabinet (right).

Table 6. Recovery percentages for each herbicide and metabolite in MM1, unamended (S1, S2) and MM1-amended (S1+MM1, S2+MM1) soils.

Herbicide/ Metabolite	MM1	S1	S2	S1+MM1	S2+MM1
SMOC	100	116	122	87.0	89.6
SMOC-ESA	95.7	92.9	93.5	92.5	104
SMOC-OA	96.0	100	110	92.5	100
FORAM	89.5	84.4	73.2	70.6	74.6
FORAM-MET	92.0	99.5	99.0	72.4	73.6
TCM	104	100	69.1	73.0	72.4

2.2.6   Evaluation of dissipation kinetics of herbicides and their main metabolites in soils under different agriculture management practices in the field

The dissipation study of herbicides and the formation of their main metabolites was analysed in soil samples collected from the topsoil (0-10 cm) of the field experimental plots under conventional (S1+CT, S2+CT) and conservation (S1+NT, S2+NT) tillage that were treated with the herbicides. The sampling times corresponded to 1, 5, 8, 13, 20, 27, 34, 41, 48, 55, 62, 69, 76, 91, 111, 139 after the first herbicides application (first maize cycle), and at 1, 5, 8, 14, 20, 29, 34, 41, 48, 57, 62, 69, 76, 84, 105, 111 and 153 days after the second herbicides application (second maize cycle). At each sampling time, five soil sub-samples were randomly taken from each plot, they were homogeneously mixed to obtain a representative average soil samples for each plot. The soil samples were transferred from the field to the laboratory in plastic bags where they were homogenized, sieved (< 2 mm) and stored at -18°C until the extraction of herbicides/metabolites. Duplicate wet soil samples (40 g) were taken from each soil segment and plot and sonicated (1h at 20°C) and intermittently shaken (24h at 20°C) with 80 mL of methanol: Milli-Q ultrapure water 50:50. Then, they were centrifugated (30 min at 5045 g) and filtered with nylon filters (< 0.22 µm). Subsequently, the herbicides contained in the extract were concentrated by solid-phase extraction (SPE). For this purpose, 50 mL of extract was mixed with 445 mL Milli-Q ultrapure water and 5 mL formic acid. The mixture was passed through Bond Elut Plexa polymeric cartridges (60 mg, Agilent) using a Gilson MINIPLUS 3 peristaltic pump (Gilson, Inc., Middleton, WI, USA) at a constant flow rate of 1 mL min^{-1} (**Figure 26**). The cartridges were previously conditioned with 5 mL of methanol and with 5 mL of deionized water. The herbicides retained on the cartridges were eluted with 5 mL of methanol that were evaporated to dryness under nitrogen stream using an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany) (**Figure 27**). Finally, the residue was redissolved in 0.75 mL methanol and transferred to glass vials to be quantified by UHPLC-QTOF-MS (see **Section 2.2.9**) (**Figure 24**). In order to express the results per gram of dry soil, the soil humidity of each soil sample was determined by weight difference after drying 5 g of the corresponding soil segment at 110ºC for 24 h.

The amounts of SMOC, FORAM, TCM determined were expressed as percentages of the initial amount of applied herbicides. Dissipation parameters were determined by fitting the experimental data to the corresponding degradation kinetic models (SFO or FOMC model) (**section 2.2.11**).

Figure 26. Dissipation and mobility experiment (from left to right, and from up to down): Intermittent shaking of soil samples for 24 h, filtered supernatant, herbicides concentration by solid-phase extraction, and elution of herbicides.
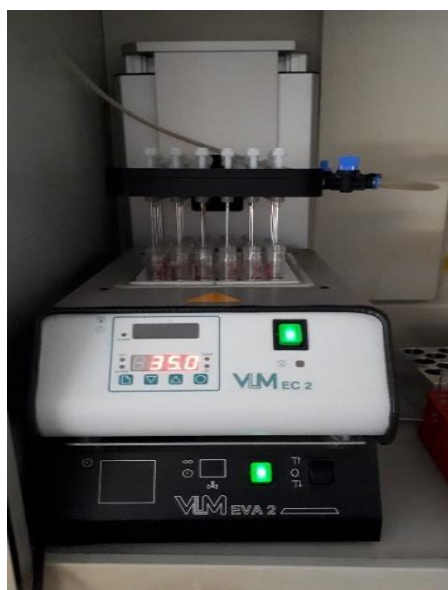
Figure 27. EVA-EC2-L evaporator.

2.2.7 Evaluation of biochemical parameters indicators of activity, abundance and structure of soil microbial communities during the dissipation process of herbicides in the field

The changes of microbial communities in soils non-treated and treated with herbicides and subjected to the two different soil management practices, CT and NT, was evaluated by the biochemical parameters: dehydrogenase activity (DHA), respiration, microbial biomass and the phospholipid fatty acids (PLFAs) profile. These parameters are an important indicator of the activity, abundance, and structure of soil microbial communities. The analysis was carried out with fresh soil samples collected from the surface horizon (0-10 cm) of all experimental field plots at different times, 0, 34 and 153 days after the second herbicides application. Soil samples were sieved (< 2 mm) and their humidity was determined by weight difference after drying 5 g (by duplicate) of each soil sample at 110ºC for 24 h.

Determination of dehydrogenase activity

Dehydrogenase enzymes are one of the most important soil enzymes linked with microbial oxidoreduction processes. They are characterized by their biological oxidation of soil OM, and are used as an indicator of overall soil microbial activity (Wolińska and Stepniewska, 2012). The DHA of field soil samples was determined using the Tabatabai (1994) method. It is a colorimetric method, where 2,3,5-triphenyltetrazolium chloride (TTC) is reduced by soil microorganisms resulting in the formation of 1,3,5-triphenyl formazan (TPF), which is a red compound.

Six grams of fresh and sieved soil samples collected from all the experimental field plots at the different times previously indicated were weighed and 60 mg of calcium carbonate ($CaCO_3$), 1 mL of a 3% aqueous solution of TTC and 2.5 mL of Milli-Q ultrapure water (Millipore) were added. They were vortexed gently and incubated at 37°C in the dark under anaerobic conditions for 24 h. After this incubation time, the red-coloured compound TPF originated from the reduction of TTC was extracted with three consecutive methanol extractions (**Figure 28**). For this purpose, 7 mL of methanol were added to each soil sample, vortexed and centrifuged at 5045 g for 10 min. The supernatant was transferred to a 25 mL volumetric flask using a glass Pasteur pipette. The above procedure was repeated twice, and the flask was finally filled up to 25 mL with methanol. The calibration curve was prepared with standard solutions

prepared in methanol with concentrations between 0 and 40 µg TPF mL^{-1}. TTC and TPF reagents were supplied by Sigma-Aldrich S.A (Spain).
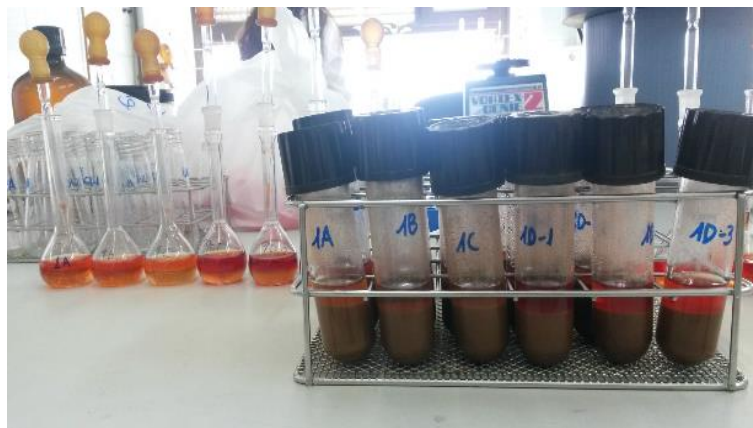
Figure 28. Soil samples after the reduction of TTC to TPF as an indicator of dehydrogenase activity.

The DHA is determined by the quantification of the absorbance of TPF compound within the range of visible light at $\lambda = 485$ nm by ultraviolet-visible (UV/VIS) spectrophotometry. The spectrophotometer used was a Cary 100 Conc model (Varian Optical Spectroscopy Instruments) with Cary Win UV software (**Figure 29**). The values of the results are expressed in µg TPF g^{-1} of dry soil.
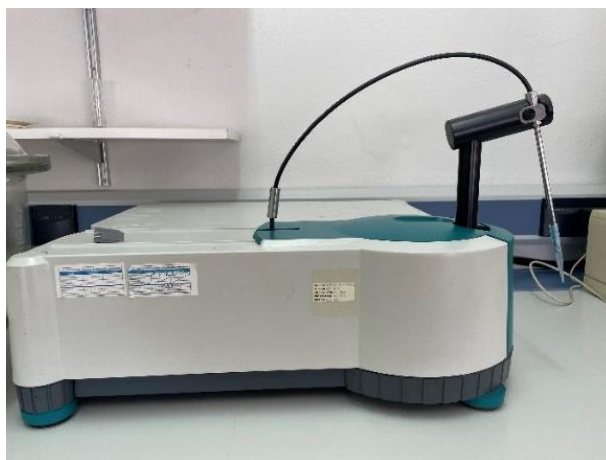
Figure 29. Ultraviolet-visible (UV/VIS) spectrophotometer for DHA quantification.

Determination of the soil respiration

Soil respiration was determined for all experimental field plots at the different times previously indicated by measuring the pressure drop caused by the O_2 consumed by microorganisms in 50 g of fresh soil over four days using OxiTop Control BM6 containers fitted with an OxiTop Control OC 110 measurement system (WTW, Weilheim, Germany) (**Figure 30**). The CO_2 produced by the metabolism of soil microorganisms was trapped in 10 mL of NaOH 1 M. The metabolic activity of microorganisms was measured based on O_2 consumption. The results were expressed as mg O_2 kg^{-1} dry soil.

Figure 30. OxiTop measurement system for the determination of the soil respiration.

Determination of the soil phospholipid fatty acids profile and the microbial biomass

Phospholipid fatty acid profiling is a method that has been developed for a quantitative analyses of soil biotic diversity (fungi and bacteria) based on the variability of fatty acids in cell membrane of the microorganisms. This allows the profiling of soil microbial communities and delivers an overall vision of the soil microbial composition, structure and biomass (Frostegård et al., 1993). Thirty grams of fresh and sieved soil samples collected from all the experimental field plots at the different times previously indicated were freezed at -79ºC for 24 h and then lyophilized for 48 h prior to their analyses (**Figure 31**).

Figure 31. Freezing of soil samples at -79ºC (left) and soil sample lyophilization (right).

Lyophilized soil samples were extracted by sonication with a one-phase chloroform-methanol-phosphate buffer solvent. The samples were then purified by solid-phase extraction (SPE), and polar lipids were transesterified with methanol-KOH. Finally, hexane extracts containing the resultant fatty acid methyl esters (FAMEs) were analyzed by gas chromatography coupled to a flame ionization detector (GC-FID) (**Figure 32**). The chromatograph used was an Agilent model 7890 (Agilent technologies, Wilmington, DE, USA) equipped with a 25 m Ultra 2 (5% phenyl)-methylpolysiloxane column (J andW Scientific, Folsom, CA, USA). Phospholipids were identified using bacterial and fungal fatty acid standards and a microbial identification system software (Microbial ID, Inc., Newark, DE, USA). Neodecanoic acid (19:0) was used as an internal standard for the quantitative determination of PLFAs. Some specific fatty acids were used as biomarkers to quantify the relative abundance of Gram-positive (iso and anteiso saturated branched-chain fatty acids), Gram-negative (monounsaturated and 17:0 cyclopropyl fatty acids), Actinobacteria (10-methyl fatty acids) and saprophytic and arbuscular mycorrhizal fungi (18:2 ω6 cis and 16:1ω5, respectively). **Total microbial biomass** was estimated by the total sum of PLFAs and expressed as nmol g^{-1}.

Figure 32. Gas chromatograph coupled to a flame ionization detector (GC-FID) for the quantification of phospholipids (PLFAs).

2.2.8   Evaluation of the mobility and distribution of herbicides and their metabolites in the soil profiles under the different soil management practices

The study of herbicides mobility was carried out on profiles of soils (0-50 cm) in each of the experimental plots under conventional tillage (S1+CT, S2+CT) and non-tillage (S1+NT, S2+NT) treated with the herbicides. The samples were taken at different times throughout the 2-year experiment corresponding to 1, 13, 27, 41, 62, 76 and 139 days after the first herbicide application (first maize cycle), and at 1, 14, 29, 41, 57, 69, 84, and 111 days after the second herbicides application (second maize cycle). At each sampling time, five soil profiles up to 50 cm depth were randomly taken with a 3 cm i.d. probe in each plot and sectioned into 5 segments (each with a depth of 10 cm) (**Figure 33**). The five soil sub-samples contained in each segment corresponding to the same depth were homogeneously mixed to obtain a representative average soil samples for each plot. The soil samples were transferred from the field in plastic bags to the laboratory, where they were homogenized, sieved (< 2 mm) and stored at -18°C until the extraction of herbicides. The extraction and analyses of herbicides were carried out as it is indicated for the samples collected for the study of their dissipation previously described in **Section 2.2.6**.

Figure 33. Soil sampling up to 50 cm depth.

The DOC content was determined in soil samples at different times after the herbicide application (13, 41 and 139 days after the first application, and 14, 41 and 111 days after the second application) to evaluate the influence of this parameter on the mobility of the herbicides. These analyses were carried out as indicated in **Section 2.2.2**.

2.2.9   Quantitative determination of herbicides and metabolites

The extraction and analyses of the herbicides and metabolites was performed with soil samples taken from the field experimental plots for the different processes at selected time periods. The herbicides/metabolites were quantitatively determined by UHPLC-QTOF-MS (**Figure 24**). The equipment used was an Agilent chromatograph (Agilent Technologies, Avondale, AZ, USA) equipped with a UHPLC (HPCL Infinity II), an Agilent 6546A QTOF mass spectrometer, and Mass Hunter Qualitative and Quantitative Analysis software as the data acquisition and processing system. The chromatographic separation of herbicides involved a Zorbax® Eclipse Plus C18 column from Agilent (2.1 × 50 mm inner diameter, 1.8 μm), maintained at 30 ℃. The gradient profile was as follows: 0 - 0.25 min, 95% water with 0.1% formic acid (A) and 5% acetonitrile (B); 0.25 – 2.5 min, 55% A and 45% B; 2.5 – 3.5 min, 100% B; 3.5 – 4 min, 95% A and 5% B. The flow rate was 0.4 mL min^{-1} and the sample injection volume was 4 μL. The Q-TOF mass spectrometer operated in positive electrospray ionisation mode (ESI) ion source with Jet Stream Technology (AJS) under multiple-reaction monitoring mode (MRM). Ultra-pure nitrogen (N_2) was used as the nebulising and sheath gas. Ultra-high-purity N_2 was used as collision gas in product ion scanning experiments. The ESI parameters

were set as follows: the capillary voltage was 3.5 kV; the temperature of the sheath gas and the flow rate were 350 ºC and 11 L min^{-1}, respectively; the source temperature was set at 225 ºC and the flow rate of the drying gas at 12 L min^{-1}; the nebulizer gas pressure was 30 psi; the fragmentation voltage was 110 V; the mass analyser scanned from 100 to 1050 (*m/z*); the QTOF acquisition rate was 1.5 Hz; the energies for collision-induced dissociation (CID) experiments were set at 10, 20, and 40 eV, respectively.

All MS data were acquired with reference masses at *m/z* 121.05 and 922.01 in the positive ESI mode to ensure mass accuracy and reproducibility; quantification involved monitoring the positive molecular ion *m/z* [M+H]$^+$ 284.14 (SMOC), 330.14 (SMOC-ESA), 280.15 (SMOC-OA), 453.12 (FORAM), 156.08 (FORAM-MET), and 391.39 (TCM). Under these conditions, the retention times of the herbicides and metabolites were 3.81 (SMOC), 2.58 (SMOC-ESA), 3.20 (SMOC-OA), 2.90 (FORAM), 1.45 (FORAM-MET), and 3.17 (TCM) min. (**Figure 34**). The range of the detection (LOD) and quantification (LOQ) limits for each herbicide/metabolite and treatment studied are shown in **Table 7**.
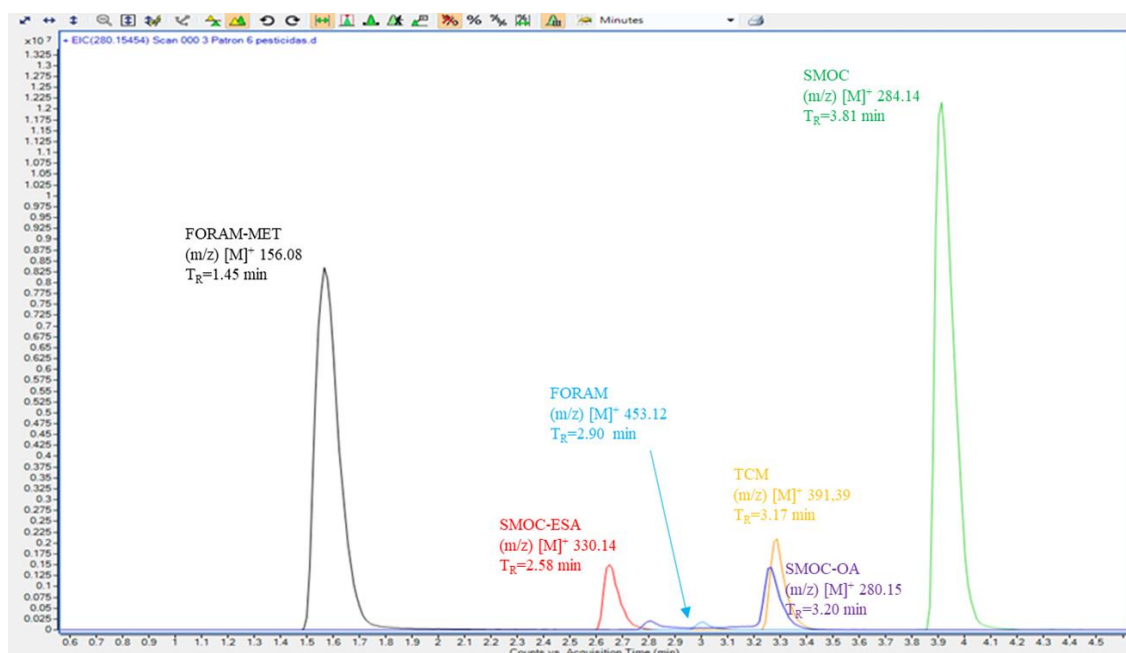
Figure 34. Chromatogram obtained by UHPLC-QTOF-MS showing the peaks of S-metolachlor (SMOC) and its metabolites (SMOC-ESA and SMOC-OA), foramsulfuron (FORAM) and its metabolite (FORAM-MET) and thiencarbazone methyl (TCM) with different retention times in response to the intensity of the analytes as a function of time.

Table 7. Range of the detection (LOD) and quantification (LOQ) limits for each herbicide and metabolite in the different treatments assayed.

Herbicide/ Metabolite	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)
SMOC	0.231 - 6.106	0.700 - 18.50
SMOC-ESA	0.141 - 6.447	0.428 - 19.54
SMOC-OA	0.151 - 4.132	0.457 - 12.52
FORAM	0.482 - 3.097	1.462 - 9.385
FORAM-MET	0.059 - 1.033	0.180 - 3.132
TCM	0.058 - 1.117	0.177 - 3.386

2.2.10 Modelling of herbicides behaviour in the field

Modelling strategy

The simulations of the behaviour of herbicides in field were conducted from 30 October 2019 to 31 December 2021, and the modelling strategy was carried out through two steps. The first step was the models' calibration of water and herbicides (SMOC, FORAM and TCM) content in the soil profiles of plots subjected to conventional (S1+CT, S2+CT) and conservation (S1+NT, S2+NT) tillage against field measurements, during the experimental period of 30 October 2019 to 31 December 2020 (first year). The second step was the models' validation, where water content and herbicide transport were simulated without any additional model calibration from 01 January 2021 to 31 December 2021, and the results were compared with the field observation of the second year.

Parameterization of mathematical models

The parameterization of the models was mainly based on experimental data of soils, herbicides, crop, irrigation, and climate that were measured in the field. The data that were not measured in the field, such as hydrological parameters, were estimated by pedotransfer

functions using data from the literature or default values from the corresponding user manuals of the model.

The physical presence of the mulch layer at the topsoil in NT plots was not considered in the simulation but its impact on the potential evapotranspiration (ETP) and on the adsorption and degradation of the herbicides intercepted by the mulch layer was considered in the meteorological file and in the herbicide application module of the models, respectively. The soil profiles were divided into five horizons of different depths (**Table 8**).

The soil physicochemical characteristics such as pH, bulk density, OC, OM, sand, silt, and clay were measured from 0 to 50 cm depth (**Table 3**) while values for these characteristics were taken from Carpio et al. (2020) for samples of the rest of horizons (51-160 cm depth). For PRZM parameterization, water content at field capacity (θ_{FC}, pF = 2) and at wilting point (θ_{WP}, pF = 4.2) were estimated using Rosetta pedotransfer functions (Šimůnek et al., 2008). Meanwhile for MACRO parameterization, the pedotransfer functions MACRO 5.0/5.1 included in MACRO 5.2 were used to estimate the van Genuchten soil-water parameters (θ_r, θ_s, α and n), the saturated hydraulic conductivities (K_{sat}), and the soil characteristics of the macropore domain such as: the water content corresponding to the boundary soil water pressure head between micropores and macropores (θ_b), the boundary hydraulic conductivity (K_b), the parameter controlling the exchange of both water and solute between the micropore and macropore flows (ASCALE) and the size distribution index in the macropores (ZN). For the boundary soil water pressure head between micropores and macropores, it was set to MACRO default value (CTEN = 10 cm) (**Table 8**).

Adsorption coefficients (K_f) of SMOC, FORAM and TCM in the CT and NT soil profiles and the effect of temperature on herbicides degradation rate (Q_{10} in PRZM and TRESP in MACRO) were obtained from the laboratory experiments, and their topsoil half-lives (DT_{50}) from field experiments aforementioned, respectively (see **Section 2.2.5** and **Section 2.2.6**) (**Table 9**). However, a calibration step involving SMOC K_d values was done to improve the goodness-of-fit statistics of the models for this herbicide. The variation of DT_{50} with depth was calculated according to the recommendations of FOCUS (2000) and the K_f values for deeper soil layers were estimated assuming this coefficient was proportional to OC (**Section 3.5**).

Table 8. Physicochemical and hydraulic characteristics of soil profiles (S1, S2) under conventional tillage (CT) and non-tillage (NT).

Treatment	S1+CT					S2+CT		S1+NT		S2+NT	
Parameter/ soil layer (cm)	0-10	11-30	31-50	51-90	91-160	0-10	11-30	0-10	11-30	0-10	11-30
Sand (%)[a]	80.4	79.7	77.4	72.9	68.3	76.7	78.8	80.4	79.7	76.7	78.8
Silt (%)[a]	4.7	4.9	6.0	7.4	9.7	6.8	5.00	4.7	4.9	6.8	5.0
Clay (%)[a]	14.9	15.4	16.6	19.7	22.0	16.5	16.2	14.9	15.4	16.5	16.2
pH[a]	6.81	6.79	7.13	7.36	7.74	7.67	7.59	6.8	6.76	7.67	7.53
BD (g cm^{-3})[a]	1.50	1.49	1.54	1.61	1.60	1.43	1.40	1.55	1.55	1.48	1.45
OC (%)[a]	0.69	0.71	0.51	0.27	0.29	1.01	1.24	0.68	0.69	1.01	1.24
$\Theta_{initial}$ (m^3 m^{-3})[b,c]	0.197	0.196	0.161	0.167	0.202	0.160	0.217	0.177	0.170	0.182	0.190
Θ_{FC} (m^3 m^{-3})[d]	0.219	0.227	0.239	0.259	0.275	0.252	0.246	0.219	0.229	0.249	0.244
Θ_{WP} (m^3 m^{-3})[d]	0.069	0.068	0.075	0.094	0.108	0.073	0.070	0.069	0.068	0.071	0.071
Θ_r (m^3 m^{-3})[e]	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Θ_S (m^3 m^{-3})[e]	0.380	0.380	0.370	0.350	0.360	0.410	0.410	0.370	0.370	0.390	0.400
α (cm^{-1})[e]	0.087	0.086	0.096	0.094	0.088	0.080	0.080	0.090	0.090	0.080	0.090
n[e]	1.32	1.30	1.27	1.22	1.19	1.29	1.31	1.33	1.32	1.28	1.26
K_{sat} (mm h^{-1})[e]	427	377	298	178	390	355	382	328	326	323	349
CTEN (cm)[f]	10	10	10	10	10	10	10	10	10	10	10
Θ_b (m^3 m^{-3})[e]	0.32	0.33	0.32	0.31	0.33	0.35	0.36	0.31	0.31	0.34	0.34
K_b (mm h^{-1})[e]	7.72	7.41	6.55	5.02	3.93	6.4	7.01	7.72	7.41	6.4	7.01
ASCALE (mm)[e]	2	2	50	50	70	2	2	2	2	2	2
ZN (-)[e]	4	4	3	3	4	4	4	4	4	4	4

[a] Parameters measured in the laboratory for 0–50 cm depth. The values for 51–160 cm depth were taken from Carpio et al. (2020); [b] Data for 0–20, 20–40, 40–60, 60–80 and 80-100 cm depth soil layers, respectively. The data measured for the 80-100 cm layer were used to parameterize the 100–160 cm layer; [c] $\Theta_{initial}$ at 40–60, 60–80 and 80-100 cm depth were 0.269/0.269/0.312 m^3 m^{-3} for S2+CT, 0.163/0.159/0.190 m^3 m^{-3} for S1+NT and 0.203/0.193/0.223 for S2+NT, respectively; [d] Estimated by Rosetta's pedotransfer functions (Šimůnek et al., 2008); [e] Estimated by the pedotransfer functions MACRO 5.0/5.1 included in MACRO 5.2; [f] Default value (Larsbo and Jarvis, 2003).

Given that PRZM and MACRO were not designed for modelling the environmental fate of herbicides under conservation tillage practices involving a mulch layer where a fraction of herbicide is intercepted during the application process and can be adsorbed and degraded, an approach was necessary to be considered to simulate the experimental behaviour of the herbicides in NT plots.

The herbicides were applied experimentally once per year; however, two herbicide applications were considered in the herbicide application module of the models. The first application rate corresponded to the experimental amount of herbicide that reached the soil in the real date of application. The second application was assumed to happen on the date when the first irrigation or precipitation event was recorded as a result of the herbicide wash-off that had been intercepted by the mulch layer in the real (experimental) application date. This approach allows us assuming that there is a difference between the total rate applied of herbicides and those determined experimentally on the soil surface. This difference between the real rate of herbicide applied and the sum of the first and second rate of herbicide used as input in the models is due to the irreversible adsorption and/or degradation in the mulch layer.

The dispersivity (DV for MACRO) and the hydrodynamic dispersion (DISP for PRZM) coefficients for each soil treatment were fitted according to the data obtained in the previous study conducted in the field (**Table 9**) (Marín-Benito et al., 2020).

Table 9. Main herbicide input parameters used in the simulations for PRZM and MACRO.

Parameter	Soil layer (cm)	SMOC				FORAM				TCM			
		S1+CT	S1+NT	S2+CT	S2+NT	S1+CT	S1+NT	S2+CT	S2+NT	S1+CT	S1+NT	S2+CT	S2+NT
Adsorption													
K_f (mL g^{-1})[a]	0-10	1.34	1.34	2.00	2.00	0	0	0.090	0.090	0.010	0.010	0.400	0.400
		0.80*	0.80*	0.80*	0.80*								
	11-30	1.39	1.39	2.46	2.46	0	0	0.090	0.090	0.008	0.008	0.380	0.395
		0.82*	0.83*	0.97*	0.97*								
	31-50	1.00	0.99	1.00	1.00	0	0	0.037	0.037	0.007	0.007	0.160	0.163
		0.60*	0.59*	0.40*	0.40*								
	51-90	0.53	0.53	0.53	0.53	0	0	0.020	0.020	0.004	0.004	0.080	0.087
		0.31*	0.31*	0.21*	0.21*								
	91-160	0	0	0	0	0	0	0	0	0	0	0	0
n_f [b]	0-10	0.63	0.63	0.63	0.63	0	0	1.18	1.18	1.89	1.89	1.11	1.11
Degradation													
DT_{50} (days) [c]	0-10	0.023	0.073	0.033	0.05	0.158	0.112	0.117	0.073	0.060	0.048	0.024	0.018
	11-30	0.023	0.073	0.033	0.05	0.158	0.112	0.117	0.073	0.060	0.048	0.024	0.018
	31-51	0.012	0.036	0.017	0.24	0.079	0.056	0.059	0.036	0.030	0.024	0.012	0.009
Q_{10} [d]		3.80	3.80	2.70	2.70	2.61	2.6	2.34	2.3	2.80	2.82	2.00	2.00
TRESP (K^{-1})[e]		0.13	0.13	0.10	0.10	0.10	0.10	0.09	0.08	0.10	0.10	0.07	0.07
Other characteristics													
DISP (cm^2 day^{-1})[f]		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
DV (cm)[f]		10	10	12	12	10	10	12	12	10	10	12	12

[a] Adsorption coefficient taken from the adsorption-desorption laboratory experiment (**section 3.1**). The values for deeper soil layers were estimated assuming adsorption coefficients are proportional to OC content. Values in asterisk (*) correspond to calibrated values for PRZM and MACRO; [b] Freundlich exponent taken from adsorption-desorption laboratory experiment (**section 3.1**). The n_f values determined in the top 0-10 cm were used in 31-160 cm depth; [c] Herbicide half-lives were taken from the field dissipation experiment for soils under conventional tillage (S1+CT, S2+CT) and non-tillage (S1+NT, S2+NT) after the first application (**Section 3.3**). Variation of the degradation rate k (k (d^{-1}) = ln (2) / DT_{50}) with depth: k for 0–30 cm, k × 0.5 for 30–60 cm, k × 0.3 for 60–100 cm, k = 0 for >100 cm (FOCUS, 2000); [d] Q_{10} factor taken from herbicides degradation experiment under controlled laboratory conditions (**Section 3.2**); [e] Exponent in the temperature response function estimated from TRESP = (ln Q_{10}) / 10; [f] DISP: Pesticide hydrodynamic solute dispersion coefficient, DV: Dispersivity taken from Marín-Benito et al. (2020).

Crop parameters including emergence, flowering and harvest dates of the winter wheat and maize plants, root distribution, the maximum soil cover fraction (COVMAX in PRZM) and the maximum crop height corresponded to field site observations. The maximum rooting depth was estimated according to FOCUS (2000) recommendations for winter wheat and maize. The leaf area index (LAI) values were taken from Porto scenario (FOCUS, 2000) (**Table 10**).

Table 10. Crop input parameters for winter wheat and maize in soil under conventional tillage (S1+CT, S2+CT) and non-tillage (S1+NT, S2+NT).

Crop	Date	Crop stage	Root distribution[c]	COVMAX (%)	Crop height (m)	Root depth (m)	LAI (m^2m^{-2})
Winter wheat	30/10/2019	Sowing	0.60	-	-	-	-
	07/11/2019	Emergence		3	0.01	0.01	0.1
	23/05/2020	Flowering		95	0.5	0.8	6.5
	02/06/2020[a]	Harvest		90	0.5	0.8	2
Maize	08/06/2020	Sowing	0.67	-	-	-	-
	15/06/2020[b]	Emergence		3	0.1	0.01	0.1
	17/08/2020[b]	Flowering		70	2.5	0.8	3
	20/11/2020	Harvest		70	2.5	0.8	2
Winter wheat	26/02/2021	Sowing	0.60	-	-	-	-
	13/03/2021	Emergence		3	0.01	0.01	0.1
	14/03/2021	Flowering		10	0.1	0.1	0.3
	15/03/2021	Harvest		10	0.1	0.1	0.3
Maize	03/06/2021	Sowing	0.67	-	-	-	-
	10/06/2021[b]	Emergence		3	0.1	0.01	0.1
	17/08/2021[b]	Flowering		90	2.5	0.8	3
	19/11/2021	Harvest		90	2.5	0.8	2

[a] The cover crop (winter wheat) destruction date was considered as harvest date; [b] The maize emergence and flowering dates in NT plots was observed 15 days later than those in CT plots; [c] Fraction of root density in the uppermost 25% of the root depth.

Soil humidity and topsoil temperature monitored at the beginning of the experiment through the soil profiles were used as initial conditions for the simulations. Soil temperature in deep soil layers was assumed to be 1°C below those observed on the topsoil (Marín-Benito et al., 2020). For MACRO, a constant hydraulic gradient equal to 1 was assumed as bottom boundary condition.

Meteorological data (rainfall, maximum, minimum and average air temperature) were daily monitored using a meteorological station located at the field site (**Figure 35**). Solar radiation, evapotranspiration of reference (ET_{ref}) and wind speed data were obtained from the station of Matacan airport (23 km away from Muñovela farm). Both meteorological stations are operated by the AEMET (Spanish Agency of Meteorology).
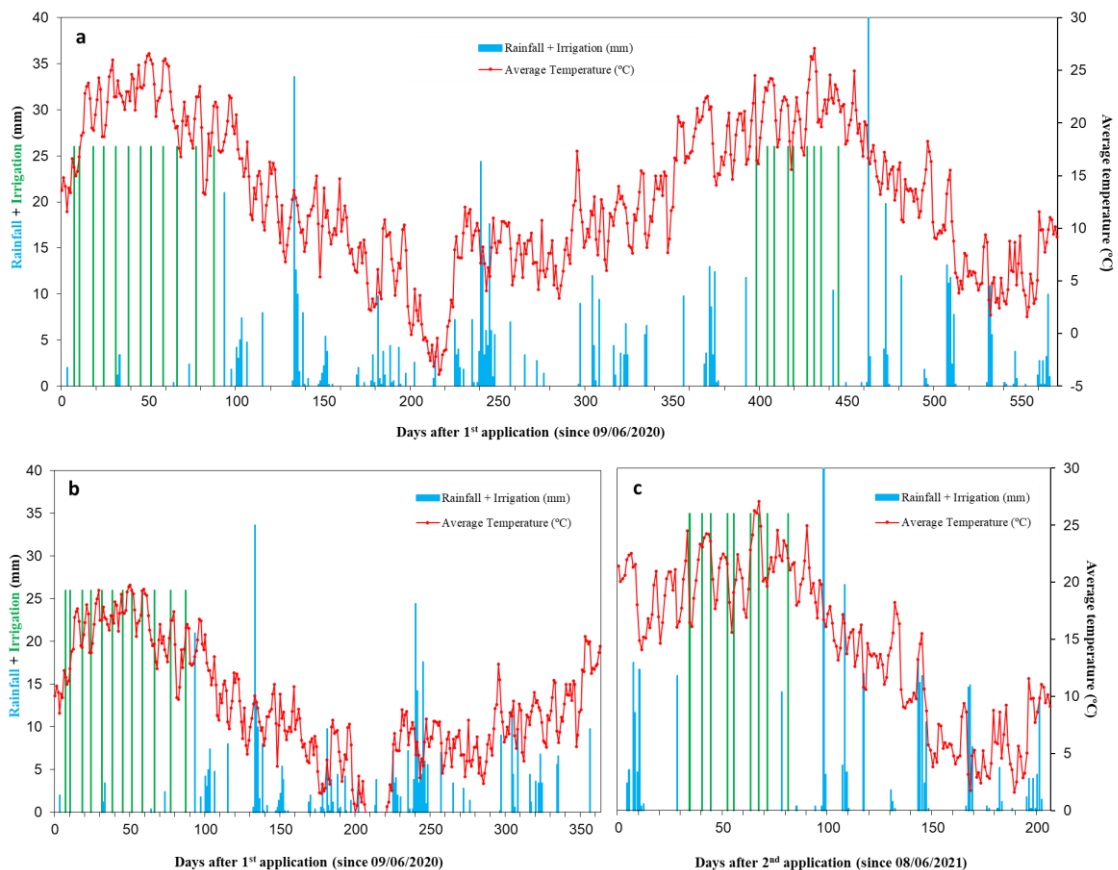
Figure 35. Measured Rainfall, irrigation and average temperature monitored over the 2-year experiment (a), and after the first (b) and second (c) application of herbicides.

The ETP was calculated applying a crop factor (k_c) corresponding to cover crop (winter wheat) and maize to ET_{ref} values according to FOCUS (2000) recommendation, and k_c was set to one where the soil was bare. In plots under NT, the impact of the mulch layer on ETP was determined by calculating the daily difference between the experimental soil water content in S+NT plots and their corresponding S+CT plots. Then, the daily difference was normalized with respect to the difference in the initial water content observed between S+NT and S+CT plots. To obtain new ETP values for S+NT plots, daily ETP values used as input in the meteorological file of the S+CT plots simulations were deducted by the difference previously estimated. These new ETP values were then used in the corresponding meteorological file for the simulations in S+NT plots.

2.2.11 Determination of parameters to characterize the different processes studied and statistical analysis of the results obtained

Adsorption-desorption study

The adsorption and desorption data for the herbicides were fit to the linearised form of the Freundlich equation: $\log C_s = \log K_f + n_f \log C_e$ (**Section 1.5.1, eq. 2**) and $\log C_s = \log K_{fd} + n_{fd} \log C_e$ (**Section 1.5.1, eq. 6**), respectively. The distribution coefficients K_d (mL g^{-1}) were also calculated from the relationship C_s/C_e (**Section 1.5.1, eq. 3**) for a C_e of 25 µg mL^{-1} for comparison with the adsorption behaviour of herbicides at low concentrations (K_f) because the isotherms were nonlinear (**Section 3.1**). Values of K_f or K_d normalised to 100% OC were determined as $K_{foc} = 100\ K_f/\%OC$ or $K_{doc} = 100\ K_d/\%OC$ (**Section 1.5.1, eq. 4**), respectively.

Standard deviation (SD) was used to indicate variability in the adsorption and desorption coefficient values among replicates. Analysis of variance (ANOVA) was performed to determine significant differences between adsorption-desorption constants. Means were compared by the Tuckey post-hoc test ($p < 0.05$). Simple and multiple linear regression models were used to relate the adsorption-desorption coefficients of the herbicides to adsorbent and herbicide characteristics ($p < 0.05$). IBM SPSS Statistics 29.0 (IBM Inc. Chicago, ILL) software was used.

Degradation and dissipation studies

The herbicide degradation kinetics of the field and laboratory studies were fitted to a SFO (**Section 1.5.2, eq. 9**) or FOMC (**Section 1.5.2, eq. 13**) model, based on the recommendations of FOCUS (2006) work group guidelines. Herbicide half-life or DT_{50} values (days) and DT_{90} were calculated for each of the tested treatments from the kinetic model that best fitted the degradation data, to compare variations in herbicide dissipation rates in different soil treatments and to characterize the degradation curves. To indicate the goodness of fit, the coefficient of determination (r^2) and the chi-square test (χ^2) were calculated. The χ^2 test considers the deviations between the observed and calculated values relative to the uncertainty of the measurements for a specific fit and was used to compare the goodness-of-fit of the two models tested. To validate the model, the calculated χ^2 values must be equal to or less than 15% for a given number of degrees of freedom at a significance level of 95%. The kinetic models parameters were estimated using the Excel Solver adding Package (FOCUS, 2006; Marín-Benito et al., 2019). The incubation temperature's effect on herbicide degradation was determined by the factor $Q_{10} = DT_{50}$ (14 °C)/DT_{50} (24 °C). SD was used to indicate variability in the dissipation coefficient values among replicates. One-way ANOVA was performed to determine significant differences between dissipation coefficients. Means were compared by the Tuckey post-hoc test ($p < 0.05$). Simple linear regression models were used to relate the dissipation coefficients to adsoprtion parameters of herbicides and/or soil characteristics ($p < 0.05$). IBM SPSS Statistics 29.0 (IBM Inc. Chicago, ILL) software was used.

Leaching study

SD was used to indicate variability among replicates in the residual amounts of herbicides in soil profiles. One-way ANOVA was performed to determine significant differences between these amounts and compare the effects of the different soil management practices and times. Simple linear regression models were used to relate the residual amounts of herbicides and/or soil characteristics ($p < 0.05$). IBM SPSS Statistics 29.0 (IBM Inc. Chicago, ILL) software was used.

The performance of PRZM and MACRO models was evaluated by calculating four statistical indexes: the root mean square error (*RMSE*), the coefficient of residual mass (*CRM*), the Pearson correlation coefficient (*r*) and the efficiency (*EF*) (Equations 15-18) (Smith et al., 1996):

$$RMSE = (100 / O_m) [\sum_{i=1}^{n}(S_i - O_i)^2 / n]^{1/2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\text{[eq.15]}$$

$$CRM = (\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} S_i)/\sum_{i=1}^{n} O_i \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{[eq.16]}$$

$$r = \sum_{i=1}^{n}(O_i - O_m) \times (S_i - S_m)/[\sum_{i=1}^{n}(O_i - O_m)^2]^{1/2}\dots\dots\dots\dots\dots\text{[eq.17]}$$

$$EF = 1 - [\sum_{i=1}^{n}(S_i - O_i)^2 / \sum_{i=1}^{n}(O_i - O_m)^2]\dots\dots\dots\dots\dots\dots\dots\dots\text{[eq.18]}$$

where O_i and S_i are the observed and simulated values, respectively, O_m and S_m are the mean observed and simulated values, respectively, and n is the number of data. The optimum value of *RMSE* and *CRM* is zero and that of EF and r is +1. If *CRM* >0 (<0), it indicates that there is and under(over)estimation of observed values.

Microbiological studies

SD was used to indicate variability among replicates in the soil DHA, respiration, microbial biomass and PLFAs. One -way ANOVA and two-way ANOVA was performed and Tukey's or Games-Howell's post hoc test (according to Levene's test for homogeneity of variance) at $p < 0.05$ was used to determine significant differences between these parameters and compare the effects of the different soil management practices at the same sampling time and different sampling times within the same soil treatment. Simple linear regression models were used to relate the residual amounts of herbicides and/or soil characteristics ($p < 0.05$). IBM SPSS Statistics 29.0 (IBM Inc. Chicago, ILL) software was used.

RESULTS AND DICUSSION

3. RESULTS AND DISCUSSION

3.1 MULCHING VS. ORGANIC SOIL AMENDMENT: EFFECTS ON ADSORPTION-DESORPTION OF HERBICIDES (Annex I)

3.1.1 Adsorption of herbicides by mulches and soils

Figure 36 includes the adsorption isotherms of SMOC, FORAM, and TCM for mulches M1, M2 and M3, milled M1 (MM1), and unamended and MM1-amended soils. They were well described by the Freundlich equation with $r^2 \geq 0.91$ ($p < 0.02$), and the n_f, K_f, and K_d parameters determined from this equation are shown in **Tables 11− 13**.

A wide variety of isotherm types were obtained depending on the adsorbent **(Figure 36)**, and they agreed with the wide range of n_f values obtained (0.34 – 1.10 for SMOC; 0.87 – 1.83 for FORAM, and 1.09 – 2.37 for TCM) **(Tables 11− 13)**. L-type isotherms with n_f values < 1 were obtained for the adsorption of SMOC by M3, S1, S2, S1+MM1, S2+MM1 (with total adsorption of the herbicide at $C_i \leq 5$ µg mL^{-1}) and L-C-type isotherms were obtained for MM1. However, S-type isotherms with n_f values > 1 were obtained solely for M1 and M2. L-type isotherms ($n_f < 1$) or close to C-type ($n_f \geq 0.9$) also characterised the adsorption of FORAM by MM1, S1+MM1, and S2+MM1, generally indicating that the adsorption of water by these adsorbents could be similar to that of FORAM molecules. In contrast, S-type isotherms ($n_f > 1$) described the adsorption of FORAM by S2, M1, M2, and M3, whereas no herbicide adsorption was determined for S1. These results indicate different mechanisms of adsorption for SMOC and FORAM depending on the adsorbent. In contrast to SMOC and FORAM, TCM showed a more homogeneous adsorption mechanism by the different adsorbents, as the adsorption isotherms were always of S-type ($n_f > 1$) (**Table 13**). A broad range of isotherm types has also been reported for the adsorption of SMOC by different adsorbents with different characteristics. Aslam et al. (2013) have obtained almost linear adsorption isotherms ($n_f \geq 0.9$) for SMOC on decomposed maize mulch residues with OC content ranging between 34% and 42%, whereas Marín-Benito et al. (2021) and Peña et al. (2019) have reported mainly L-type isotherms or C-type isotherms, respectively, for the adsorption of SMOC by unamended soils and soils amended with different organic residues whose OC content varied from 22% – 24% to 38% – 53%, respectively.
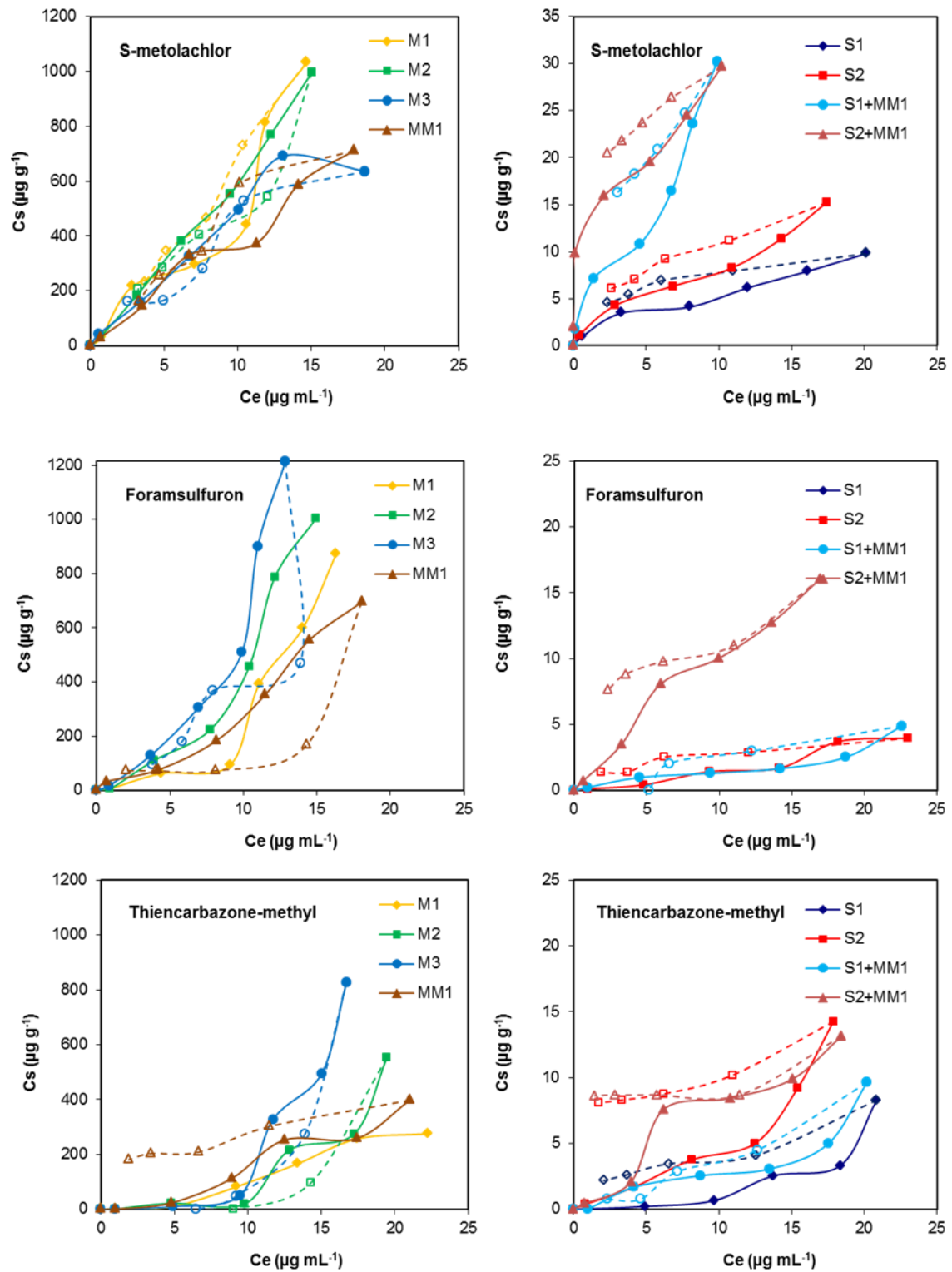
Figure 36. Adsorption-desorption isotherms of S-metolachlor, foramsulfuron, and thiencarbazone-methyl for mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1 + MM1 and S2 + MM1). Closed symbols and continuous line correspond to adsorption, and open symbols and dashed line correspond to desorption.

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As regards FORAM, and as far as we know, the only n_f values reported in the literature range from 0.82 to 0.96, and they correspond to its adsorption in unamended soils with OC contents in the range 0.47% − 1.47%, respectively (EFSA, 2016). In turn, Gul et al. (2020) have reported lower n_f values (0.49 - 0.92) for the adsorption of TCM in ten natural soils with low OC content (0.17% − 0.58%) and with a predominantly more sandy-loam texture than in the current study. EFSA (2013) has also reported lower n_f values (0.89 − 0.93) for soils with a higher variation in OC content (0.9% − 4.1%).

The K_f values obtained for the adsorption of SMOC by soils and mulches ranged between 1.34 and 65.8, with the highest K_f values corresponding to mulches (43.7 − 65.8), and the lowest ones to unamended soils (1.34 − 2.00). Cassigneul et al. (2018) have also observed a significantly lower adsorption of SMOC by soil than by mulch from different cover crop residues. The K_f values increased in the order: S1 < S2 < S1+MM1 < S2+MM1 << MM1 < M1 < M2 < M3 according to the increase in the OC content (r = 0.971, $p < 0.001$) and/or DOC (r = 0.830, $p < 0.05$) of the adsorbents (**Tables 4** and **14**). OC is reported to be the most important soil component affecting the adsorption of this hydrophobic herbicide (Alletto et al., 2013; Marín-Benito et al., 2021; Westra et al., 2015). The application of MM1 as a soil amendment increased the K_f values up to 4.5 times in S1+MM1 and up to 6.4 times in S2+MM1 (**Table 11**). An increase in SMOC K_f values has frequently been observed after the addition of organic soil amendments of different origins (Marín-Benito et al., 2021; Peña et al., 2019). The stage of mulch decomposition also had a significant ($p < 0.05$) influence on the adsorption of SMOC by increasing the K_f values from 45.6 (M1) to 65.8 (M3) after a 2.5 month-mulch decomposition period and according to their decrease in DOC content (M1 > M2 > M3) (**Tables 4 and 14**). A positive impact on the adsorption of SMOC and other herbicides by different kinds of mulches according to their decomposition stage has been also reported (Aslam et al., 2013; Cassigneul et al., 2015, 2016, 2018). However, the particle size of the fresh mulch (M1) did not have a significant impact on the adsorption of SMOC with similar K_f values for M1 and MM1 (**Table 11**), indicating that the mulch composition is more important than the increased surface for the adsorption of the hydrophobic herbicide SMOC.

Table 11. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of S-metolachlor by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1+MM1 and S2+MM1) 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	K_{foc}	$K_d \pm$ SD	K_{doc}	$n_f \pm$ SD	r^2	$K_{fd} \pm$ SD	$n_{fd} \pm$ SD	r^2	H
M1	45.6 ± 3.37B	102	62.6 ± 3.95A	140	1.10 ± 0.07	0.95	55.3 ± 3.63A	1.08 ± 0.25	0.99	1.01 ± 0.17
M2	49.7 ± 3.13AB	113	68.4 ± 0.37A	155	1.10 ± 0.10	0.99	65.1 ± 3.54A	0.93 ± 0.30	0.94	1.18 ± 0.25
M3	65.8 ± 0.79A	148	39.0 ± 3.69B	87.7	0.84 ± 0.03	0.98	64.1 ± 3.69A	0.79 ± 0.05	0.88	1.06 ± 0.10
MM1	43.7 ± 3.54B	105	39.0 ± 2.33B	93.7	0.96 ± 0.08	0.99	60.8 ± 3.25A	0.89 ± 0.08	0.95	1.08 ± 0.18
S1	1.34 ± 0.01b	194	0.41 ± 0.01a	59.4	0.63 ± 0.01	0.98	3.39 ± 0.31c	0.36 ± 0.14	0.98	1.77 ± 0.71
S2	2.00 ± 0.06b	198	0.65 ± 0.01a	64.4	0.65 ± 0.01	0.98	3.69 ± 0.30c	0.48 ± 0.10	0.99	1.35 ± 0.27
S1+MM1	6.05 ± 1.16b	96.6	1.60 ± 0.46a	25.6	0.59 ± 0.20	0.96	8.81 ± 0.64b	0.52 ± 0.09	0.97	1.13 ± 0.20
S2+MM1	12.9 ± 1.35a	113	1.53 ± 0.18a	13.4	0.34 ± 0.07	0.92	16.2 ± 0.58a	0.26 ± 0.01	0.99	1.32 ± 0.30
CV (%)	89.8	31.1	109	62.7						

SD = standard deviation of replicates; H = n_f /n_{fd}; CV= coefficients of variation.

Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

The K_d distribution coefficients for SMOC ranged from 0.41 to 68.4. They varied in the same direction as the K_f constants for unamended and amended soils, while some changes in the order were observed for mulches (**Table 11**). The K_d values followed the order: S1 ~ S2 < S2+MM1 ~ S1+MM1 << M3 = MM1 < M1 < M2, and they were lower (1.1 – 8.4 times) than the 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 or S-type, respectively) indicating a decrease or increase in adsorption with the herbicide concentration in solution, respectively (Alletto et al., 2013; Aslam et al., 2013; Cassigneul et al., 2015; Marín-Benito et al., 2021).

Lower K_f values were obtained for the adsorption of FORAM by mulches and soils compared to SMOC (**Tables 11 − 12**). The 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 SMOC except for the mulch MM1, with the lowest OC and DOC content, which recorded the highest K_f value for FORAM but the lowest affinity by the most hydrophobic herbicide, SMOC. This high adsorption of FORAM by MM1 led to a significant increase in herbicide adsorption ($p < 0.05$) by S1 and S2 after the addition of MM1 to these soils. The effect of mulch decomposition and particle size on FORAM K_f values was more significant than that previously indicated for SMOC (**Tables 11 − 12**). M1 recorded the lowest K_f value, and it increased by 1.3 (M2) and 3.5 (M3) times after its decomposition, and up to 6.3 times (MM1) after milling. The K_f values determined for S1 and S2 were lower than the range of values (0.31 - 2.61) reported for unamended soils by EFSA (2016), and no additional adsorption-desorption studies have been found in the literature for FORAM. However, some studies have reported a similar low or very low adsorption of other sulfonylurea herbicides by unamended soils (Cueff et al., 2021; Delgado-Moreno and Peña, 2008; Marín-Benito et al., 2018b; Sunulahpašić et al., 2020), slightly promoted by the addition to soil of fresh and composted olive cake or green compost (Delgado-Moreno and Peña, 2008; Marín-Benito et al., 2018b). No adsorption-desorption studies involving FORAM or other sulfonylureas and mulches have been found in the literature.

Table 12. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of foramsulfuron by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1+MM1 and S2+MM1) soils, distribution coefficients (K_d), K_f or K_d normalized to 100% OC (K_{foc}, K_{doc}), and hysteresis coefficients (H).

Sample	$K_f \pm SD$	K_{foc}	$K_d \pm SD$	K_{doc}	$n_f \pm SD$	r^2	$K_{fd} \pm SD$	$n_{fd} \pm SD$	r^2	H
M1	5.48 ± 0.05C	12.3	50.3 ± 0.10B	113	1.69 ± 0.03	0.94	-	-	-	-
M2	6.89 ± 0.21C	15.6	101 ± 4.25A	229	1.83 ± 0.07	0.99	-	-	-	-
M3	19.4 ± 2.14B	43.5	105 ± 6.76A	235	1.52 ± 0.05	0.98	11.0 ± 0.92B	1.63 ± 0.43	0.85	0.93 ± 0.20
MM1	34.3 ± 0.49A	82.3	28.5 ± 1.20B	68.5	0.94 ± 0.02	0.91	26.3 ± 1.74A	0.84 ± 0.47	0.66	1.13 ± 0.50
S1	0d	0	0b	0	-	-	-	-	-	-
S2	0.09 ± 0.01c	8.91	0.16 ± 0.01b	15.8	1.18 ± 0.01	0.97	0.94 ± 0.03b	0.46 ± 0.01	0.91	2.58 ± 0.07
S1+MM1	0.22 ± 0.01b	3.51	0.14 ± 0.01b	2.24	0.87 ± 0.02	0.94	0c	3.22 ± 0.25	0.61	0.27 ± 0.03
S2+MM1	1.19 ± 0.01a	10.4	0.97 ± 0.10a	8.49	0.94 ± 0.03	0.99	5.60 ± 0.01a	0.33 ± 0.01	0.90	2.81 ± 0.07
CV (%)	146	125	127	118						

SD = standard deviation of replicates; H = n_f /n_{fd}; CV= coefficients of variation; "-" No adsorption or desorption isotherms were obtained.
Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

According to the shape of its isotherms, FORAM showed lower K_d values than the corresponding K_f values obtained for MM1, S1+MM1, and S2+MM1, and vice versa for the adsorbents M1, M2, M3, and S2 (**Table 12**). These K_d values ranged from 0 to 105, and they were in the same order of magnitude as the corresponding K_f values determined for MM1, S1, S2, S1+MM1, and S2+MM1. In contrast, there was a significant increase in the K_f values compared to the K_d values for M1, M2, and M3 (up to 9.2, 14.7, and 5.4 times, respectively).

TCM had the lowest K_f value ($K_f \leq 1.10$) for all the adsorbents, in general, compared to SMOC and FORAM (**Table 13**). It is consistent with the lowest hydrophobicity of TCM among the three herbicides studied. The adsorption of this herbicide increased in the order: S1 ~ S1+MM1 < S2 < S2+MM1 = M3 < M2 ~ M1 < MM1. The K_f values determined for S1 and S2 were lower than the range of values (0.4 – 9.3) found in the literature for TCM in unamended soils (EFSA, 2013; Gul et al., 2020), whereas no adsorption-desorption studies are available in the literature for this herbicide in amended soils or in mulches. The increase in the MM1 surface area after the milling of M1 and the application of MM1 to soils slightly increased the adsorption of TCM by this adsorbent and by amended soils compared to M1 (1.3 times) and unamended soils (1.5 - 4 times), respectively. The opposite effect was observed with mulch decomposition. This non-hydrophobic herbicide recorded the highest K_f adsorption value for MM1, as observed for FORAM (**Table 13**).

According to S-type isotherms, the adsorption of TCM by all the adsorbents assayed was favoured by the increase in the herbicide concentration in solution. The K_d values (0.26 – 27.6) increased from 1.3 (S2+MM1) to 39.7 (M3) times the corresponding K_f adsorption coefficients (**Table 13**). The high n_f values resulting from TCM adsorption isotherms, exceeding those obtained for SMOC and FORAM, explain the biggest variation between the K_f and K_d values for this herbicide. In a TCM adsorption study involving unamended soils with similar properties to S1 and S2, (Gul et al. (2020) have found higher K_d values (4.3 – 26.4) than those obtained here, possibly because of the different experimental conditions used (unclearly defined in the study).

Table 13. Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of thiencarbazone-methyl by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1+MM1 and S2+MM1) 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	K_{foc}	$K_d \pm$ SD	K_{doc}	$n_f \pm$ SD	r^2	$K_{fd} \pm$ SD	$n_{fd} \pm$ SD	r^2	H
M1	0.86 ± 0.10A	1.93	17.4 ± 1.77A	39.0	1.93 ± 0.17	0.98	-	-	-	-
M2	0.84 ± 0.26A	1.90	21.2 ± 1.30A	48.0	2.00 ± 0.08	0.91	0B	14.6 ± 0.45	0.93	0.14 ± 0.01
M3	0.61 ± 0.02A	1.37	24.2 ± 3.68A	54.4	2.37 ± 0.19	0.92	0B	11.2 ± 1.20	0.87	0.21 ± 0.01
MM1	1.10 ± 0.07A	2.64	27.6 ± 2.24A	66.2	2.00 ± 0.04	0.99	135 ± 1.20A	0.33 ± 0.08	0.91	6.15 ± 1.52
S1	0.01 ± 0.00b	1.45	0.26 ± 0.04b	37.7	1.89 ± 0.06	0.96	1.34 ± 0.27b	0.53 ± 0.02	0.91	3.58 ± 0.01
S2	0.40 ± 0.07a	39.6	0.58 ± 0.09ab	57.4	1.11 ± 0.18	0.97	6.50 ± 1.34a	0.22 ± 0.05	0.91	4.96 ± 0.25
S1+MM1	0.04 ± 0.00b	0.64	0.57 ± 0.00ab	9.11	1.85 ± 0.02	0.91	0.19 ± 0.03b	1.26 ± 0.35	0.90	1.47 ± 0.37
S2+MM1	0.61 ± 0.08a	5.34	0.80 ± 0.13a	7.00	1.09 ± 0.09	0.95	7.65 ± 0.79a	0.12 ± 0.02	0.47	8.89 ± 2.28
CV (%)	69.8	194	105	54.6						

SD = standard deviation of replicates; H = n_f / n_{fd}; CV= coefficients of variation; "-" No adsorption or desorption isotherms were obtained.
Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

Table 14. 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	N
K_f/S-metolachlor (n=8)	-0.632[d]	0.971[a]	0.830[c]	0.884[b]
K_d/S-metolachlor (n=8)	-0.715[c]	0.934[a]	0.988[a]	0.819[c]
K_{fd}/S-metolachlor (n=8)	-0.686[d]	0.994[a]	0.875[b]	0.944[a]
K_f/foramsulfuron (n=8)	-0.280	0.670[d]	0.341	0.874[b]
K_d/foramsulfuron (n=8)	-0.535	0.843[b]	0.792[c]	0.711[c]
K_{fd}/foramsulfuron (n=5)	0.400	0.829	0.781	0.941[c]
K_f/thiencarbazone-methyl (n=8)	-0.482	0.826[c]	0.711[c]	0.839[b]
K_d/thiencarbazone-methyl (n=8)	-0.406	0.843[b]	0.606	0.830[c]
K_{fd}/thiencarbazone-methyl (n=5)	-0.375	0.970[a]	0.991[a]	0.999[a]

[a] $p < 0.001$, [b] $p < 0.01$, [c] $p < 0.05$, [d] $p < 0.1$.

3.1.2 Desorption of herbicides from mulches and soils

Desorption isotherms from the different adsorbents were obtained after herbicide adsorption at initial concentrations of 25 mg L^{-1} (**Figure 36**). They fit the Freundlich equation with r^2 values ranging from 0.88 to 0.99 for SMOC; 0.61 – 0.91 for FORAM, and 0.47 – 0.93 for TCM. The K_{fd} and n_{fd} parameters determined from this equation are shown in **Tables 11 − 13**. A poor fit was observed for FORAM desorption from MM1 and S1+MM1 ($r^2 = 0.61 – 0.66$) due to a very fast initial desorption followed by the non-desorption of the herbicide (**Figure 36, Table 12**). In addition, non-desorption isotherms were observed for M2 and M3 for the initial total desorption, and in S1 as result of the non-adsorption of the herbicide by this soil (**Figure 36, Table 12**). A poor fit to the Freundlich desorption equation for TCM was observed solely for S2+MM1 ($r^2 = 0.47$) (**Table 13**).

All the isotherms exhibited hysteresis to a greater or lesser extent because desorption data did not coincide with the adsorption isotherms (**Figure 36**). The

hysteresis coefficients (H) were always higher than one for SMOC, recording greater irreversibility (higher H values, lower desorption) of the adsorption by soils, especially by unamended ones, than by mulches (**Table 11**). Other authors have also reported a higher irreversibility of SMOC adsorption in soils amended with fresh by-products from olive oil extraction compared to the corresponding unamended soil (Cañero et al., 2015; Peña et al., 2019). The H values obtained for the desorption of SMOC from M1, M2, and M3 were similar, although an increase in irreversibility could be expected, as reported by Aslam et al. (2013) for the adsorption of SMOC by maize mulch at a later stage of decomposition. Possible changes in the functional groups of mulch in our study were not relevant (**Table 5**) compared to those registered by Aslam et al. (2013) for maize mulch maintained under more extreme laboratory conditions (28 ºC and soil humidity at field capacity) or in the field (up to 300 days). Under these conditions, Aslam et al. (2013) have reported a negative correlation between the O-alkyl-C groups of mulch after decomposition and the irreversibility of SMOC adsorption. However, this study has found a significant positive correlation between O-alkyl-C groups (r = 0.990, *p* < 0.05) of mulches and the H coefficients of SMOC, and a negative correlation with the alkyl-C groups (r = -0.956, *p* < 0.05). García-Delgado et al. (2020) have also described an enhanced hysteresis of the adsorption of herbicides with contrasting solubility and hydrophobicity properties in soils amended with different organic residues due to the abundance of O-alkyl (and N-alkyl) groups in these organic amendments.

A wide range of positive and negative hysteresis was observed for the desorption isotherms of FORAM and TCM from the different adsorbents (**Table 12**), although no correlation could be established between H coefficients and functional groups of mulch OC due to the few H observations. Gul et al. (2020) have also reported hysteresis for TCM in the adsorption-desorption experiment conducted on unamended soils with H values ranging from 0.6 to 1.9.

The K_{fd} values ranged between 3.39 and 65.1 for SMOC desorption from the different adsorbents, and between 0 - 26.3 for FORAM (excluding S1, M1, and M2 because of the absence of desorption isotherms), and they were significantly higher (*p* < 0.05) for mulches than for soils (unamended and amended). A lower hydrophobicity and/or higher solubility of FORAM than SMOC would explain the lower K_{fd} values determined for FORAM than for SMOC (**Tables 11 − 12**). The K_{fd} values of SMOC varied in the same direction as the K_f adsorption constants for unamended and amended

soils, although not for mulches (S1 < S2 < S1+MM1 < S2+MM1 << M1 < MM1 < M3 ≈ M2). Aslam et al. (2013) have observed a clear decrease in the desorption of SMOC after mulch (maize) decomposition due to greater irreversibility, as previously indicated. TCM showed intermediate K_{fd} values (0.19 - 7.65) to those determined for SMOC and FORAM when the herbicides were desorbed from unamended and MM1-amended soils. As regards mulches, MM1 recorded a very high K_{fd} value (= 135), while it was 0 for M2 and M3, corresponding to a total desorption of the amount of herbicide initially adsorbed (**Table 13**). However, it should be noted that the TCM 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 desorption step (no desorption isotherm), and second, and third ones, respectively (**Figure 36**). This behaviour seems to be related to the loss of DOC content in the mulches following their decomposition (**Table 4**).

3.1.3 Influence of mulch, soil, and herbicide properties on the adsorption-desorption of herbicides

The simple correlation coefficient (r) revealed the existence of a highly significant positive correlation between the K_f and K_d adsorption constants of the most hydrophobic herbicide (SMOC) and the OC or N content of the mulches, and unamended and MM1-amended soils (**Table 14**). The correlation with N content was derived from its significant correlation with OC ($p < 0.01$). Based on the determination coefficient, r^2, OC accounted for 94.3% or 87.2% of the variance in the adsorption of SMOC 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 (Peña et al., 2019; Sharipov et al., 2021). In turn, non-significant correlations were observed between the K_f and K_d values and the functional OC groups in the mulches (**Table 5**) ($p > 0.1$, data not shown) indicating that the OC content was more important than its actual nature. It was also confirmed by the CVs of the K_{foc} and K_{doc} values, which were lower than those for the K_f and K_d parameters (**Table 11**).

In addition, a significant ($p < 0.05$) or highly significant ($p < 0.001$) positive correlation was also observed between K_f and K_d values and the DOC contents of the adsorbents, respectively, and a significant ($p < 0.05$) negative correlation was determined between the adsorbents' pH and SMOC K_d values (**Table 14**). These results are consistent

with previous studies reporting an increase in the adsorption of SMOC by amended soils with a high DOC content in solution (Marín-Benito et al., 2021; Singh, 2003) or a decrease in adsorption with pH for agricultural soils cultivated with different conservation tillage systems (Alletto et al., 2013).

The results indicate that both OC and DOC are the main variables involved in the adsorption of SMOC by the different adsorbents, with OC content explaining the higher variability of K_f values ($r^2 = 94.3\%$) than DOC (68.9%), and the opposite effect explaining the variability of K_d values (97.6% by DOC vs. 87.2% by OC). In some cases, an adjusted R^2 coefficient higher than the simple correlation coefficient was obtained when the results were subject to multiple linear regression analysis by combining two or more adsorbent properties to determine their relative importance when they vary simultaneously (**Table 15**). A highly significant relationship ($p < 0.001$) was found between the K_d adsorption constant and the variables OC and DOC. The coefficient of determination, $R^2 = 97.8\%$, accounts for a slightly higher percentage of variance in the K_d than that explained when the OC or the DOC content of the adsorbents is individually considered as the responsible variable. A highly significant relationship ($p < 0.001$) was also found between the K_f adsorption constant and the variables OC and DOC (**Table 15**), although its R^2 value (93.8%) explained a lower percentage of the variability in K_f than that explained by the OC as the single variable (94.3%).

A very significant positive correlation ($p < 0.01$) was also observed between the adsorption of FORAM at high concentrations of herbicide in solution (K_d) and mulch and soil OC content (**Table 14**), while a non-significant relationship was determined at low herbicide concentrations (K_f). Some studies also reported that the adsorption of sulfonylurea herbicides is positively correlated with adsorbent OC content (Grey and McCullough, 2012; Pavão et al., 2021). The OC content accounts for a lower percentage of variance in the adsorption of K_d (71.1%) than that of SMOC, suggesting that other mulch and soil parameters may influence the adsorption of this non-hydrophobic herbicide. This is consistent with the considerable variability in the K_{foc} and K_{doc} values (CV = 125% and 118%, respectively) (**Table 12**), indicating that the nature of mulch and soil OC plays a more important role in the adsorption of FORAM than indicated previously for SMOC. In fact, both positive and negative relationships were respectively observed between K_f or K_d values and N-alkyl-C and aromatic-C groups of mulch OC, although they did not become significant (data not shown).

A significant positive correlation ($p < 0.05$) was also found between FORAM K_d values and the DOC content of the adsorbents (**Table 14**). However, the combination of OC and DOC variables did not improve the explanation of the K_d variability (60.2%) compared to that explained by the OC content as a single variable (71.1%). No relationship was found between FORAM adsorption constants (K_f and K_d) and adsorbent pH in keeping with data from EFSA (2016). The opposite effects have been observed for other sulfonylurea herbicides. Delgado-Moreno and Peña (2008) have reported that the adsorption of bensulfuron-methyl, chlorsulfuron, and prosulfuron by unamended and amended soils was affected mainly by the pH of the soil solution, with the OC content having no significant effect on herbicide retention. However, in most cases, sulfonylurea adsorption is greater in soils with a low pH and high OC content (Grey and McCullough, 2012; Kumari et al., 2020; Pavão et al., 2021).

Despite the low hydrophobicity of TCM, a significant ($p < 0.05$) and a very significant positive correlation ($p < 0.01$) was also observed between the adsorption of this herbicide (K_f and K_d) and adsorbent OC content, respectively (**Table 14**). However, the OC content accounts for a lower percentage of variability in the adsorption of TCM by mulches and soils (K_f, 68.3%) than for SMOC (94.3%) or FORAM (71.1%). As previously indicated, other mulch and soil parameters may influence the adsorption of this other non-hydrophobic herbicide (**Tables 11** and **15**). This is also confirmed by the higher CV of the K_{foc} values compared to the K_f values, suggesting that the nature of mulch and soil OC plays a more important role than their OC content in the adsorption of TCM. Within this context, there was a positive relationship between the N-alkyl-C and aromatic-C groups of mulches and the K_f values of TCM, although it was non-significant (data not shown). Therefore, a statistically non-significant correlation was found between the K_f or K_d values of the three herbicides studied and the functional groups of OC in mulches. However, other authors have observed this type of correlation in pesticide adsorption studies on different organic residues or mulches (Aslam et al., 2013; Cassigneul et al., 2015; García-Delgado et al., 2020).

Table 15. Best 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 (organic carbon, OC; and dissolved organic carbon, DOC).

Constant/Herbicide	Regression equation	p	R^2
K_f/S-metolachlor (n=8)	$-1.144 \pm 3.662 + (1.471 \pm 0.269) \%OC - (1.330 \pm 1.093) \%DOC$	<0.001	0.938
K_d/S-metolachlor (n=8)	$-1.488 \pm 2.468 + (0.309 \pm 0.181) \%OC + (4.430 \pm 0.740) \%DOC$	<0.001	0.978
K_{fd}/S-metolachlor (n=8)	$0.998 \pm 1.908 + (1.530 \pm 0.140) \%OC - (0.747 \pm 0.569) \%DOC$	<0.001	0.987
K_f/foramsulfuron (n=8)	$-3.668 \pm 3.378 + (1.169 \pm 0.248) \%OC - (3.490 \pm 1.010) \%DOC$	0.011	0.773
K_d/foramsulfuron (n=8)	$-7.170 \pm 16.445 + (1.496 \pm 1.207) \%OC + (1.420 \pm 4.910) \%DOC$	0.043	0.602
K_{fd}/foramsulfuron (n=5)	$-4.113 \pm 6.460 + (1.565 \pm 1.280) \%OC - (7.463 \pm 8.359) \%DOC$	0.223	0.554
K_f/thiencarbazone-methyl (n=8)	$0.176 \pm 0.148 + (0.019 \pm 0.011) \%OC - (0.015 \pm 0.044) \%DOC$	0.050	0.566
K_d/thiencarbazone-methyl (n=8)	$-2.564 \pm 1.897 + (0.794 \pm 0.139) \%OC - (1.102 \pm 0.566) \%DOC$	<0.001	0.926
K_{fd}/thiencarbazone-methyl (n=5)	$0.328 \pm 7.035 - (1.307 \pm 1.827) \%OC + (33.76 \pm 13.10) \%DOC$	0.014	0.972

A significant positive correlation ($p < 0.05$) was also determined between TCM K_f values and the DOC content of the adsorbents (**Table 14**), but the combination of the variables OC and DOC of mulches and soils explained a higher percentage (92.6%) of the K_d variability for TCM compared to that explained individually by the OC (71.1%) (**Tables 14 − 15**). According to EFSA (2013), no correlation was found between TCM adsorption constants (K_f and K_d) and adsorbent pH.

The OC and DOC variables were also involved in the desorption of SMOC according to a very significant ($p < 0.01$) or highly significant ($p < 0.001$) positive correlation between these variables and the K_{fd} of SMOC, respectively (**Table 14**). However, by combining both variables the multiple linear regression model (**Table 15**) explained the similar variability of K_{fd} (98.7%) compared to OC content (98.8%). No simple or combined correlation was found for FORAM between the K_{fd} values and OC and/or DOC content of the adsorbents (**Tables 14 − 15**), but a highly significant positive correlation ($p < 0.001$) was found for TCM between K_{fd} desorption constants and the OC and DOC content from MM1, and unamended and MM1-amended soils (**Table 14**). It should be noted, however, that DOC content explained a higher variability in K_{fd} values ($R^2 = 98.2\%$) than OC (94.1%) or even the combination of both variables (97.2%) (**Table 14**). The DOC content of adsorbents was therefore the main variable controlling TCM desorption, whereas it was OC content for SMOC. A positive, albeit non-significant, relationship was found for TCM (because of the few samples) between the aromatic-C or N-alkyl-C groups in mulches and the K_{fd} values, but not for SMOC and FORAM (data not shown).

A multiple linear regression analysis was also carried out combining the two most significant absorbent variables involved in the adsorption-desorption processes (OC and DOC) and herbicide characteristics (water solubility- S_w - and hydrophobicity-K_{ow}) to evaluate the relative importance of mulch, soil, and herbicide parameters on the adsorption of the compounds studied. A highly significant multiple linear regression ($p < 0.001$) was obtained between the K_f or K_d adsorption and K_{fd} desorption constants and the K_{ow} of the herbicides and the OC content of adsorbents when jointly considering all the herbicides and adsorbents (n = 24). The R^2 statistic revealed that 62.7% of the variability in the K_f values could be explained by the combination of K_{ow} and OC according to Equation 19 [**eq. 19**], while the R^2 statistic showed that 61.3% of the

variability in the K_d could be explained by the herbicide S_w and the OC content of adsorbents according to Equation 20 [**eq. 20**]:

$$K_f = (-0.869 \pm 3.893) + (5.452 \pm 1.143) \, K_{ow} + (0.527 \pm 0.124) \, \%OC \dots \dots \text{[eq. 19]}$$

$$K_d = (-13.243 \pm 7.761) + (0.006 \pm 0.003) \, S_w + (1.218 \pm 0.207) \, \%OC \dots \dots \text{[eq. 20]}$$

For the desorption process, Equation 22 [**eq. 21**] reveals a highly significant ($p < 0.001$) relationship between the K_{fd} desorption constants ($n = 18$), the S_w of the herbicides, and the OC content of the adsorbents for a confidence level of 95%:

$$K_{fd} = (9.567 \pm 9.136) - (0.009 \pm 0.004) \, S_w + (1.411 \pm 0.279) \, \%OC \dots \dots \text{[eq. 21]}$$

The R^2 statistic shows that this equation explains 62.1% of the variability in the K_{fd} of the herbicides.

Previous adsorption studies involving pesticides and organic residues with contrasting properties have also reported the relevance of the K_{ow} of pesticides and the OC content of adsorbents together with their polarity index for predicting the adsorption capacity of the organic residues tested (García-Delgado et al., 2020; Marín-Benito et al., 2012).

3.1.4 Mulching vs. organic soil amendment as a strategy for supporting eco-friendly agricultural practices

Figure 37 includes adsorbed amounts expressed as percentages of herbicide (SMOC, FORAM, or TCM) in aqueous solution at an initial concentration of 25 µg mL^{-1}, and the residual amounts adsorbed after desorption (four steps) expressed as percentages of the herbicide adsorbed by the mulches, and unamended and MM1-amended soils. The amounts of herbicide remaining adsorbed after desorption were used to calculate the efficiency of the mulches, and unamended and MM1-amended soils as adsorbents to compare the real impact of using cover crop residues as mulches or as soil organic amendment on the adsorption of herbicides studied.
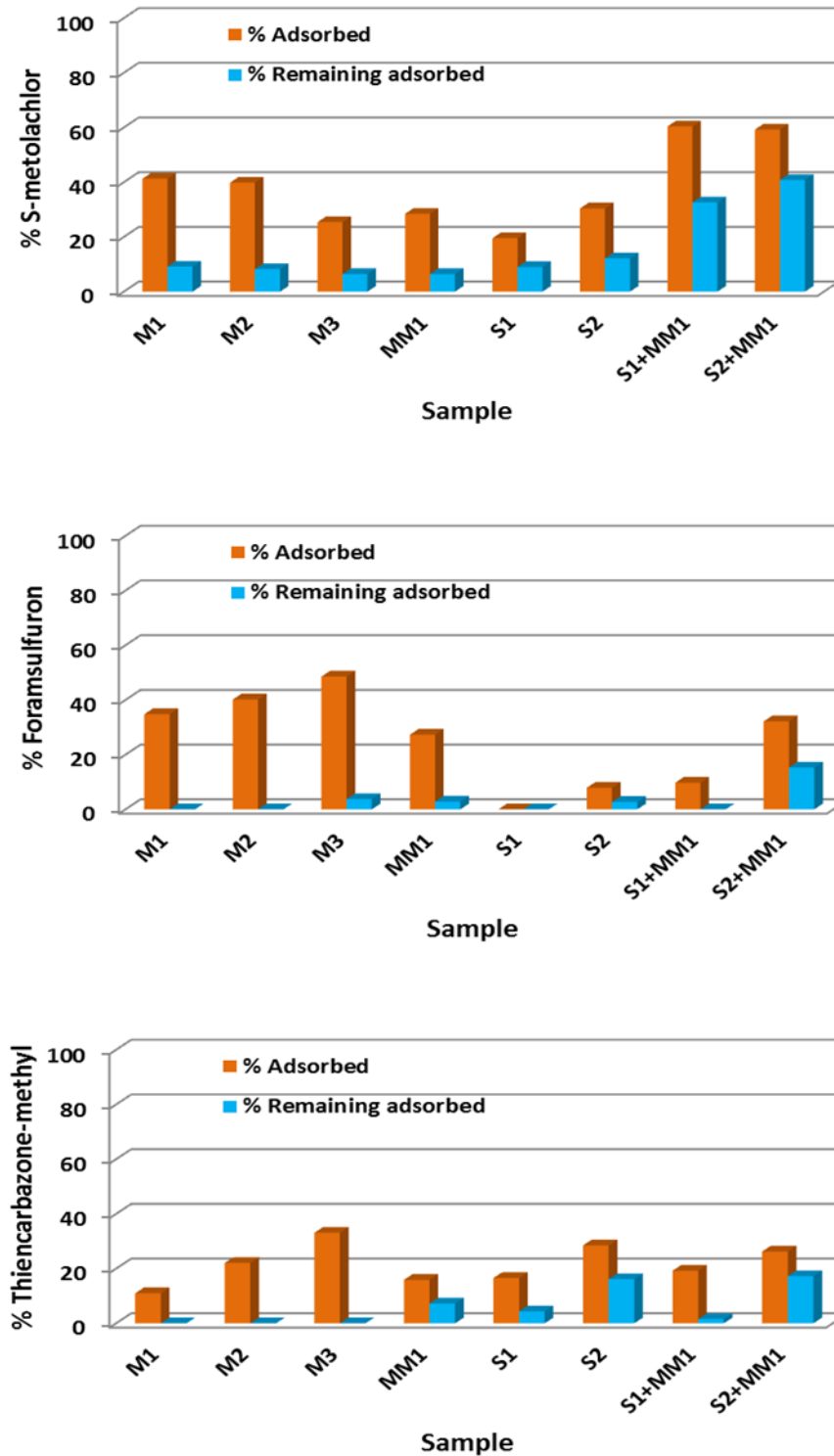
Figure 37. Adsorbed amounts expressed as percentages of herbicide (S-metolachlor, foramsulfuron or thiencarbazone-methyl) in aqueous solution at an initial concentration of 25 μg mL−1 , and the residual amounts adsorbed after desorption (four steps) expressed as percentages of the herbicide adsorbed by the mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1 + MM1 and S2 + MM1).

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The hydrophobic herbicide SMOC recorded residual amounts < 10% after its desorption from the mulches M1, M2, and M3. However, no residual amounts of the non-hydrophobic herbicides FORAM or TCM were found in the three mulches except for a low percentage (3.8%) of FORAM in M3 after four successive desorption steps.

These results indicate that the real influence of mulching on the adsorption of these non-hydrophobic herbicides, and consequently on their fate, would be negligible at field scale under precipitation events or under irrigation practices. The wash-off of these non-hydrophobic herbicides intercepted by the mulch during their application is totally or almost totally independent of the mulch's decomposition stage. This preserves the agronomic efficacy of the herbicides, although it could lead to a possible risk of water pollution (Alletto, et al., 2012; Sperry et al., 2022).

The application of SMOC on mulch with various stages of decomposition involved a residual amount (6.45% – 9.1% of the initial application) because total desorption did not occur. This means the choice of the timing of SMOC application in real field conditions in the presence of mulch is crucial from an environmental and agronomic perspective. A positive decrease in its leaching risk would be noted because of its variable adsorption of the amount initially applied (**Figure 37**), but also an undesirable loss of herbicide due to a lack of desorption by the mulch. Aslam et al. (2013) have also reported residual amounts of absorbed SMOC (24% – 38%) in maize mulch at various and higher stages of decomposition than those considered here. It should be noted that the timing and quantity of precipitation or irrigation could be also critical for the wash off of herbicides from the mulch. Aslam et al. (2015) observed that the leaching of SMOC in soil columns covered by mulch and under two different simulated rainfall (light but frequent rainfall and a less frequent but more intense rainfall) was controlled by the rainfall regime.

The application of MM1 as an organic soil amendment recorded an increasing amount of the three herbicides remaining adsorbed in S2. After the entire desorption process, the residual amounts in S2+MM1 increased up to 3.4 times for SMOC, 5.6 times for FORAM, and 1.1 times for TCM compared to unamended S2. However, this increase was found solely for the most hydrophobic herbicide, SMOC, in S1+MM1 (up to 3.6 times). The amendment of soils with organic residue materials has frequently been cited in the literature as a potential strategy for preventing the point pollution of soils and waters by pesticides (Álvarez-Martín et al., 2016; García-Delgado et al., 2020; Marín-Benito et al., 2016). Nevertheless, MM1 was not an effective adsorbent for herbicides with a high

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solubility in water and/or a low hydrophobicity when used as an organic amendment in soils with a low natural OC content. Other organic residues assessed as adsorbents for environmental purposes have proven more effective for different pesticides than those obtained for MM1 here (García-Delgado et al., 2020; Karanasios et al., 2010; Marín-Benito et al., 2012). Some authors, however, have also observed that the beneficial environmental impact of organic residues as soil amendment could be limited under field conditions or similar in presence of preferential macropore flow in soil (Dollinger et al., 2022) or rainfall events shortly after the pesticides' application (Carpio et al., 2020) since these processes may minimize the retention of pesticides by organic residues and favour their leaching.

CONCLUSIONS

4. CONCLUSIONS

1. A significant and positive impact of the mulch at different decomposition stage on the adsorption of SMOC and FORAM and by milled mulch after on the adsorption of FORAM was found. The OC and/or DOC content of the soils and mulches or milled mulch-amended soils and the characteristics of herbicides such as their hydrophobicity and/or their water solubility controlled the adsorption and/or desorption of each herbicide.

2. The real impact of mulch residues on the soil surface under NT management or the use of mulch as a potential organic amendment of soils revealed that a higher amount of herbicide remained adsorbed by the mulch-amended soils than by the mulches after the desorption experiment. Therefore, the effect of the mulch on the net balance of the herbicide adsorption-desorption process could be defined as a delay in the time that the compounds need to reach the soil surface. This delay will depend on the precipitation and/or irrigation recorded after the application of the herbicides and their interception by the mulch.

3. The application of milled mulch to soil decreased the degradation rates of SMOC, FORAM and TCM under laboratory conditions due to the higher adsorption and lower bioavailability for their degradation in mulch-amended soils. An expected faster degradation rate was observed for the herbicides at 24°C than at 14°C, possibly because the microbiological activity increased with the temperature. The presence of some herbicide metabolites was detected simultaneously to their degradation in all the soil treatments and incubation temperatures.

4. The effect of the mulch applied to soils as an organic amendment on the herbicide degradation was different depending on the herbicide and incubation temperature. However these factors (incubation temperature and mulch) had non-significant impact on the kinetic model that best fits the experimental degradation curves of herbicides in the agricultural soils. This impact depended solely on the herbicide.

5. The properties of soils without mulch and in presence of mulch (CT and NT managements) showed no influence on the best kinetic model fitting the dissipation of the three herbicides under field conditions. It depended solely on the herbicide, being, in general, SMOC kinetics fitted best to the FOMC model, and FORAM and TCM to the SFO model after the first application (the first experimental year). However, dissipation fitting was more heterogeneous after the second application (the second experimental year) in NT treatments when a highest amount of mulch on the soil surface controlled the herbicides' dissipation mechanism. The

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dissipation of herbicides via degradation was consistent with the detection and quantification of some SMOC and FORAM metabolites in the soils under CT and NT practices over the two experimental periods. No detection of TCM metabolites was possible under any soil treatment.

6. The soil physicochemical characteristics (OC and DOC) and the herbicide properties (solubility and hydrophobicity) played a key role in the dissipation of the herbicides under CT and NT managements, because they control the adsorption behaviour of the herbicides after their application as observed in the laboratory experiment. The dissipation of FORAM and TCM was delayed or accelerated under NT compared to CT managements after the first and second application of herbicides, respectively, while it was always accelerated for SMOC. In addition, the irrigation (first year) and rainfall (second year) events shortly recorded after the herbicides' application to the soil controlled strongly the dissipation of the three herbicides via leaching in all the soil treatments.

7. The presence of mulch on the soil surface in a higher amount in the second year than in the first one showed a strong impact on the dissipation of the herbicides. It was explained considering that more than 56% of the herbicides dissipation occurred on the mulch surface before reaching the soil through different potential pathways (mineralization, formation of bound residues, photodegradation, and/or volatilization) in addition to degradation, which could accelerate this process in soils+NT in comparison with that observed in soils+CT.

8. The adoption of a NT management generally enhanced the biological parameters that were assessed in the soil microbial community compared to the CT management. Under NT, both soil microbial activity (DHA) and biomass increased as compared to CT treatments. However, an adverse effect was observed on soil microbial respiration. The microbial structure showed no significant changes under NT treatments, mainly due to the short transition period (two years) to this soil management.

9. The application of herbicides to soils significantly decreased soil microbial biomass, respiration, and activity in all treatments, with a greater effect in CT than in NT managements. However, their impact did not persist over time. Herbicides triggered stress on microbial structure, resulting in a decrease in Actinomycetes and fungi, while having a positive effect on Gram-negative and Gram-positive bacteria.

10. A high and rapid mobility was observed for the three herbicides through the whole soil profile (0-50 cm depth) of all treatments favoured by the irrigation and/or rainfall events shortly recorded after the first and second herbicides' application to the soil. However, a slower and

lower wash-off of the herbicides in soils+NT profiles was observed due to the partial (first year) or almost total (second year) interception of herbicides by the mulch layer that decreased the concentration in the topsoils as well as at any depth under this management compared to soils+CT.

11. Herbicides mobility was reduced in S2 soils compared to S1 soils due to its retention by the higher OC content in all soil profile than in that of S1. However, mobility of SMOC and TCM could be favoured by the DOC content, higher in S2 soils and in NT treatments.

12. The modelling strategy followed can be considered correct to simulate the soil moisture and the mobility behaviour of the herbicides in soils+NT with the two pesticide fate models at a bi-annual scale, especially with MACRO that showed a higher performance than PRZM, which did not simulate satisfactorily the water dynamics.

13. The decrease in models' efficiency with simulation time to predict the fate of the herbicides in soils+NT under different percentage of soil surface covered by the mulch each year suggests the need of implementing a module in the models allowing to correct the DT_{50} values according to the amount of mulch covering the soil annually.

14. Finally, it is highlighted that the present study shows the results of two-year field experiment in agricultural soils that have moved from a CT management for more than 20 years to a NT management. The experimental period for this trial is probably short to observe the impact that this type of agricultural practices has on the long-term soil properties and consequently on its influence on the behaviour of herbicides applied. The processes of adsorption-desorption, dissipation and mobility of herbicides are widely influenced by these agricultural managements and at the same time by the impacts on the soil microbial communities. All these processes determine the final environmental fate of the herbicides as well as their efficacy. In this sense, laboratory studies including mulch with different decomposition stage and field studies implying longer experimental periods under non-tillage management and considering different degrees of soil surface covered by mulch should be assayed and simulated in order to stablish the sturdiness of the modelling strategy followed in this study.

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ANNEX I

Mulching vs. organic soil amendment: Effects on adsorption-desorption of herbicides

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HIGHLIGHTS

- Potential of mulching and organic soil amendment to retain herbicides was compared.
- Net retention of herbicides was higher in amended soils than in mulches.
- Mulch decomposition enhanced the adsorption of S-metolachlor and foramsulfuron.
- Foramsulfuron and thiencarbazone-methyl adsorption were increased after the mulch milling.
- Herbicide retention may be predicted using their hydrophobicity and water solubility, and the adsorbent OC content.

GRAPHICAL ABSTRACT
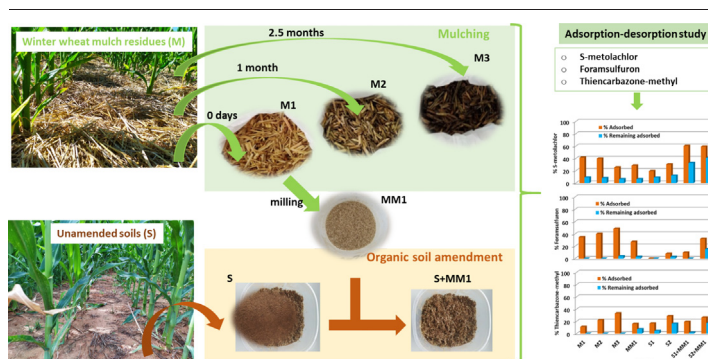
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ABSTRACT

Mulching and organic soil amendment are two agricultural practices that are being increasingly used to preserve soil from degradation, although they may modify the fate of herbicides when applied in soils subjected to these practices. This study has set out to compare the impact of both agricultural practices on the adsorption-desorption behaviour of the herbicides S-metolachlor (SMOC), foramsulfuron (FORAM), and thiencarbazone-methyl (TCM) involving winter wheat mulch residues at different stages of decomposition and particle size, and unamended soils or those amended with mulch. The Freundlich K_f adsorption constants of the three herbicides by mulches, and unamended and amended soils ranged between 1.34 and 65.8 (SMOC), 0–34.3 (FORAM), and 0.01–1.10 (TCM). The adsorption of the three compounds was significantly higher in mulches than in soils (unamended and amended). The adsorption of SMOC and FORAM increased significantly with mulch decomposition, with this positive impact also being observed on the adsorption of FORAM and TCM after mulch milling. Simple and multiple correlations between mulches, soils, and herbicide properties, and adsorption-desorption constants (K_f, K_d, K_{fd}) reflected the organic carbon (OC) content and/or dissolved organic carbon (DOC) content of the adsorbents as main variables controlling the adsorption and/or desorption of each herbicide. The statistic R^2 revealed that >61 % of the variability in the adsorption-desorption constants could be explained by jointly considering the OC of mulches and soils and the hydrophobicity (for K_f) or water solubility of herbicides (for K_d or K_{fd}). The same trend observed for K_{fd} desorption constants as for K_f adsorption ones resulted in higher percentages of herbicide remaining adsorbed after desorption in amended soils (33 %–41 % of SMOC, 0 %–15 % of FORAM, and 2 %–17 % of TCM) than in mulches (< 10 %). The results reveal a higher efficiency of organic soil amendment than mulching as an agricultural practice for immobilising the herbicides studied when winter wheat mulch residues are used as a common adsorbent, and as a better strategy for avoiding groundwater contamination.

1. Introduction

Intensive agriculture involves excess soil tillage, heavy irrigation, and the application of pesticides for rapidly obtaining high yields. Nevertheless, intensive soil management practices in agriculture have changed substantially in recent years to reduce their high pressure on the different environmental compartments (Gil Ribes et al., 2017; Pereira et al., 2018). This is leading to the implementation of more sustainable soil management practices focused mainly on the short- and long-term preservation of soil health and fertility (Bonanomi et al., 2020; Ravichandran et al., 2022) and as potential strategies to avoid degrading the environment in general and the soil in particular (https://ejpsoil.eu/soil-research/i-sompe).

Two management practices that have been attracting growing attention for some years now involve covering the soil surface with crop residues after harvest (mulching) and the application of organic residues as soil amendments because of their environmental and agronomic benefits (Bonanomi et al., 2020; Carpio et al., 2023; Iqbal et al., 2020; Lugato et al., 2014; Siedt et al., 2021; Urra et al., 2019). Mulching improves the retention of water in the soil by limiting its evaporation; and other soil properties by increasing nutrient holding capacity, weed control, soil microbial and macro- and mesofauna diversity, lessening the impact of precipitation and potential erosion, and reducing the need for crop-boosting products (Gil Ribes et al., 2017; Iqbal et al., 2020). Physical, chemical, and biological soil properties are also improved by the application of organic amendments, and a better soil structure, cation exchange capacity, and microbial biomass have frequently been reported in the literature as beneficial effects of this agricultural practice (Siedt et al., 2021; Urra et al., 2019). In addition, both mulching and organic amendments promote the restoration and maintenance of the organic matter (OM) content of agricultural soils, greatly enhancing long-term soil fertility and performance, as well as helping to tackle climate change through carbon sequestration (Carpio et al., 2023; Gil Ribes et al., 2017; Govindasamy et al., 2020; Lugato et al., 2014).

Both soil management practices provide similar or related benefits for soil properties, although their implementation is different. Organic amendments are incorporated into the soil bulk, whereas mulching is located on the soil surface where the mulch layer acts mainly as a physical barrier (Gil Ribes et al., 2017). This is the main difference between both agricultural practices, and the consequences could be significant when these practices are simultaneous to other agronomic practices, such as the application of herbicides. A mulch layer and amended soils immobilise herbicides in soils, controlling their degradation and leaching, and therefore modifying their environmental fate and/or decreasing water contamination (Carpio et al., 2022). Nevertheless, the mulch layer may also intercept and adsorb the herbicides, decreasing their agronomic performance when precipitation or irrigation fail to reverse the adsorption process and allow herbicides to reach the soil (Sperry et al., 2022).

Herbicides accounted in 2020 for 52.5 % of the total pesticides used worldwide (FAOSTAT, 2023). It is therefore of interest to understand the influence that new management practices might have in herbicide environmental and/or agronomic behaviour. The ability to immobilise herbicides in amended soils has often been reported by adsorption studies involving a wide range of organic residues of different origins, nature, composition, maturity, and properties (Álvarez-Martín et al., 2016; Cañero et al., 2015; García-Delgado et al., 2020; Marín-Benito et al., 2021; Peña et al., 2019). Studies of the adsorption of different herbicides by similar materials to mulch, such as wood or its components, have been evaluated and their retention capacity has been evidenced (Jing et al., 2021; Mandal et al., 2017; Rodríguez-Cruz et al., 2007). In addition, the adsorption of some herbicides by no-till soils usually located under the mulch layer have been reported (Alletto et al., 2012, 2013; Cueff et al., 2020, 2021; Porfiri et al., 2015), although the effect of mulch applied as an organic soil amendment on the behaviour of herbicides has not been addressed. Accordingly, these processes have scarcely been studied, although mulch should be evaluated as an herbicide interceptor and adsorbent (Alletto et al., 2012; Jing et al., 2021), as well as the impact of its evolution or degree of decomposition over time (Aslam et al., 2013; Cassigneul et al., 2016).

SMOC, FORAM, and TCM are pre- and/or postemergence herbicides used to control grasses and some broadleaf weeds in a wide range of crops (Lewis et al., 2016). They are widely applied nowadays in soils subject to new management practices, which largely justifies their selection for this study (Leonie et al., 2014; Wendt et al., 2017; Whalen et al., 2019). SMOC has moderate water solubility and high hydrophobicity. FORAM is a weak acid (pK_a = 4.6, 25 °C) with high water solubility and very low hydrophobicity, belonging to the sulfonylurea group. TCM is also a weak acid (pK_a = 3.0, 25 °C) with very low hydrophobicity but moderate water solubility. This herbicide belongs to the triazolone group. All three compounds are considered non-persistent in soil with half-life (DT_{50}) values lower than 52 days under laboratory conditions. According to the groundwater ubiquity score (GUS), FORAM is classified as a highly leachable herbicide and SMOC and TCM are moderately mobile, with values of 2.95, 2.32, and 2.46, respectively (Lewis et al., 2016). The properties of the three herbicides enable them to leach into ground and/or surface waters, where they have been detected (Bexfield et al., 2021; Chèvre et al., 2008; Herrero-Hernández et al., 2017).

According to the current state-of-the-art, the knowledge on the environmental fate of SMOC, FORAM, and TCM when they are intercepted by crop residues in mulching practice or when they reach the amended soils is limited. The study of the adsorption-desorption processes that mainly control their behaviour therefore needs to be evaluated and compared within the context of these agronomic practices. The adsorption-desorption behaviour of SMOC has been documented on unamended and amended soils (Cañero et al., 2015; Delgado-Moreno and Peña, 2008; Marín-Benito et al., 2021; Peña et al., 2019; Sharipov et al., 2021), while there are very few studies that have explored this herbicide's adsorption and desorption processes or even others in mulches (Alletto et al., 2012; Aslam et al., 2013). Most studies have evaluated solely the adsorption process, disregarding subsequent SMOC desorption and therefore missing the net balance of mulching as an agronomic practice for herbicide immobilisation (Cassigneul et al., 2015, 2018). Within this context, Cassigneul et al. (2015, 2018) have also assessed the effect that the nature and stage of decomposition of mulch has on SMOC adsorption, although it was determined for a single concentration. However, adsorption isotherms for mulching at different stages of decomposition are required for better understanding the adsorption behaviour for a range of herbicide concentrations and obtaining parameters for simulating their environmental fate. Complete and adequate parameterisation data are needed for recent pesticide fate modelling studies when considering organic amendment and mulching practices (Marín-Benito et al., 2018a, 2020). To the best of our knowledge, no information about the adsorption-desorption behaviour of FORAM and TCM is available, apart from their corresponding pesticide risk assessment report by the European Food Safety Authority (EFSA, 2013, 2016). Only one additional adsorption-desorption study has been reported in the literature for TCM in unamended soils (Gul et al., 2020).

Accordingly, the aim here has been to evaluate the adsorption-desorption behaviour of the herbicides SMOC, FORAM, and TCM with contrasting properties involving different agricultural practices as an indicator of their potential environmental fate. The adsorption-desorption behaviour of these compounds was compared for: (1) winter wheat mulch residues at different stages of decomposition and particle size, and (2) unamended soils and those amended with mulch. A statistical approach was adopted to study the effects that the mulch, soil, and herbicide properties had on herbicide adsorption-desorption. The purpose of this research is to find efficient and environmentally friendly agricultural practices and determine adsorption parameters in high demand in pesticide fate modelling.

2. Materials and methods

2.1. Winter wheat mulches and soil samples

Winter wheat residues were sampled immediately after harvest (mulch 1, M1) on a plot subject to conservation tillage at the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of

Salamanca (IRNASA-CSIC), Spain. Additionally, winter wheat residues left on the soil surface and decomposed under field conditions and irrigation (~26 mm per week) were collected one month (mulch 2, M2) and 2.5 months (mulch 3, M3) after harvest. Multiple sub-samples (500 g) of each mulch type were collected, mixed, dry cleaned to remove soil particles, and cut into 1–2-cm pieces. Mulch 1 was also milled (<1 mm) (MM1) to evaluate its individual adsorbent capacity as a mulch with a different particle size and its efficiency as an organic soil amendment. The physicochemical characteristics of the mulch were determined by standard analytical methods (Carpio et al., 2020; Sparks, 1996) (Table 1). The mulches were also analysed by cross-polarization and magic angle spinning nuclear magnetic resonance (CP-MAS ^{13}C NMR) to determine the main functional groups contained in the OC and their evolution with mulch decomposition, according to García-Delgado et al. (2020). Chemical shifts were reported relative to tetramethyl silane at 0 ppm. Spectra were divided into five chemical shift regions as follows: 0–45 ppm alkyl-C; 45–60 ppm N-alkyl-C; 60–110 ppm O-alkyl-C; 110–160 ppm aromatic-C; 160–220 ppm usually associated with carboxyl and carboxylic-C. The carbon distribution of mulches is shown in Table 2.

A soil with sandy-loam texture (80.4 % sand, 4.7 % silt, and 14.9 % clay) was sampled from two sites at the same location (the Muñovela experimental farm) with different OC content in the surface horizon. They were labelled soil S1 (0.69 %OC) and soil S2 (1.01 %OC). These soil samples were collected from the surface horizon (0–10 cm), air dried, and sieved (<2 mm). The soils were then amended with the milled mulch by uniformly mixing S1 or S2 with MM1 at a rate of 10 % *w*/w on a dry weight basis in the laboratory (S1 + MM1 and S2 + MM1), as performed with other organic residues (García-Delgado et al., 2020). The physicochemical characteristics of soil (unamended and amended) samples were determined by standard analytical methods (Carpio et al., 2020; Sparks, 1996) (Table 1).

2.2. Herbicides

The herbicides SMOC, FORAM, and TCM (>98 % purity) were supplied by Sigma Aldrich Química S.A. (Madrid, Spain). The chemical structures and selected properties of the three compounds are presented in Table 3 (Lewis et al., 2016). Based on the frequently reported adsorption-desorption behaviour of SMOC, it was chosen as a reference herbicide to compare it with FORAM and TCM, which have hardly been explored.

2.3. Adsorption-desorption experiments

The adsorption-desorption isotherms of herbicides for mulches at different stages of decomposition and particle size, and by the unamended and MM1-amended soils were obtained using the batch equilibrium technique. Duplicate samples of dry mulch (0.1 g) or soil (5 g) were equilibrated with 10 mL of an ultrapure water solution of each herbicide at concentrations of 1, 5, 10, 15, 20, and 25 mg L^{-1}. The suspensions were shaken at 24.0 ± 0.1 °C for 24 h in a thermostated chamber, with intermittent shaking for 2 h at three-hour intervals. Preliminary experiments revealed that contact for 24 h was long enough for reaching equilibrium. The suspensions were subsequently centrifuged at 5045*g* for 30–40 min, and the supernatant was filtered through 0.22-μm Minisart nylon filters (Sartorius Stedim

Table 2
Carbon distribution of mulches calculated by relative areas of the chemical shift regions (ppm) in ^{13}C cross-polarization and magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra.

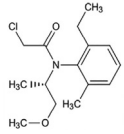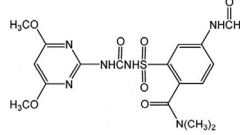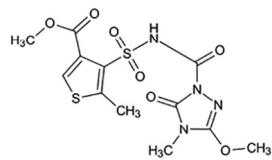| Mulch	Alkyl-C 0–45	N-alkyl-C 45–60	O-alkyl-C 60–110	Aromatic-C 110–160	Carboxyl/carbonyl-C 160–220
M1	11.1	0.56	80.4	2.77	5.17
M2	6.23	0.52	87.0	2.35	3.90
M3	9.43	0.46	82.0	2.16	5.95
MM1	7.80	1.15	83.8	4.23	3.02

Biotech, Germany) prior to the determination of the equilibrium concentration of each herbicide in the supernatant by ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS), as indicated in Section 2.4. The amount of herbicide adsorbed was taken to be the difference between that initially present in solution and that remaining after equilibration with the mulch or soil. Calculations assumed that the herbicides did not degrade during the adsorption studies.

The desorption isotherms of the herbicides were obtained from 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, and after adsorption equilibrium had been reached, a 5 mL aliquot was taken from the solution and immediately replaced by 5 mL of ultrapure water. The resuspended samples were shaken as indicated above, after which the suspensions were centrifuged, filtered, and the desorbed herbicide was calculated as the difference between that initially adsorbed and the amounts desorbed measured by UHPLC-QTOF-MS.

2.4. Herbicide analysis

The herbicides were quantitatively determined by UHPLC-QTOF-MS. The equipment used was an Agilent chromatograph (Agilent Technologies, Avondale, AZ, USA) equipped with a UHPLC (HPCL Infinity II), an Agilent 6546A QTOF mass spectrometer, and Mass Hunter Qualitative and Quantitative Analysis software as the data acquisition and processing system. The chromatographic separation of herbicides involved a Zorbax® Eclipse Plus C18 column from Agilent (2.1 × 50 mm inner diameter, 1.8 μm), maintained at 30 °C. The gradient profile was as follows: 0–0.25 min, 95 % water with 0.1 % formic acid (A) and 5 % acetonitrile (B); 0.25–2.5 min, 55 % A and 45 % B; 2.5–3.5 min, 100 % B; 3.5–4 min, 95 % A and 5 % B. The flow rate was 0.4 mL min^{-1} and the sample injection volume was 4 μL. The Q-TOF mass spectrometer operated in positive electrospray ionisation mode (ESI) ion source with Jet Stream Technology (AJS) under multiple-reaction monitoring mode (MRM). Ultra-pure nitrogen (N$_2$) was used as the nebulising and sheath gas. Ultra-high-purity N$_2$ was used as collision gas in product ion scanning experiments. The ESI parameters were set as follows: the capillary voltage was 3.5 kV; the temperature of the sheath gas and the flow rate were 350 °C and 11 L min^{-1}, respectively; the source temperature was set at 225 °C and the flow rate of the drying gas at 12 L min^{-1}; the nebulizer gas pressure was 30 psi; the fragmentor voltage was 110 V; the mass analyser scanned from 100 to 1050 (*m/z*); the QTOF acquisition rate was 1.5 Hz; the energies for collision-induced dissociation

Table 1
Main characteristics of the mulches at different stages of decomposition (M1, M2, and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1 + MM1 and S2 + MM1) soils.

Sample	pH	OC (%)	N (%)	C/N	DOC (mg/g)
M1	5.38 ± 0.04	44.6 ± 0.05	1.21 ± 0.03	36.8 ± 0.78	125 ± 3
M2	5.43 ± 0.02	44.1 ± 0.26	1.56 ± 0.06	28.3 ± 0.90	114 ± 4
M3	6.09 ± 0.07	44.5 ± 0.06	1.53 ± 0.02	29.1 ± 0.48	66.0 ± 1.40
MM1	5.95 ± 0.05	41.7 ± 0.11	2.22 ± 0.03	18.8 ± 0.18	55.8 ± 17.5
S1	6.81 ± 0.13	0.69 ± 0.02	0.09 ± 0.00	7.93 ± 0.17	0.14 ± 0.03
S2	7.67 ± 0.09	1.01 ± 0.06	0.12 ± 0.01	8.27 ± 0.30	0.14 ± 0.01
S1 + MM1	5.85 ± 0.09	6.26 ± 0.31	0.13 ± 0.01	47.2 ± 1.8	5.81 ± 0.10
S2 + MM1	6.15 ± 0.09	11.4 ± 0.96	0.14 ± 0.01	79.6 ± 2.5	5.96 ± 0.25

Table 3
Chemical structure and main characteristics of herbicides.

Herbicide	Chemical structure	WS[a] (mg L^{-1})	Log K$_{ow}$[b]	K$_f$[c] (mL g^{-1})	DT$_{50}$[d] (days)	GUS index[e]
S-metolachlor [2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-meth-oxy-1-methylethyl] acetamide]		480	3.05	3.63	51.8	2.32
Foramsulfuron [2-[[[[(4,6-Dimethoxy-2-pyrimidinyl) amino] carbonyl]amino] sulfony]-4-(formylamino)-N,N-dimethylbenzamide]		3293	−0.78	1.08	25.3	2.95
Thiencarbazone-methyl [Methyl 4-[[[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl) carbonyl] amino] sulfonyl]-5-methyl-3-thiophenecarboxylic acid]		436	−1.98	2.01	51.5	2.46

[a] WS, water solubility at 20 °C.
[b] Octanol/water partition coefficient at pH 7 and 20 °C.
[c] Freundlich adsorption coefficient.
[d] Time to degradation 50 % of compound.
[e] Gustafson mobility index (Lewis et al., 2016).

(CID) experiments were set at 10, 20, and 40 eV, respectively; all MS data were acquired with reference masses at *m/z* 121.05 and 922.01 in the positive ESI mode to ensure mass accuracy and reproducibility; quantification involved monitoring the positive molecular ion [m/z] [M + H]$^+$ 284.14 (SMOC), 391.39 (TCM), and 453.12 (FORAM). Under these conditions, the retention times of the herbicides were 2.90 (FORAM), 3.17 (TCM), and 3.81 (SMOC) min, respectively.

2.5. Data analysis

The adsorption and desorption data for the herbicides were fit to the linearised form of the Freundlich equation: log Cs = log K$_f$ + n$_f$ log C$_e$ or log C$_s$ = log K$_{fd}$ + n$_{fd}$ log C$_e$. Cs (µg g^{-1}) is the amount of adsorbed herbicide and Ce (µg mL^{-1}) is the equilibrium concentration of herbicide in solution. K$_f$ or K$_{fd}$ (mL^n µg^{1-n} g^{-1}) and n$_f$ or n$_{fd}$ are the Freundlich adsorption or desorption coefficients and non-linearity coefficients, respectively. The distribution coefficients K$_d$ (mL g^{-1}) were also calculated from the relationship C$_s$/C$_e$ for a C$_e$ of 25 µg mL^{-1} for comparison with the adsorption behaviour of herbicides at low concentrations (K$_f$) because the isotherms were nonlinear. 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. Analysis of variance (ANOVA) was performed to determine significant differences between adsorption-desorption constants. Means were compared by the Tuckey post-hoc test ($p < 0.05$). Simple and multiple linear regression models were used to relate the adsorption-desorption coefficients of the herbicides to adsorbent and herbicide characteristics ($p < 0.05$). IBM SPSS Statistics 29.0 software was used.

3. Results and discussion

3.1. Adsorption of herbicides by mulches and soils

Fig. 1 includes the adsorption isotherms of SMOC, FORAM, and TCM for mulches M1, M2 and M3, milled M1 (MM1), and unamended and MM1-amended soils. They were well described by the Freundlich equation

with r^2 ≥ 0.91 ($p < 0.02$), and the n$_f$, K$_f$, and K$_d$ parameters determined from this equation are shown in Tables 4–6.

A wide variety of isotherm types were obtained depending on the adsorbent (Fig. 1), and they agreed with the wide range of n$_f$ values obtained (0.34–1.10 for SMOC; 0.87–1.83 for FORAM, and 1.09–2.37 for TCM) (Tables 4–6). L-type isotherms with n$_f$ values <1 were obtained for the adsorption of SMOC by M3, S1, S2, S1 + MM1, S2 + MM1 (with total adsorption of the herbicide at C$_i$ ≤ 5 µg mL^{-1}) and L-C-type isotherms were obtained for MM1. However, S-type isotherms with n$_f$ values >1 were obtained solely for M1 and M2. L-type isotherms (n$_f$ < 1) or close to C-type (n$_f$ ≥ 0.9) also characterised the adsorption of FORAM by MM1, S1 + MM1, and S2 + MM1, generally indicating that the adsorption of water by these adsorbents could be similar to that of FORAM molecules. In contrast, S-type isotherms (n$_f$ > 1) described the adsorption of FORAM by S2, M1, M2, and M3, whereas no herbicide adsorption was determined for S1. These results indicate different mechanisms of adsorption for SMOC and FORAM depending on the adsorbent. In contrast to SMOC and FORAM, TCM showed a more homogeneous adsorption mechanism by the different adsorbents, as the adsorption isotherms were always of S-type (n$_f$ > 1) (Table 6).

A broad range of isotherm types has also been reported for the adsorption of SMOC by different adsorbents with different characteristics. Aslam et al. (2013) have obtained almost linear adsorption isotherms (n$_f$ ≥ 0.9) for SMOC on decomposed maize mulch residues with OC content ranging between 34 % and 42 %, whereas Marín-Benito et al. (2021) and Peña et al. (2019) have reported mainly L-type isotherms or C-type isotherms, respectively, for the adsorption of SMOC by unamended soils and soils amended with different organic residues whose OC content varied from 22 %–24 % to 38 %–53 %, respectively. As regards FORAM, and as far as we know, the only n$_f$ values reported in the literature range from 0.82 to 0.96, and they correspond to its adsorption in unamended soils with OC contents in the range 0.47 %–1.47 %, respectively (EFSA, 2016). In turn, Gul et al. (2020) have reported lower n$_f$ values (0.49–0.92) for the adsorption of TCM in ten natural soils with low OC content (0.17 %–0.58 %) and with a predominantly more sandy-loam texture than in the current study. EFSA (2013) has also reported lower n$_f$ values (0.89–0.93) for soils with a higher variation in OC content (0.9 %–4.1 %).
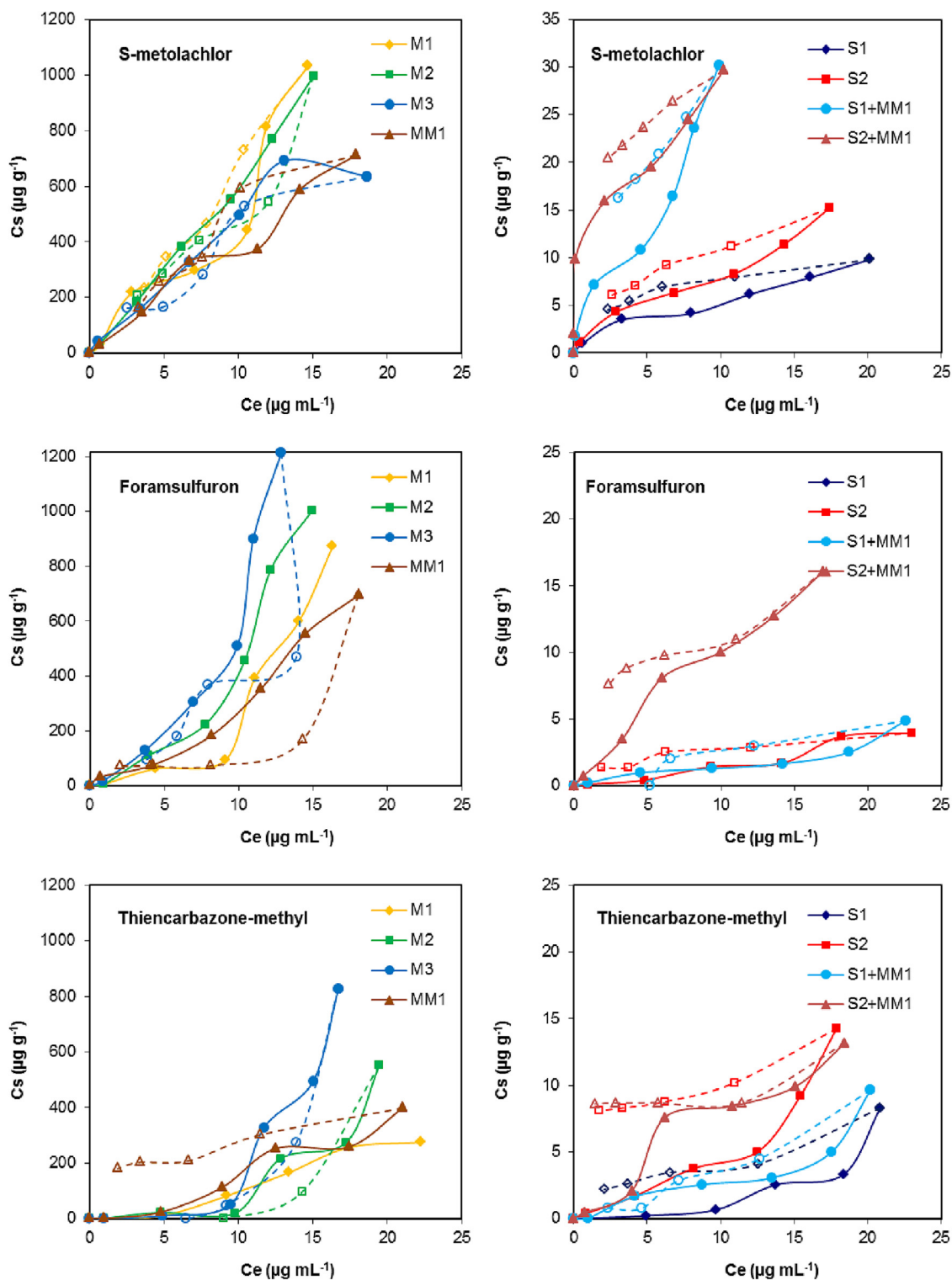
Fig. 1. Adsorption-desorption isotherms of S-metolachlor, foramsulfuron, and thiencarbazone-methyl for mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1 + MM1 and S2 + MM1). Closed symbols and continuous line correspond to adsorption and open symbols and dashed line correspond to desorption.

The K_f values obtained for the adsorption of SMOC by soils and mulches ranged between 1.34 and 65.8, with the highest K_f values corresponding to mulches (43.7–65.8), and the lowest ones to unamended soils (1.34–2.00). Cassigneul et al. (2018) have also observed a significantly lower adsorption of SMOC by soil than by mulch from different cover crop residues. The K_f values increased in the order: S1 < S2 < S1 + MM1 < S2 + MM1 << MM1 < M1 < M2 < M3 according to the increase in the OC content ($r = 0.971$, $p < 0.001$) and/or DOC ($r = 0.830$, $p < 0.05$) of the adsorbents

(Tables 1 and 7). OC is reported to be the most important soil component affecting the adsorption of this hydrophobic herbicide (Alletto et al., 2013; Marín-Benito et al., 2021; Westra et al., 2015). The application of MM1 as a soil amendment increased the K_f values up to 4.5 times in S1 + MM1 and up to 6.4 times in S2 + MM1 (Table 4). An increase in SMOC K_f values has frequently been observed after the addition of organic soil amendments of different origins (Marín-Benito et al., 2021; Peña et al., 2019). The stage of mulch decomposition also had a significant ($p < 0.05$)

Table 4
Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of S-metolachlor by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1 + MM1 and S2 + MM1) 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	K_{foc}	$K_d \pm$ SD	K_{doc}	$n_f \pm$ SD	r^2	$K_{fd} \pm$ SD	$n_{fd} \pm$ SD	r^2	H
M1	45.6 ± 3.37B	102	62.6 ± 3.95A	140	1.10 ± 0.07	0.95	55.3 ± 3.63A	1.08 ± 0.25	0.99	1.01 ± 0.17
M2	49.7 ± 3.13AB	113	68.4 ± 0.37A	155	1.10 ± 0.10	0.99	65.1 ± 3.54A	0.93 ± 0.30	0.94	1.18 ± 0.25
M3	65.8 ± 0.79A	148	39.0 ± 3.69B	87.7	0.84 ± 0.03	0.98	64.1 ± 3.69A	0.79 ± 0.05	0.88	1.06 ± 0.10
MM1	43.7 ± 3.54B	105	39.0 ± 2.33B	93.7	0.96 ± 0.08	0.99	60.8 ± 3.25A	0.89 ± 0.08	0.95	1.08 ± 0.18
S1	1.34 ± 0.01b	194	0.41 ± 0.01a	59.4	0.63 ± 0.01	0.98	3.39 ± 0.31c	0.36 ± 0.14	0.98	1.77 ± 0.71
S2	2.00 ± 0.06b	198	0.65 ± 0.01a	64.4	0.65 ± 0.01	0.98	3.69 ± 0.30c	0.48 ± 0.10	0.99	1.35 ± 0.27
S1 + MM1	6.05 ± 1.16b	96.6	1.60 ± 0.46a	25.6	0.59 ± 0.20	0.96	8.81 ± 0.64b	0.52 ± 0.09	0.97	1.13 ± 0.20
S2 + MM1	12.9 ± 1.35a	113	1.53 ± 0.18a	13.4	0.34 ± 0.07	0.92	16.2 ± 0.58a	0.26 ± 0.01	0.99	1.32 ± 0.30
CV (%)	89.8	31.1	109	62.7						

SD = standard deviation of replicates; H = n_f/n_{fd}; CV = coefficients of variation.
Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

Table 5
Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of foramsulfuron by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1 + MM1 and S2 + MM1) 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	K_{foc}	$K_d \pm$ SD	K_{doc}	$n_f \pm$ SD	r^2	$K_{fd} \pm$ SD	$n_{fd} \pm$ SD	r^2	H
M1	5.48 ± 0.05C	12.3	50.3 ± 0.10B	113	1.69 ± 0.03	0.94	–	–	–	–
M2	6.89 ± 0.21C	15.6	101 ± 4.25A	229	1.83 ± 0.07	0.99	–	–	–	–
M3	19.4 ± 2.14B	43.5	105 ± 6.76A	235	1.52 ± 0.05	0.98	11.0 ± 0.92B	1.63 ± 0.43	0.85	0.93 ± 0.20
MM1	34.3 ± 0.49A	82.3	28.5 ± 1.20B	68.5	0.94 ± 0.02	0.91	26.3 ± 1.74A	0.84 ± 0.47	0.66	1.13 ± 0.50
S1	0d	0	0b	0	–	–	–	–	–	–
S2	0.09 ± 0.01c	8.91	0.16 ± 0.01b	15.8	1.18 ± 0.01	0.97	0.94 ± 0.03b	0.46 ± 0.01	0.91	2.58 ± 0.07
S1 + MM1	0.22 ± 0.01b	3.51	0.14 ± 0.01b	2.24	0.87 ± 0.02	0.94	0c	3.22 ± 0.25	0.61	0.27 ± 0.03
S2 + MM1	1.19 ± 0.01a	10.4	0.97 ± 0.10a	8.49	0.94 ± 0.03	0.99	5.60 ± 0.01a	0.33 ± 0.01	0.90	2.81 ± 0.07
CV (%)	146	125	127	118						

SD = standard deviation of replicates; H = n_f/n_{fd}; CV = coefficients of variation; "–" No adsorption or desorption isotherms were obtained.
Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

influence on the adsorption of SMOC by increasing the K_f values from 45.6 (M1) to 65.8 (M3) after a 2.5 month-mulch decomposition period and according to their decrease in DOC content (M1 > M2 > M3) (Tables 1 and 4). A positive impact on the adsorption of SMOC and other herbicides by different kinds of mulches according to their decomposition stage has been also reported (Aslam et al., 2013; Cassigneul et al., 2015, 2016, 2018). However, the particle size of the fresh mulch (M1) did not have a significant impact on the adsorption of SMOC with similar K_f values for M1 and MM1 (Table 4), indicating that the mulch composition is more important than the increased surface for the adsorption of the hydrophobic herbicide SMOC.

The K_d distribution coefficients for SMOC ranged from 0.41 to 68.4. They varied in the same direction as the K_f constants for unamended and amended soils, while some changes in the order were observed for mulches

(Table 4) (Alletto et al., 2013; Aslam et al., 2013; Cassigneul et al., 2015; Marín-Benito et al., 2021).

Lower K_f values were obtained for the adsorption of FORAM by mulches and soils compared to SMOC (Tables 4 and 5). The 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 SMOC except for the mulch MM1, with the lowest OC and DOC content, which recorded the highest K_f value for FORAM but the lowest affinity by the most hydrophobic herbicide, SMOC. This high adsorption of FORAM by MM1 led to a significant increase in herbicide adsorption ($p < 0.05$) by S1 and S2 after the addition of MM1 to these soils. The effect of mulch decomposition and particle size on FORAM K_f values was more significant than that previously indicated for SMOC (Tables 4 and 5). M1 recorded the lowest K_f value, and it increased by 1.3 (M2) and 3.5 (M3) times after

Table 6
Freundlich constants for adsorption (K_f and n_f) and desorption (K_{fd} and n_{fd}) of thiencarbazone-methyl by mulches at different stages of decomposition (M1, M2 and M3), milled M1 (MM1), unamended (S1 and S2) and MM1-amended (S1 + MM1 and S2 + MM1) 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	K_{foc}	$K_d \pm$ SD	K_{doc}	$n_f \pm$ SD	r^2	$K_{fd} \pm$ SD	$n_{fd} \pm$ SD	r^2	H
M1	0.86 ± 0.10A	1.93	17.4 ± 1.77A	39.0	1.93 ± 0.17	0.98	–	–	–	–
M2	0.84 ± 0.26A	1.90	21.2 ± 1.30A	48.0	2.00 ± 0.08	0.91	0B	14.6 ± 0.45	0.93	0.14 ± 0.01
M3	0.61 ± 0.02A	1.37	24.2 ± 3.68A	54.4	2.37 ± 0.19	0.92	0B	11.2 ± 1.20	0.87	0.21 ± 0.01
MM1	1.10 ± 0.07A	2.64	27.6 ± 2.24A	66.2	2.00 ± 0.04	0.99	135 ± 1.20A	0.33 ± 0.08	0.91	6.15 ± 1.52
S1	0.01 ± 0.00b	1.45	0.26 ± 0.04b	37.7	1.89 ± 0.06	0.96	1.34 ± 0.27b	0.53 ± 0.02	0.91	3.58 ± 0.01
S2	0.40 ± 0.07a	39.6	0.58 ± 0.09ab	57.4	1.11 ± 0.18	0.97	6.50 ± 1.34a	0.22 ± 0.05	0.91	4.96 ± 0.25
S1 + MM1	0.04 ± 0.00b	0.64	0.57 ± 0.00ab	9.11	1.85 ± 0.02	0.91	0.19 ± 0.03b	1.26 ± 0.35	0.90	1.47 ± 0.37
S2 + MM1	0.61 ± 0.08a	5.34	0.80 ± 0.13a	7.00	1.09 ± 0.09	0.95	7.65 ± 0.79a	0.12 ± 0.02	0.47	8.89 ± 2.28
CV (%)	69.8	194	105	54.6						

SD = standard deviation of replicates; H = n_f/n_{fd}; CV = coefficients of variation; "-" No adsorption or desorption isotherms were obtained.
Note: K_f, K_d or K_{fd} values in the same column followed with a different capital letter indicate significant differences ($p < 0.05$) between mulches, and K_f, K_d or K_{fd} values in the same column followed with a different lowercase letter indicate significant differences ($p < 0.05$) between unamended and amended soils.

Table 7

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	N
K_f/S-metolachlor ($n = 8$)	−0.632[d]	0.971[a]	0.830[c]	0.884[b]
K_d/S-metolachlor ($n = 8$)	−0.715[c]	0.934[a]	0.988[a]	0.819[c]
K_{fd}/S-metolachlor ($n = 8$)	−0.686[d]	0.994[a]	0.875[b]	0.944[a]
K_f/foramsulfuron ($n = 8$)	−0.280	0.670[d]	0.341	0.874[b]
K_d/foramsulfuron ($n = 8$)	−0.535	0.843[b]	0.792[c]	0.711[c]
K_{fd}/foramsulfuron ($n = 5$)	0.400	0.829	0.781	0.941[c]
K_f/thiencarbazone-methyl ($n = 8$)	−0.482	0.826[c]	0.711[c]	0.839[b]
K_d/thiencarbazone-methyl ($n = 8$)	−0.406	0.843[b]	0.606	0.830[c]
K_{fd}/thiencarbazone-methyl ($n = 5$)	−0.375	0.970[a]	0.991[a]	0.999[a]

[a] $p < 0.001$.
[b] $p < 0.01$.
[c] $p < 0.05$.
[d] $p < 0.1$.

its decomposition, and up to 6.3 times (MM1) after milling. The K_f values determined for S1 and S2 were lower than the range of values (0.31–2.61) reported for unamended soils by EFSA (2016), and no additional adsorption-desorption studies have been found in the literature for FORAM. However, some studies have reported a similar low or very low adsorption of other sulfonylurea herbicides by unamended soils (Cueff et al., 2021; Delgado-Moreno and Peña, 2008; Marín-Benito et al., 2018b; Sunulahpašić et al., 2020), slightly promoted by the addition to soil of fresh and composted olive cake or green compost (Delgado-Moreno and Peña, 2008; Marín-Benito et al., 2018b). No adsorption-desorption studies involving FORAM or other sulfonylureas and mulches have been found in the literature.

According to the shape of its isotherms, FORAM showed lower K_d values than the corresponding K_f values obtained for MM1, S1 + MM1, and S2 + MM1, and vice versa for the adsorbents M1, M2, M3, and S2 (Table 5).

TCM had the lowest K_f value ($K_f \leq 1.10$) for all the adsorbents, in general, compared to SMOC and FORAM (Table 6). It is consistent with the lowest hydrophobicity of TCM among the three herbicides studied. The adsorption of this herbicide increased in the order: S1 ~ S1 + MM1 < S2 < S2 + MM1 = M3 < M2 ~ M1 < MM1. The K_f values determined for S1 and S2 were lower than the range of values (0.4–9.3) found in the literature for TCM in unamended soils (EFSA, 2013; Gul et al., 2020), whereas no adsorption-desorption studies are available in the literature for this herbicide in amended soils or in mulches. The increase in the MM1 surface area after the milling of M1 and the application of MM1 to soils slightly increased the adsorption of TCM by this adsorbent and by amended soils compared to M1 (1.3 times) and unamended soils (1.5–4 times), respectively. The opposite effect was observed with mulch decomposition. This non-hydrophobic herbicide recorded the highest K_f adsorption value for MM1, as observed for FORAM (Table 6).

According to S-type isotherms, the adsorption of TCM by all the adsorbents assayed was favoured by the increase in the herbicide concentration in solution. The K_d values (0.26–27.6) increased from 1.3 (S2 + MM1) to 39.7 (M3) times the corresponding K_f adsorption coefficients (Table 6). The high n_f values resulting from TCM adsorption isotherms, exceeding those obtained for SMOC and FORAM, explain the biggest variation between the K_f and K_d values for this herbicide. In a TCM adsorption study involving unamended soils with similar properties to S1 and S2, Gul et al. (2020) have found higher K_d values (4.3–26.4) than those obtained here, possibly because of the different experimental conditions used (unclearly defined in the study).

3.2. Desorption of herbicides from mulches and soils

Desorption isotherms from the different adsorbents were obtained after herbicide adsorption at initial concentrations of 25 mg L^{-1} (Fig. 1). They fit the Freundlich equation with r^2 values ranging from 0.88 to 0.99 for SMOC; 0.61–0.91 for FORAM, and 0.47–0.93 for TCM. The K_{fd} and n_{fd} parameters determined from this equation are shown in Tables 4–6. A poor fit was observed for FORAM desorption from MM1 and S1 + MM1 ($r^2 = 0.61$–0.66) due to a very fast initial desorption followed by the non-desorption of the herbicide (Fig. 1, Table 5). In addition, non-desorption isotherms were observed for M2 and M3 for the initial total desorption, and in S1 as result of the non-adsorption of the herbicide by this soil (Fig. 1, Table 5). A poor fit to the Freundlich desorption equation for TCM was observed solely for S2 + MM1 ($r^2 = 0.47$) (Table 6).

All the isotherms exhibited hysteresis to a greater or lesser extent because desorption data did not coincide with the adsorption isotherms (Fig. 1). The hysteresis coefficients (H) were always higher than one for SMOC, recording greater irreversibility (higher H values, lower desorption) of the adsorption by soils, especially by unamended ones, than by mulches (Table 4). Other authors have also reported a higher irreversibility of SMOC adsorption in soils amended with fresh by-products from olive oil extraction compared to the corresponding unamended soil (Cañero et al., 2015; Peña et al., 2019). The H values obtained for the desorption of SMOC from M1, M2, and M3 were similar, although an increase in irreversibility could be expected, as reported by Aslam et al. (2013) for the adsorption of SMOC by maize mulch at a later stage of decomposition. Possible changes in the functional groups of mulch in our study were not relevant (Table 2) compared to those registered by Aslam et al. (2013) for maize mulch maintained under more extreme laboratory conditions (28 °C and soil humidity at field capacity) or in the field (up to 300 days). Under these conditions, Aslam et al. (2013) have reported a negative correlation between the O-alkyl-C groups of mulch after decomposition and the irreversibility of SMOC adsorption. However, this study has found a significant positive correlation between O-alkyl-C groups ($r = 0.990$, $p < 0.05$) of mulches and the H coefficients of SMOC, and a negative correlation with the alkyl-C groups ($r = -0.956$, $p < 0.05$). García-Delgado et al. (2020) have also described an enhanced hysteresis of the adsorption of herbicides with contrasting solubility and hydrophobicity properties in soils amended with different organic residues due to the abundance of O-alkyl (and N-alkyl) groups in these organic amendments.

A wide range of positive and negative hysteresis was observed for the desorption isotherms of FORAM and TCM from the different adsorbents (Table 5), although no correlation could be established between H coefficients and functional groups of mulch OC due to the few H observations. Gul et al. (2020) have also reported hysteresis for TCM in the adsorption-desorption experiment conducted on unamended soils with H values ranging from 0.6 to 1.9.

The K_{fd} values ranged between 3.39 and 65.1 for SMOC desorption from the different adsorbents, and between 0 and 26.3 for FORAM (excluding S1, M1, and M2 because of the absence of desorption isotherms), and they were significantly higher ($p < 0.05$) for mulches than for soils (unamended and amended). A lower hydrophobicity and/or higher solubility of FORAM than SMOC would explain the lower K_{fd} values determined for FORAM than for SMOC (Tables 4 and 5). The K_{fd} values of SMOC varied in the same direction as the K_f adsorption constants for unamended and amended soils, although not for mulches (S1 < S2 < S1 + MM1 < S2 + MM1 < < M1 < MM1 < M3 ≈ M2). Aslam et al. (2013) have observed a clear decrease in the desorption of SMOC after mulch (maize) decomposition due to greater irreversibility, as previously indicated. TCM showed intermediate K_{fd} values (0.19–7.65) to those determined for SMOC and FORAM when the herbicides were desorbed from unamended and MM1-amended soils. As regards mulches, MM1 recorded a very high K_{fd} value ($= 135$), while it was 0 for M2 and M3, corresponding to a total desorption of the amount of herbicide initially adsorbed (Table 6). However, it should be noted that the TCM 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 desorption step (no desorption isotherm), and second, and third ones, respectively (Fig. 1). This behaviour seems to be related to the loss of DOC content in the mulches following their decomposition (Table 1).

3.3. Influence of mulch, soil, and herbicide properties on the adsorption-desorption of herbicides

The simple correlation coefficient (r) revealed the existence of a highly significant positive correlation between the K_f and K_d adsorption constants of the most hydrophobic herbicide (SMOC) and the OC or N content of the mulches, and unamended and MM1-amended soils (Table 7). The correlation with N content was derived from its significant correlation with OC ($p < 0.01$). Based on the determination coefficient, r^2, OC accounted for 94.3 % or 87.2 % of the variance in the adsorption of SMOC 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 (Peña et al., 2019; Sharipov et al., 2021). In turn, non-significant correlations were observed between the K_f and K_d values and the functional OC groups in the mulches (Table 2) ($p > 0.1$, data not shown) indicating that the OC content was more important than its actual nature. It was also confirmed by the CVs of the K_{foc} and K_{doc} values, which were lower than those for the K_f and K_d parameters (Table 4).

In addition, a significant ($p < 0.05$) or highly significant ($p < 0.001$) positive correlation was also observed between K_f and K_d values and the DOC contents of the adsorbents, respectively, and a significant ($p < 0.05$) negative correlation was determined between the adsorbents' pH and SMOC K_d values (Table 7). These results are consistent with previous studies reporting an increase in the adsorption of SMOC by amended soils with a high DOC content in solution (Marín-Benito et al., 2021; Singh, 2003) or a decrease in adsorption with pH for agricultural soils cultivated with different conservation tillage systems (Alletto et al., 2013).

The results indicate that both OC and DOC are the main variables involved in the adsorption of SMOC by the different adsorbents, with OC content explaining the higher variability of K_f values ($r^2 = 94.3$ %) than DOC (68.9 %), and the opposite effect explaining the variability of K_d values (97.6 % by DOC vs. 87.2 % by OC). In some cases, an adjusted R^2 coefficient higher than the simple correlation coefficient was obtained when the results were subject to multiple linear regression analysis by combining two or more adsorbent properties to determine their relative importance when they vary simultaneously (Table 8). A highly significant relationship ($p < 0.001$) was found between the K_d adsorption constant and the variables OC and DOC. The coefficient of determination, $R^2 = 97.8$ %, accounts for a slightly higher percentage of variance in the K_d than that explained when the OC or the DOC content of the adsorbents is individually considered as the responsible variable. A highly significant relationship ($p < 0.001$) was also found between the K_f adsorption constant and the variables OC and DOC (Table 8), although its R^2 value (93.8 %) explained a lower percentage of the variability in K_f than that explained by the OC as the single variable (94.3 %).

A very significant positive correlation ($p < 0.01$) was also observed between the adsorption of FORAM at high concentrations of herbicide in solution (K_d) and mulch and soil OC content (Table 7), while a non-significant relationship was determined at low herbicide concentrations (K_f). Some studies also reported that the adsorption of sulfonylurea herbicides is positively correlated with adsorbent OC content (Grey and

McCullough, 2012; Pavão et al., 2021). The OC content accounts for a lower percentage of variance in the adsorption of K_d (71.1 %) than that of SMOC, suggesting that other mulch and soil parameters may influence the adsorption of this non-hydrophobic herbicide. This is consistent with the considerable variability in the K_{foc} and K_{doc} values (CV = 125 % and 118 %, respectively) (Tables 5), indicating that the nature of mulch and soil OC plays a more important role in the adsorption of FORAM than indicated previously for SMOC. In fact, both positive and negative relationships were respectively observed between K_f or K_d values and N-alkyl-C and aromatic-C groups of mulch OC, although they did not become significant (data not shown).

A significant positive correlation ($p < 0.05$) was also found between FORAM K_d values and the DOC content of the adsorbents (Table 7). However, the combination of OC and DOC variables did not improve the explanation of the K_d variability (60.2 %) compared to that explained by the OC content as a single variable (71.1 %). No relationship was found between FORAM adsorption constants (K_f and K_d) and adsorbent pH in keeping with data from EFSA (2016). The opposite effects have been observed for other sulfonylurea herbicides. Delgado-Moreno and Peña (2008) have reported that the adsorption of bensulfuron-methyl, chlorsulfuron, and prosulfuron by unamended and amended soils was affected mainly by the pH of the soil solution, with the OC content having no significant effect on herbicide retention. However, in most cases, sulfonylurea adsorption is greater in soils with a low pH and high OC content (Grey and McCullough, 2012; Kumari et al., 2020; Pavão et al., 2021).

Despite the low hydrophobicity of TCM, a significant ($p < 0.05$) and a very significant positive correlation ($p < 0.01$) was also observed between the adsorption of this herbicide (K_f and K_d) and adsorbent OC content, respectively (Table 7). However, the OC content accounts for a lower percentage of variability in the adsorption of TCM by mulches and soils (K_f, 68.3 %) than for SMOC (94.3 %) or FORAM (71.1 %). As previously indicated, other mulch and soil parameters may influence the adsorption of this other non-hydrophobic herbicide (Tables 4 and 6). This is also confirmed by the higher CV of the K_{foc} values compared to the K_f values, suggesting that the nature of mulch and soil OC plays a more important role than their OC content in the adsorption of TCM. Within this context, there was a positive relationship between the N-alkyl-C and aromatic-C groups of mulches and the K_f values of TCM, although it was non-significant (data not shown). Therefore, a statistically non-significant correlation was found between the K_f or K_d values of the three herbicides studied and the functional groups of OC in mulches. However, other authors have observed this type of correlation in pesticide adsorption studies on different organic residues or mulches (Aslam et al., 2013; Cassigneul et al., 2015; García-Delgado et al., 2020).

A significant positive correlation ($p < 0.05$) was also determined between TCM K_f values and the DOC content of the adsorbents (Table 7), but the combination of the variables OC and DOC of mulches and soils explained a higher percentage (92.6 %) of the K_d variability for TCM compared to that explained individually by the OC (71.1 %) (Tables 7 and 8). According to EFSA (2013), no correlation was found between TCM adsorption constants (K_f and K_d) and adsorbent pH.

The OC and DOC variables were also involved in the desorption of SMOC according to a very significant ($p < 0.01$) or highly significant

Table 8
Best 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 (organic carbon, OC; and dissolved organic carbon, DOC).

Constant/herbicide	Regression equation	p	R^2
K_f/S-metolachlor (n = 8)	$-1.144 \pm 3.662 + (1.471 \pm 0.269)\,\%OC - (1.330 \pm 1.093)\,\%DOC$	<0.001	0.938
K_d/S-metolachlor (n = 8)	$-1.488 \pm 2.468 + (0.309 \pm 0.181)\,\%OC + (4.430 \pm 0.740)\,\%DOC$	<0.001	0.978
K_{fd}/S-metolachlor (n = 8)	$0.998 \pm 1.908 + (1.530 \pm 0.140)\,\%OC - (0.747 \pm 0.569)\,\%DOC$	<0.001	0.987
K_f/foramsulfuron (n = 8)	$-3.668 \pm 3.378 + (1.169 \pm 0.248)\,\%OC - (3.490 \pm 1.010)\,\%DOC$	0.011	0.773
K_d/foramsulfuron (n = 8)	$-7.170 \pm 16.445 + (1.496 \pm 1.207)\,\%OC + (1.420 \pm 4.910)\,\%DOC$	0.043	0.602
K_{fd}/foramsulfuron ($n = 5$)	$-4.113 \pm 6.460 + (1.565 \pm 1.280)\,\%OC - (7.463 \pm 8.359)\,\%DOC$	0.223	0.554
K_f/thiencarbazone-methyl (n = 8)	$0.176 \pm 0.148 + (0.019 \pm 0.011)\,\%OC - (0.015 \pm 0.044)\,\%DOC$	0.050	0.566
K_d/thiencarbazone-methyl (n = 8)	$-2.564 \pm 1.897 + (0.794 \pm 0.139)\,\%OC - (1.102 \pm 0.566)\,\%DOC$	<0.001	0.926
K_{fd}/thiencarbazone-methyl (n = 5)	$0.328 \pm 7.035 - (1.307 \pm 1.827)\,\%OC + (33.76 \pm 13.10)\,\%DOC$	0.014	0.972

($p < 0.001$) positive correlation between these variables and the K_{fd} of SMOC, respectively (Table 7). However, by combining both variables the multiple linear regression model (Table 8) explained the similar variability of K_{fd} (98.7 %) compared to OC content (98.8 %). No simple or combined correlation was found for FORAM between the K_{fd} values and OC and/or DOC content of the adsorbents (Tables 7 and 8), but a highly significant positive correlation ($p < 0.001$) was found for TCM between K_{fd} desorption constants and the OC and DOC content from MM1, and unamended and MM1-amended soils (Table 7). It should be noted, however, that DOC content explained a higher variability in K_{fd} values ($r^2 = 98.2$ %) than OC (94.1 %) or even the combination of both variables (97.2 %) (Table 7). The DOC content of adsorbents was therefore the main variable controlling TCM desorption, whereas it was OC content for SMOC. A positive, albeit non-significant, relationship was found for TCM (because of the few samples) between the aromatic-C or N-alkyl-C groups in mulches and the K_{fd} values, but not for SMOC and FORAM (data not shown).

A multiple linear regression analysis was also carried out combining the two most significant absorbent variables involved in the adsorption-desorption processes (OC and DOC) and herbicide characteristics (water solubility- S_w - and hydrophobicity-K_{ow}) to evaluate the relative importance of mulch, soil, and herbicide parameters on the adsorption of the compounds studied. A highly significant multiple linear regression ($p < 0.001$) was obtained between the K_f or K_d adsorption and K_{fd} desorption constants and the K_{ow} of the herbicides and the OC content of adsorbents when jointly considering all the herbicides and adsorbents ($n = 24$). The R^2 statistic revealed that 62.7 % of the variability in the K_f values could be explained by the combination of K_{ow} and OC according to Eq. (1), while the R^2 statistic showed that 61.3 % of the variability in the K_d could be explained by the herbicide S_w and the OC content of adsorbents according to Eq. (2):

$$K_f = (-0.869 \pm 3.893) + (5.452 \pm 1.143)\, K_{ow} + (0.527 \pm 0.124)\%OC \tag{1}$$

$$K_d = (-13.243 \pm 7.761) + (0.006 \pm 0.003)\, S_w + (1.218 \pm 0.207)\%OC \tag{2}$$

For the desorption process, Eq. (3) reveals a highly significant ($p < 0.001$) relationship between the K_{fd} desorption constants ($n = 18$), the S_w of the herbicides, and the OC content of the adsorbents for a confidence level of 95 %.

$$K_{fd} = (9.567 \pm 9.136) - (0.009 \pm 0.004)\, S_w + (1.411 \pm 0.279)\%OC \tag{3}$$

The R^2 statistic shows that this equation explains 62.1 % of the variability in the K_{fd} of the herbicides.

Previous adsorption studies involving pesticides and organic residues with contrasting properties have also reported the relevance of the K_{ow} of pesticides and the OC content of adsorbents together with their polarity index for predicting the adsorption capacity of the organic residues tested (García-Delgado et al., 2020; Marín-Benito et al., 2012).

3.4. Mulching vs. organic soil amendment as a strategy for supporting eco-friendly agricultural practices

Fig. 2 includes adsorbed amounts expressed as percentages of herbicide (SMOC, FORAM, or TCM) in aqueous solution at an initial concentration of 25 μg mL^{-1}, and the residual amounts adsorbed after desorption (four steps) expressed as percentages of the herbicide adsorbed by the mulches, and unamended and MM1-amended soils as adsorbents to compare the real impact of using cover crop residues as mulches or as soil organic amendment on the adsorption of herbicides studied.

The hydrophobic herbicide SMOC recorded residual amounts <10 % after its desorption from the mulches M1, M2, and M3. However, no
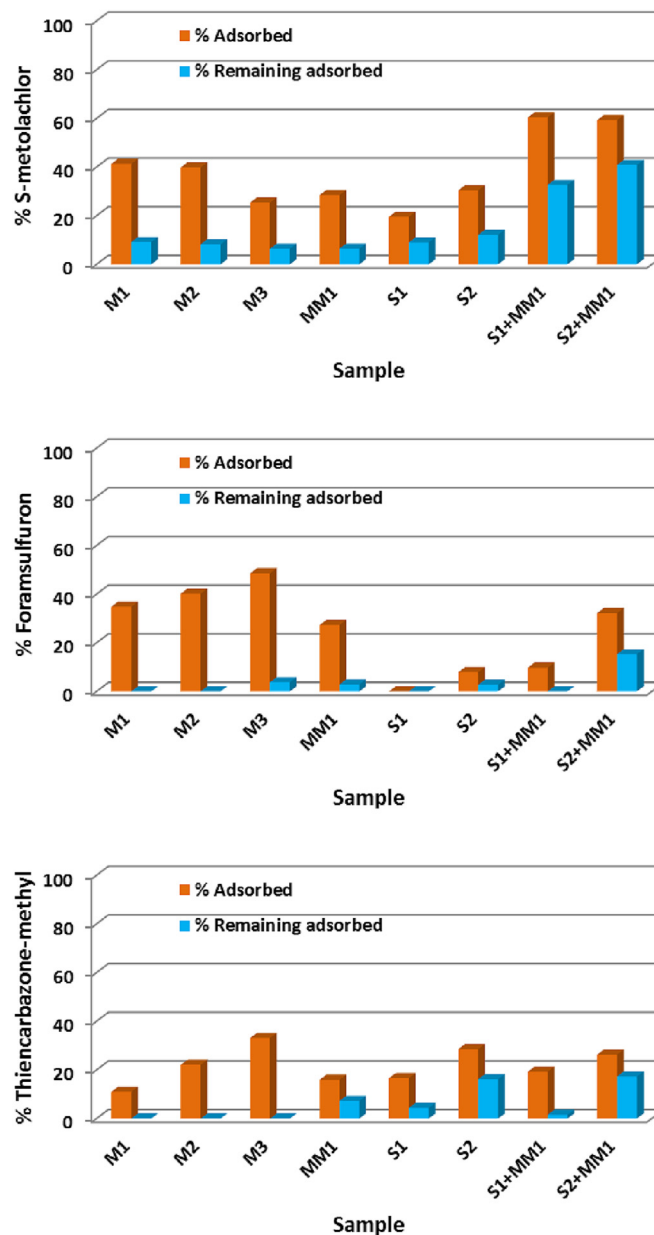

Fig. 2. Adsorbed amounts expressed as percentages of herbicide (S-metolachlor, foramsulfuron or thiencarbazone-methyl) in aqueous solution at an initial concentration of 25 μg mL^{-1}, and the residual amounts adsorbed after desorption (four steps) expressed as percentages of the herbicide adsorbed by the mulches (M1, M2, M3 and MM1), unamended (S1 and S2) and MM1-amended soils (S1 + MM1 and S2 + MM1).

residual amounts of the non-hydrophobic herbicides FORAM or TCM were found in the three mulches except for a low percentage (3.8 %) of FORAM in M3 after four successive desorption steps. These results indicate that the real influence of mulching on the adsorption of these non-hydrophobic herbicides, and consequently on their fate, would be negligible at field scale under precipitation events or under irrigation practices. The wash off of these non-hydrophobic herbicides intercepted by the mulch during their application is totally or almost totally independent of the mulch's decomposition stage. This preserves the agronomic efficacy of the herbicides, although it could lead to a possible risk of water pollution (Alletto et al., 2012; Sperry et al., 2022).

The application of SMOC on mulch with various stages of decomposition involved a residual amount (6.45 %–9.1 % of the initial application)

because total desorption did not occur. This means the choice of the timing of SMOC application in real field conditions in the presence of mulch is crucial from an environmental and agronomic perspective. A positive decrease in its leaching risk would be noted because of its variable adsorption of the amount initially applied (Fig. 2), but also an undesirable loss of herbicide due to a lack of desorption by the mulch. Aslam et al. (2013) have also reported residual amounts of absorbed SMOC (24 %–38 %) in maize mulch at various and higher stages of decomposition than those considered here. It should be noted that the timing and quantity of precipitation or irrigation could be also critical for the wash off of herbicides from the mulch. Aslam et al. (2015) observed that the leaching of SMOC in soil columns covered by mulch and under two different simulated rainfall (light but frequent rainfall and a less frequent but more intense rainfall) was controlled by the rainfall regime.

The application of MM1 as an organic soil amendment recorded an increasing amount of the three herbicides remaining adsorbed in S2. After the entire desorption process, the residual amounts in S2 + MM1 increased up to 3.4 times for SMOC, 5.6 times for FORAM, and 1.1 times for TCM compared to unamended S2. However, this increase was found solely for the most hydrophobic herbicide, SMOC, in S1 + MM1 (up to 3.6 times). The amendment of soils with organic residue materials has frequently been cited in the literature as a potential strategy for preventing the point pollution of soils and waters by pesticides (Álvarez-Martín et al., 2016; García-Delgado et al., 2020; Marín-Benito et al., 2016). Nevertheless, MM1 was not an effective adsorbent for herbicides with a high solubility in water and/or a low hydrophobicity when used as an organic amendment in soils with a low natural OC content. Other organic residues assessed as adsorbents for environmental purposes have proven more effective for different pesticides than those obtained for MM1 here (García-Delgado et al., 2020; Karanasios et al., 2010; Marín-Benito et al., 2012). Some authors, however, have also observed that the beneficial environmental impact of organic residues as soil amendment could be limited under field conditions or similar in presence of preferential macropore flow in soil (Dollinger et al., 2022) or rainfall events shortly after the pesticides' application (Carpio et al., 2020) since these processes may minimize the retention of pesticides by organic residues and favour their leaching.

4. Conclusions

The study focuses on the impact of winter wheat mulch residues with low stage of decomposition and different particle size, together with the use of milled mulch as organic soil amendment on the adsorption-desorption processes of the herbicides SMOC, FORAM, and TCM. A significant and positive impact on the adsorption of SMOC and FORAM by the mulch after its decomposition and on the adsorption of FORAM and TCM after milling was found. The OC and/or DOC content of the adsorbents controlled the adsorption and/or desorption of each herbicide, and the OC content of mulches and soils explained the variability in K_f, K_d and K_{fd} values when the three herbicides were considered jointly. Herbicide hydrophobicity expressed as K_{ow} was involved in the variability of the K_f adsorption constant, being replaced by the water solubility of the herbicides when K_d and K_{fd} were the constants analysed. Although the K_f and K_d values of the three herbicides were higher for the mulches than for the soils (unamended and amended), this was an apparent adsorption, as the K_{fd} values generally followed the same trend as the adsorption constants. The real impact, therefore, was a higher amount of herbicide remaining adsorbed by the amended soils than by the mulches once the desorption experiment had been completed. As a result, the net balance of the mulches on the herbicide adsorption-desorption process could be defined as a delay in the time that the compounds need to reach the soil surface, with this delay depending on the precipitation and/or irrigation recorded after the application of the herbicides and their interception by the mulches. Accordingly, winter wheat mulch residues used as organic soil amendments may be a better strategy than their disposal on the soil surface for avoiding groundwater contamination by the herbicides applied in scenarios with frequent precipitation or under irrigated conditions. Nevertheless, future researches on

herbicides dissipation and leaching would be necessary in order to determine the effectiveness and viability of these techniques.

CRediT authorship contribution statement

Marwa Douibi: Investigation. **Akhil Krishtammagari:** Investigation. **María J. Sánchez-Martín:** Validation, Formal analysis, Resources, Writing – original draft, Writing – review & editing. **M. Sonia Rodríguez-Cruz:** Resources, Writing – review & editing. **Jesús M. Marín-Benito:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Data availability

The data that has been used is confidential.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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