



Tillage management effects on pesticide fate in soils. A review

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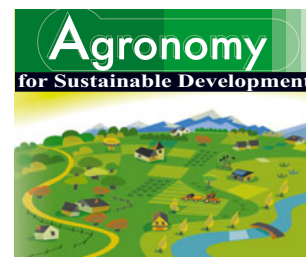
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Review article

Tillage management effects on pesticide fate in soils. A review

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Abstract – Reducing tillage intensity through the implementation of conservation practices is a way to reach a more sustainable agriculture. Reducing tillage is indeed an efficient way to control soil erosion and to decrease production costs. Nonetheless, the environmental impact of reduced tillage is not well known because conservation techniques may induce strong changes in soil physicochemical properties and biological activity. Knowledge on the fate of applied pesticides under conservation practices is particularly important from this point of view. We review here the advances in the understanding, quantification and prediction of the effects of tillage on pesticide fate in soils. We found the following major points: (1) for most dissipation processes such as retention, degradation and transfer, results of pesticide behaviour studies in soils are highly variable and sometimes contradictory. This variability is partially explained by the multiplicity of processes and contributive factors, by the variety of their interactions, and by their complex temporal and spatial dynamics. In addition, the lack of a thorough description of tillage systems and sampling strategy in most reports hampers any comprehensive interpretation of this variability. (2) Implementation of conservation tillage induces an increase in organic matter content at the soil surface and its gradual decrease with depth. This, in turn, leads to an increase in pesticide retention in the topsoil layer. (3) Increasing retention of pesticides in the topsoil layer under conservation tillage decreases the availability of the pesticides for biological degradation. This competition between retention and degradation leads to a higher persistence of pesticides in soils, though this persistence can be partially compensated for by a more intensive microbial activity under conservation tillage. (4) Despite strong changes in soil physical properties under conservation tillage, pesticide transfer is more influenced by initial soil conditions and climatic conditions than by tillage. Conservation tillage systems such as no-tillage improve macropore connectivity, which in turn increases pesticide leaching. We conclude that more knowledge is needed to fully understand the temporal and spatial dynamics of pesticide in soil, especially preferential flows, in order to improve the assessment of pesticide risks, and their relation to tillage management.

conventional tillage / conservation tillage / herbicide / retention / degradation / transport / soil carbon

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1. INTRODUCTION

Tillage can be defined as any mechanical operation on the soil and crop residues that aims at providing a suitable seedbed where crop seeds are sown. Soil preparation has always been an important component of traditional agriculture. Since 6000 BC, a wide variety of farming tools have been developed, from the simple digging stick to the paddle-shaped spade that could be pulled by humans or animals (Lal et al., 2007). In the 18th century, the mouldboard plough, a curved board that cuts and rotates the soil at a significant working depth, of more than 20 cm, was introduced in England. This tool was particularly efficient in incorporating organic residues, fertilisers and lime, in controlling weeds and helping the growing process. In the early part of the 19th century, the “initial” model of the mouldboard plough received several improvements to reach its “standardised” version by 1870, similar to current models (Hanson, 2006; Lal et al., 2007).

In the United States, between 1910 and 1930, the use of the mouldboard plough widely expanded, especially in the Great Plains of the Middle West. In Europe, its use started to be significant after 1945. These changes in tillage practices were accompanied by significant progresses in seed selection and by the development of the use of chemicals for plant protection, allowing a significant increase in crop yields. For example, wheat yields in France increased from 0.8–1 tons per hectare in 1945 to more than 8 tons in 1985. Because of its success, the mouldboard plough became a centrepiece of traditional agriculture.

In parallel with this growth of agricultural production, the widespread use of the mouldboard plough led to severe problems of soil and environmental degradation. One of the most well-known environmental problems was the drastic increase in wind erosion known as the “Dust Bowl” in 1930 in the US Great Plains (Lal et al., 2007; Masutti, 2004). Faced with this major problem, depriving some areas of any production capacity, the American reaction was swift. In 1935, the Soil Conservation Service – now called the Natural Resources Conservation Service – was created within the United States Department of Agriculture. Many important research programmes and communication efforts aimed at promoting the adoption of soil conservation techniques, grouped under the term “conservation tillage”. These techniques are defined as any tillage and planting system that leaves at least 30% of the soil surface covered by crop residue after planting to reduce soil erosion by water, or at least 1.1 tons of crop residue/ha to reduce soil erosion by wind. A broad spectrum of farming methods can thus be classified as conservation techniques: from tillage techniques with a high working depth, such as sub-soiling, to reduced tillage of 0–15 cm or direct drilling techniques without any preliminary soil tillage, called “no-

surfaces sown without ploughing (%)

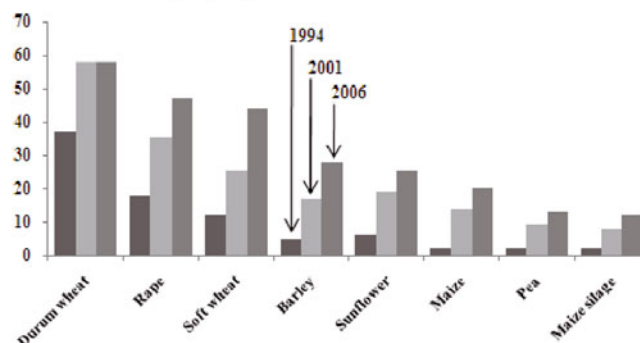


Figure 1. Evolution of cultivated surfaces without ploughing in France between 1994 and 2006. Whatever the crop, the trend is an increase of surfaces cultivated without ploughing and winter crops are more often sown without ploughing than spring crops (Agreste, 2004, 2008).

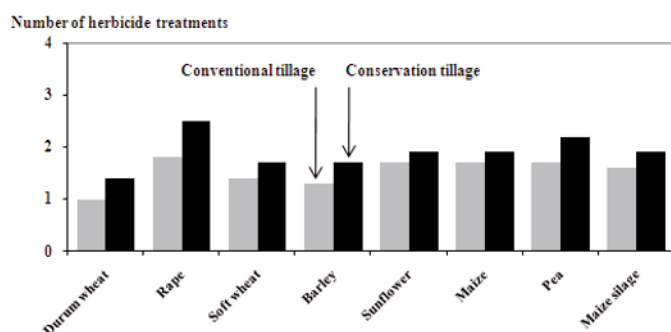
tillage”. This last type of tillage technique remained less developed until 1940 with the discovery of hormonal herbicides such as 2,4-dichlorophenoxy acetic acid (2,4D) that allowed farmers to control weeds without ploughing. Fairly quickly, these North American techniques thrived in the South American countries, particularly in Brazil where water erosion was significant (Bernoux et al., 2006), and in Argentina and Chile. Tillage practices and their codes used in this review are reported in Table I.

In Europe, because soil erosion was not as great as in the US, the interest of farmers in conservation tillage was limited. In the years 1970–1980, some attempts to develop these techniques were faced with decreases in crop yields, while, at the same time, farmers were encouraged to produce more to earn more. At the beginning of the 1990s, with the Rio conference (1992) which laid down the foundations for a sustainable agriculture, the concerns moved towards considering the vulnerability of water, soil and landscape resources. Moreover, the emergence of agricultural product surpluses led to lower prices. The control by farmers of their income more than ever implied lower production costs and a further increase in productivity, especially as the size of farms expanded. Under this economic context, soil conservation tillage, deemed to be faster and less costly in time and energy than conventional tillage, finally started to become attractive.

Progressively, surfaces sown in France without ploughing increased for all crops (Fig. 1). Spring crops are, however, more frequently sown after ploughing than winter crops. Moreover, the development of conservation techniques varies according to the regions. For example, in the south-west part of France – Aquitaine and Midi-Pyrénées regions –, more than

Table I. Tillage practice types used in this review article.

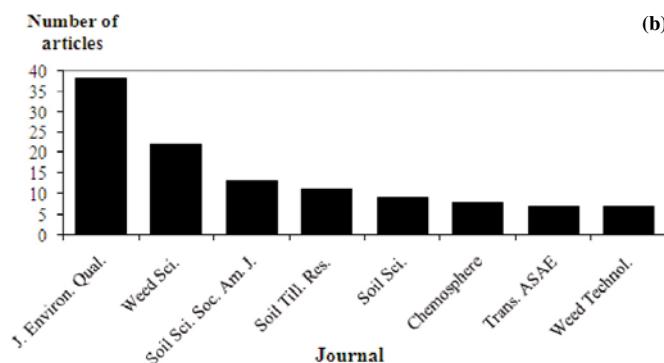
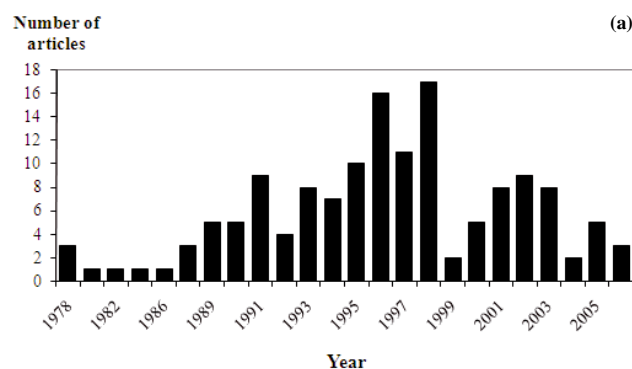
Code	Tillage practice	% soil surface covered by crop residues [†]	Agricultural tool
CT	Conventional tillage	< 30% (0–10%)	Mouldboard plough Disk plough Spading machine
CnT	Conservation tillage		
MT _{Dk}	Mulch tillage	> 30% (30–50%)	Disk harrow
MT _{Ch}	Mulch tillage	> 30% (30–50%)	Chisel plough, harrow...
SS	Sub-soiling	> 30% (30–60%)	Sub-soiler, deep ripper, paratill
RT	Ridge tillage	> 30% (40–60%)	Ridger
ST	Strip tillage	> 30% (40–60%)	Strip-till
NT	No-tillage (or direct drilling)	> 50% (depending on crop residues)	Seeding drill (with disc openers)

[†] (CTIC, 2006).**Figure 2.** Mean number of herbicide treatments applied in 2006 for several crops sown after ploughing (conventional tillage) or without ploughing (conservation tillage). Note the systematic increase of herbicide treatments with the implementation of conservation tillage (Agreste, 2004, 2008).

75% of the wheat surfaces were not ploughed in 2006 against 50% in the whole country (Agreste, 2008).

One of the main roles of tillage is to provide an efficient control of weeds. Indeed, tillage influences weed populations by the combined effects of mechanical destruction of weed seedlings and by changing the vertical distribution of weed seeds in soil (Peigné et al., 2007). It also changes the soil climatic conditions which control weed dormancy, germination and growth. Reducing tillage intensity generally tends to increase the concentration of weeds in the topsoil (Moonen and Barberi, 2004; Torresen et al., 2003; Vasileiadis et al., 2007) and is very often associated with an increase in herbicide use (Fig. 2).

Although many studies have been conducted, mainly on the North American continent, the environmental fate of pesticides under conservation tillage presents many contradictions and remains, finally, poorly understood (Aubertot et al., 2005; Réal et al., 2007). Publication of articles concerning the effects of tillage practices on pesticide fate in soils, water and air started slowly during the 1970s and showed a rapid increase at the end of the 1980s followed by a peak rate of publication at the end of the 1990s (Fig. 3a). One-third of the published articles were found in one journal, and the first three journals were from the US, illustrating the great interest of US scientists in this subject (Fig. 3b).

**Figure 3.** Articles published on the effects of tillage practices on pesticide fate in soils, water and air. (a) Time series of articles found per year; and (b) major source journals found in (a). The plot includes the top 8 journals representing 115 articles out of the 144 references cited in the review.

Reducing tillage intensity leads to significant and complex changes in soil physical, chemical and biological properties, most often interrelated with each other, thus affecting the fate of the applied pesticides. A first review, conducted by Locke and Bryson (1997), dealt with herbicide interactions in soils under plant residue-managed farming systems. Following their work, we sought to assess the current state of knowledge of the effects of tillage on the processes involved in the fate of pesticides in soils cultivated with arable crops. Figure 4 summarises

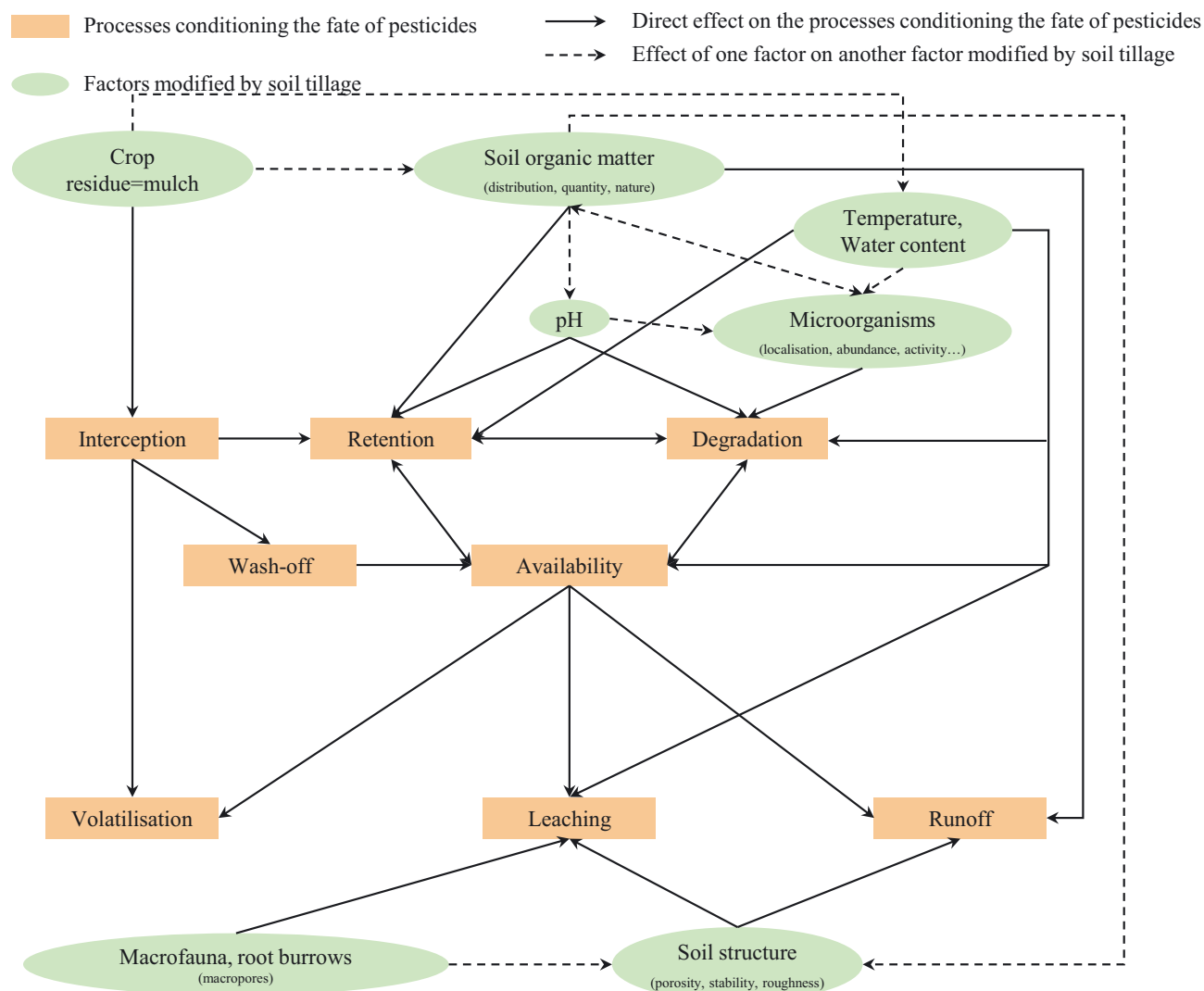


Figure 4. Relationships between the processes conditioning the fate of pesticides in soils, water and air and the soil factors modified by tillage operations.

the main changes in soil properties due to tillage practices and their effects on the mechanisms involved in pesticide fate. As shown in this figure, understanding the effects of tillage on pesticide fate in soils implies a comprehensive evaluation of all the interactions between the different dissipation processes and of all the different soil factors affected by tillage operations. Some of these interactions are now well known, but most of them are still poorly understood. In this review, for each of these processes, we paid particular attention to the understanding of the mechanisms involved, their relative importance and the origin of the contradictory results found. The lists of the molecules, mainly herbicides, mentioned in this review are shown in Table II.

2. INTERCEPTION – RETENTION

Pesticide interception depends on several factors such as the type of application (pre- or post-emergence), the presence of a

crop and, if any, plant growth stage and species, the presence of a mulch, etc. Because interception of pesticides by plant foliage and its effect on the environment have not been widely studied (Reddy and Locke, 1996), the subject developed in this part focuses mainly on the interception and retention by the mulch and by the soil. In some cases, due to the difficulty of formally separating interception and retention, these processes are discussed simultaneously.

2.1. Mulch effect

The accumulation of organic residues on soil surface (mulch) in conservation tillage generally leads to an increase in the interception of applied pesticides, more particularly for apolar pesticides or pesticides with a low polarity (Locke, 1992; Novak et al., 1996; Reddy and Locke, 1998; Reddy et al., 1997a, b; Zablotowicz et al., 2000). This interception

Table II. Chemical and common names for pesticides mentioned in this review.

Common name	Nature	Chemical name
Acetochlor	Herbicide	2'-ethyl-6'-methyl- <i>N</i> -(ethoxymethyl)-2-chloroacetylanilide
Acifluorfen	Herbicide	5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid
Alachlor	Herbicide	2-chloro- <i>N</i> -(2, 6-diethylphenyl)- <i>N</i> -(methoxymethyl)acetamide
Atrazine	Herbicide	(6-chloro- <i>N</i> -ethyl)- <i>N'</i> -(1-methylethyl)-1,3,5-triazine-2,4-diamine
Bentazone	Herbicide	3-isopropyl-1 <i>H</i> -2,1,3-benzonthiadiazain-(4) <i>3H</i> -one 2,2-dioxide
Carbofuran	Insecticide	2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate
Chlorimuron	Herbicide	Ethyl-2-[[[4-chloro-6-methoxy-2-pyrimidinyl]amino]carbonyl]amino[sulfonyl]benzoic acid
Clomazone	Herbicide	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone
Clopyralid	Herbicide	3,6-dichloropicolinic acid
Chlorpyrifos	Insecticide	<i>O</i> , <i>O</i> -diethyl- <i>O</i> -(3,5,6-trichloro-2-pyridyl) phosphorothioate
Cyanazine	Herbicide	2-4-chloro-6-(ethylamino) 1,3,5-triazin-2-yl]amino-2-methylpropanenitrile
Diazinon	Insecticide	<i>O</i> , <i>O</i> -dimethyl <i>O</i> -2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate
Dicamba	Herbicide	3,6-dichloro-2-methoxybenzoic acid
Diclofop	Herbicide	(±)-2-(4-(2,4-dichlorophenoxy)phenoxy)propanoic acid
Diclosulam	Herbicide	<i>N</i> -(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-(1,2,4)triazolo(1,5- <i>c</i>)pyrimidine-2-sulfonamide
Diketonitrile	Herbicide	2-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-3-oxopropanenitrile
Dimethipin	Defoliant	2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide
Fluometuron	Herbicide	<i>N,N</i> -dimethyl- <i>N'</i> -[3-(trifluoromethyl)-phenyl]-urea
Fonofos	Insecticide	<i>O</i> -ethyl <i>S</i> -phenyl ethylphosphonodithioate
Glyphosate	Herbicide	<i>N</i> -(phosphonomethyl)glycine
Imazapic	Herbicide	(<i>RS</i>)-2-(4,5-dihydro-4-isopropyl-4-methyl-5-oxoimidazol-2-yl)-5-methylnicotinic acid
Imazapyr	Herbicide	2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl)-3-pyridine carboxylic acid
Imazaquin	Herbicide	2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl]-3-quinolinecarboxylic acid
Imazethapyr	Herbicide	(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid
Isoproturon	Herbicide	3-(4-isopropylphenyl)-1,1-dimethylurea
Isoxaflutole	Herbicide	5-cyclopropyl-1,2-isoxazol-4-yl alpha alpha -trifluoro-2-mesyl-p-tolyl ketone
Linuron	Herbicide	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MCPA	Herbicide	4-chloro-2-methylphenoxy acetic acid
Metolachlor	Herbicide	2-chloro- <i>N</i> -(2-ethyl-6-methylphenyl)- <i>N</i> -(2-methoxy-1-methylethyl)acetamide
Metamitron	Herbicide	4-4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4 <i>H</i>)-one
Metribuzin	Herbicide	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2, 4-triazine-5(4 <i>H</i>)-one
Norflurazon	Herbicide	4-chloro-5(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2 <i>H</i>)-pyridazinone
Oxyfluorfen	Herbicide	2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoro-methyl) benzene
Pendimethalin	Herbicide	<i>N</i> -(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine
Propachlor	Herbicide	2-chloro- <i>N</i> -isopropylacetanilide
Simazine	Herbicide	2-chloro-4,6-bis[ethylamino]-s-triazine
Sulfentrazone	Herbicide	<i>N</i> -[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1 <i>H</i> -1,2,4-triazol-1-yl]phenyl]methanesulfonamide
Terbufos	Insecticide	<i>S</i> -(((1,1-dimethylethyl)thio)methyl) <i>O</i> , <i>O</i> -diethyl phosphorodithioate
Terbuthylazine	Herbicide	<i>N</i> -2-tert-butyl-6-chloro- <i>N</i> -4-ethyl-1,3,5-triazine-2,4-diamine
Thidiazuron	Defoliant	<i>N</i> -phenyl- <i>N</i> -1,2,3-thidiazol-5-yl-urea
Tribufos	Defoliant	<i>S,S,S</i> -tributyl phosphorotrithioate
2,4 D	Herbicide	(2,4-dichlorophenoxy)acetic acid
2,4-Dichlorophenol	Herbicide precursor	2,4-Dichlorophenol

depends on the amount and type of crop residues and, for example, with a proportion $\geq 30\%$ of the soil surface covered, it was found to range from 40 to 70% of the applied dose for several preemergence herbicides (Banks and Robinson, 1982; Ghadiri et al., 1984; Isensee and Sadeghi, 1994; Sadeghi and Isensee, 1997). In terms of mass of residues, for a quantity $> 4.5 \text{ t ha}^{-1}$, the interception of acetochlor, alachlor and meto-

lachlor was higher than 90% of the applied doses (Banks and Robinson, 1986). Retention processes are closely associated with the interception of pesticides. Indeed, crop residues can have sorption capacities 10 to 60 times higher than soil (Boyd et al., 1990; Reddy et al., 1995b) and can significantly modify the (bio)availability and the migration of pesticides in soil. As a result, a loss of efficacy of some pesticides has been

observed (Erbach and Lovely, 1975; Mills et al., 1989; Shelton et al., 1998) which can lead to an increase in the applied doses (Shelton et al., 1998; Worsham, 1991). By penetrating inside crop residues, most of the molecules are physically entrapped within cell wall structures, such as cellulose microfibrils embedded in a lignin-hemicellulose matrix (Dao, 1991) and, most often, lose their activity.

The nature and decomposition degree of crop residues both influence interception and retention of pesticides, but in contrasted ways depending on studies. For example, hairy vetch (*Vicia villosa* Roth) residues had a higher retention for chlorimuron than rye (*Secale cereale* L.) residues (Reddy et al., 1995) and a higher retention for fluometuron than wheat (*Triticum aestivum* L.) residues (Gaston et al., 2001) (Tab. III). This greater sorption by vetch than rye or wheat residues may be related to differences in physical state, that offered a greater surface area for herbicide sorption in the case of the vetch, and in composition of the residues that contained less cellulose and more amino acids (Gaston et al., 2001). Sigua et al. (1993) indicated that interception of atrazine was enhanced with fresh maize residues, due to a combination of a greater hydrophobicity and a higher sorption capacity of the fresh compared with the aged maize residues. In contrast, with metribuzin (Dao, 1991), chlorimuron (Reddy et al., 1995b) and cyanazine (Reddy et al., 1997a), interception was higher with aged residues. In these cases, the increase in sorption due to aging was attributed to both changes in the physical state and in the chemical composition of the crop residues. On one hand, physical alterations of the residues increase their external surface area for herbicide sorption compared with fresh residues. On the other hand, the chemical evolution of the residues during degradation leads to an increase in the lignin/cellulose ratio, resulting in an increase in the sorption of chlorimuron and metribuzin (Dao, 1991; Reddy et al., 1995b).

Interception is not only influenced by the amount of mulch. It is also conditioned by the formulation of the molecules. Compared with the commercial formulation, the use of microencapsulated or granular forms of alachlor led to a decrease in its interception and, finally, the herbicide reached the soil surface more rapidly (Johnson et al., 1989; Sadeghi et al., 1998).

Once intercepted by the mulch, the molecule can be washed off from the crop residues to reach the soil surface. This wash-off depends on the timing between pesticide treatment and the first rainfall and its intensity. On maize residues, Martin et al. (1978) reported a range of 30 to 60% wash-off by the first 5 mm of water for alachlor, atrazine, cyanazine and propachlor, which was equivalent to the wash-off by the next 30 mm of water. At the end of their experiment, most of the applied chemicals had been washed off from the mulch. Timing between treatment and first rainfall also strongly influences the quantity of pesticides that could be washed from the mulch. It was found to be the highest after heavy rainfall occurring within two weeks following the treatment (Sadeghi and Isensee, 1996; 1997). Depending on rainfall quantity and intensity, between 70 and 96% of intercepted atrazine were released between the 1st and 3rd weeks after treatment (Ghadiri et al., 1984; Isensee and Sadeghi, 1994). However, this wash-

off directly depends on the retention capacities of the pesticide on crop residues (Gaston et al., 2001). For example, metolachlor, once intercepted, seems to form stronger and less reversible bonds with crop residues than acetochlor or alachlor (Banks and Robinson, 1986). In some cases, a gradual release of the pesticide from the residues by wash-off may lead to an increase in its efficacy (Dao, 1991), but could also increase crop injuries (Barnes et al., 1989; Loux et al., 1989; Mills and Witt, 1991).

2.2. Organic carbon content effect

One of the main changes related to the implementation of conservation tillage compared with conventional tillage is the redistribution of organic carbon in the soil (Balesdent et al., 1990; Tebrügge and During, 1999). Generally, organic carbon content increases in surface soil due to the presence and decomposition of the mulch and gradually decreases with depth (Lal et al., 1994; Pinheiro et al., 2004; Six et al., 1999). For most pesticides, organic carbon content and adsorption are positively correlated, resulting in a higher adsorption in surface soil under conservation tillage than under conventional tillage (Tab. III). For molecules with low sorption capacity, such as bentazon (Gaston et al., 1996) or diclosulam (Lavorenti et al., 2003), the effect of tillage may not be significant. Very few studies aimed at analysing the effects of tillage on pesticide sorption kinetics. For acifluorfen (Gaston and Locke, 2000), chlorimuron (Reddy et al., 1995a) and cyanazine (Reddy et al., 1997b), no effect of tillage system was found on sorption kinetics and most of the sorption occurred during the first hour of contact. For some molecules, such as alachlor (Locke, 1992) and sulfentrazone (Reddy and Locke, 1998), sorption was faster under conservation tillage and was positively correlated with higher soil organic matter contents.

Tillage management also modifies pesticide desorption. For sulfentrazone and alachlor, whatever the tillage system, desorption was found to be hysteretic, but a greater proportion of the molecule, representing approximately 35% of the applied sulfentrazone, remained sorbed under no-tillage (against 20% under conventional tillage) (Locke, 1992; Reddy and Locke, 1998). For cyanazine (Reddy et al., 1997b), desorption was also more reversible under conventional tillage but, when ryegrass residues were added to the soil samples, desorption was similar under conventional and conservation tillage. As indicated by Locke (1992), desorption tends to decline with increasing contact time between soil and pesticide due to diffusion processes within the soil.

However, considering only the quantitative increase in organic carbon content in surface soil under conservation tillage is not sufficient to explain the increase in pesticide sorption found in some studies (Ding et al., 2002b; Novak et al., 1996; Zablotowicz et al., 2000). Although the analytical procedures used to extract soil organic matter can induce artefacts by modifying its molecular structure (Ding et al., 2002b; Salloum et al., 2001), it appears that the nature of soil organic matter

Table III. Sorption properties of pesticides under different tillage practices.

Pesticide	Tillage ¹	Depth. cm	Soil properties			K_D L kg ⁻¹	K_F $L^{n_F} \text{ mg}^{(1-n_F)} \text{ kg}^{-1}$	K_{OC} L kg ⁻¹ OC	Reference
			Clay	Organic carbon (OC) g kg ⁻¹	pH				
Acetochlor	NT CT	0-10	- -	16.6 13.3	- -	2.7 1.7	- -	166 126	(Ferri et al., 2002)
Acifluorfen	NT	0-10	-	10.2	5.6*	-	0.8	-	(Gaston and Locke, 2000)
	NT	10-20	-	5.6	5.3*	-	0.5	-	
	NT	20-30	-	4.4	5.7*	-	0.6	-	
	CT	0-10	-	8.7	5.8*	-	0.8	-	
	CT	10-20	-	6.4	5.8*	-	0.5	-	
	CT	20-30	-	4.9	5.8*	-	0.5	-	
Alachlor	NT	0-5	290	16.7	5.5*	5.4	5.6	323	(Locke, 1992)
	CT	0-5	260	10.2	5.5*	3.5	3.6	342	
Alachlor	NT	0-5	-	72.5	4.7*	-	6.0	-	(Clay et al., 1991)
	NT	5-10	-	29.0	5.0*	-	3.6	-	
	NT	10-15	-	29.5	6.2*	-	4.0	-	
	NT	15-20	-	32.5	6.4*	-	3.7	-	
	CT	0-5	-	30.0	5.5*	-	3.6	-	
	CT	5-10	-	26.0	6.0*	-	4.0	-	
	CT	10-15	-	29.0	5.2*	-	3.9	-	
	CT	15-20	-	28.0	5.7*	-	4.0	-	
Alachlore	NT + B ²	0-15	-	8.4	-	0.9	-	110	(Xue et al., 1997)
	NT + V ²		-	8.6	-	1.1	-	130	
	NT		-	6.7	-	1.0	-	143	
	CT + B		-	4.7	-	0.5	-	99	
	CT + V		-	5.7	-	0.5	-	95	
	CT		-	6.3	-	0.6	-	91	
Atrazine	NT	0-2.5	-	19.1	5.2	7.8	-	-	(Ghadiri et al., 1984)
	NT	2.5-5	-	15.1	5.0	7.1	-	-	
	NT	5-10	-	10.4	5.8	7.0	-	-	
	NT	10-15	-	10.4	6.2	7.3	-	-	
	NT	15-20	-	10.4	6.3	7.0	-	-	
	NT	20-25	-	8.1	6.5	6.2	-	-	
	NT	25-30	-	7.0	6.7	6.1	-	-	
	NT	30-35	-	6.4	6.8	6.1	-	-	
	NT	35-40	-	5.8	6.9	5.8	-	-	
	CT	0-2.5	-	12.8	5.6	7.4	-	-	
	CT	2.5-5	-	12.8	5.2	7.5	-	-	
	CT	5-10	-	11.6	5.7	7.6	-	-	
	CT	10-15	-	11.0	6.2	6.7	-	-	
	CT	15-20	-	10.4	6.3	6.5	-	-	
	CT	20-25	-	8.1	6.6	6.5	-	-	
	CT	25-30	-	7.0	6.7	6.0	-	-	
	CT	30-35	-	5.2	6.9	5.7	-	-	
	CT	35-40	-	4.7	7.0	5.5	-	-	
Atrazine	NT	0-15	-	10.6	-	1.7	-	-	(Novak et al., 1996)
	CT		-	9.8	-	1.4	-	-	
Bentazon	NT	0-10	-	10.2	5.6*	0.03	0.04	-	(Gaston et al., 1996)
	NT	10-20	-	5.6	5.3*			-	
	NT	20-30	-	4.4	5.7*			-	
	CT	0-10	-	8.7	5.8*			-	
	CT	10-20	-	6.4	5.8*			-	
	CT	20-30	-	4.9	5.8*			-	

Table III. Continued.

Pesticide	Tillage ¹	Depth. cm	Soil properties			K_D L kg ⁻¹	K_F L ^{n_F} mg ^(1-n_F) kg ⁻¹	K_{OC} L kg ⁻¹ OC	Reference
			Clay	Organic carbon (OC) g kg ⁻¹	pH				
Chlorimuron	NT	0-7.5	280	30.6	6.6*	-	1.0	31	(Reddy et al., 1995a)
	CT		250	17.8	6.4*	-	0.6	31	
	NT		330	46.0	6.2*	-	6.5	142	
	CT		260	19.2	4.5*	-	2.1	108	
	NT		-	15.3	5.4*	-	2.1	141	
	CT		-	13.1	5.7*	-	1.6	125	
Clopyralid	NT (9) ³	0-5	145	23.7	5.1	1.0	-	21	(Shang and Arshad, 1998)
	CT		145	22.7	5.8	0.3	-	2	
	NT (8)		532	47.0	4.9	1.6	-	51	
	CT		520	44.5	5.4	2.1	-	32	
Cyanazine	NT (10)	0-5	230	21.4	5.2	3.5	-	165	(Reddy et al., 1997b)
	CT		210	16.0	5.3	2.2	-	140	
Dicamba	NT (9)	0-5	145	23.7	5.1	0.2	-	13	(Shang and Arshad, 1998)
	CT		145	22.7	5.8	Undetected	-	Undetected	
	NT (8)		532	47.0	4.9	1.4	-	23	
	CT		520	44.5	5.4	1.6	-	23	
Diclosulam	NT	0-10	355	19.9	5.0*	1.9	1.8	98	(Lavorenti et al., 2003)
	CT	0-10	341	12.8	4.4*	2.0	1.9	159	
Fluometuron	NT+Adv ²	0-3	-	13.9	5.2	-	2.0	-	(Gaston et al., 2001)
	NT+ Adv	3-6	-	8.0	5.5	-	1.0	-	
	NT+V	0-3	-	15.6	5.5	-	1.8	-	
	NT+V	3-6	-	7.3	5.2	-	1.2	-	
	NT+B	0-3	-	11.2	6.1	-	1.8	-	
	NT+B	3-6	-	4.7	5.5	-	1.3	-	
	CT+ Adv	0-3	-	7.4	5.7	-	0.8	-	
	CT+ Adv	3-6	-	7.0	5.2	-	1.2	-	
	CT+V	0-3	-	7.4	5.5	-	0.9	-	
	CT+V	3-6	-	6.6	5.0	-	1.1	-	
	CT+B	0-3	-	7.8	5.8	-	1.0	-	
Fluometuron	CT+B	3-6	-	5.8	5.1	-	0.8	-	(Brown et al., 1994)
	NT	0-4	150	20.0	5.1	2.2	-	-	
	NT	4-8	150	10.0	5.5	1.7	-	-	
	NT	8-15	160	9.0	6.5	1.4	-	-	
	CT	0-4	130	13.0	5.5	1.7	-	-	
	CT	4-8	140	13.0	5.7	2.1	-	-	
	CT	8-15	150	11.0	6.3	1.4	-	-	
	NT+V	0-4	150	25.0	4.7	3.0	-	-	
	NT+V	4-8	150	11.0	4.9	1.0	-	-	
	NT+V	8-15	150	9.0	5.7	1.3	-	-	
	CT+V	0-4	140	15.0	5.0	2.1	-	-	
Fluometuron	CT+V	4-8	150	15.0	5.0	2.2	-	-	(Zablotowicz et al., 2000)
	CT+V	8-15	150	11.0	5.6	1.6	-	-	
	NT (11)	0-2	-	30.1	-	-	7.2	-	
	NT	2-5	-	11.8	-	-	2.0	-	
	NT	5-10	-	5.9	-	-	1.4	-	
	NT	10-25	-	3.3	-	-	1.5	-	
	CT	0-2	-	20.3	-	-	1.9	-	
	CT	2-5	-	11.2	-	-	2.2	-	
Fluometuron	CT	5-10	-	6.9	-	-	1.0	-	(Suba and Essington, 1999)
	CT	10-25	-	4.4	-	-	1.2	-	
	NT	0-8	130	24.5	5.1*	2.0	-	80	
Fluometuron	CT	0-8	100	14.2	5.2*	1.3	-	92	

Table III. Continued.

Pesticide	Tillage ¹	Depth.	Soil properties			K_D	K_F	K_{OC}	Reference
			Clay	Organic carbon (OC)	pH				
		cm		g kg^{-1}		L kg^{-1}	$\text{L}^{n_F} \text{mg}^{(1-n_F)} \text{kg}^{-1}$	$\text{L kg}^{-1} \text{OC}$	
Fluometuron	NT	0-2	-	13.9	6.7	2.4	-	-	(Locke et al., 2005)
	NT	2-10	-	6.1	5.9	1.6	-	-	
	NT+Rg ²	0-2	-	19.8	6.0	5.0	-	-	
	NT+Rg	2-10	-	6.9	5.7	1.4	-	-	
	CT	0-2	-	8.0	6.5	1.7	-	-	
	CT	2-10	-	6.0	5.8	1.6	-	-	
	CT+Rg	0-2	-	9.5	6.4	2.1	-	-	
	CT+Rg	2-10	-	7.3	5.7	2.0	-	-	
	RT	0-2	-	12.2	6.5	0.6	-	-	
	RT	2-10	-	6.7	6.7	0.4	-	-	
	RT+S [†]	0-2	-	12.6	6.6	0.7	-	-	
	RT+S	2-10	-	7.1	6.6	0.5	-	-	
	CT	0-2	-	6.4	6.1	0.4	-	-	
	CT	2-10	-	8.4	6.4	0.4	-	-	
	CT+S	0-2	-	6.8	6.1	0.4	-	-	
	CT+S	2-10	-	7.9	6.6	0.5	-	-	
	RT	0-2	-	10.3	5.5	0.5	-	-	
	RT	2-10	-	9.5	5.5	0.5	-	-	
	RT+S	0-2	-	8.8	5.5	0.4	-	-	
	RT+S	2-10	-	8.5	5.9	0.5	-	-	
	CT	0-2	-	9.0	5.6	0.4	-	-	
	CT	2-10	-	8.6	5.4	0.4	-	-	
	CT+S	0-2	-	8.7	5.7	0.4	-	-	
	CT+S	2-10	-	8.6	5.5	0.4	-	-	
MCPA	NT (9)		145	23.7	5.1	2.0	-	63	(Shang and Arshad, 1998)
	CT		145	22.7	5.8	0.7	-	40	
	NT (8)	0-5	532	47.0	4.9	7.3	-	168	
	CT		520	44.5	5.4	10.4	-	182	
Metolachlor	NT	0-5	-	15.4	-	-	3.5	230	(Ding et al., 2002b)
	NT	10-15	-	3.5	-	-	1.3	360	
	CT	0-5	-	8.5	-	-	2.0	240	
	CT	10-15	-	5.4	-	-	1.4	256	
Norflurazon	NT	0-8	130	24.5	5.1*	12.1	-	496	(Suba and Essington, 1999)
	CT	0-8	100	14.2	5.2*	6.5	-	456	
Norflurazon	NT	0-2	-	13.9	6.7	2.2	-	-	(Locke et al., 2005)
	NT	2-10	-	6.1	5.9	1.6	-	-	
	NT+Rg	0-2	-	19.8	6.0	3.6	-	-	
	NT+Rg	2-10	-	6.9	5.7	1.6	-	-	
	CT	0-2	-	8.0	6.5	1.6	-	-	
	CT	2-10	-	6.0	5.8	1.8	-	-	
	CT+Rg	0-2	-	9.5	6.4	2.3	-	-	
	CT+Rg	2-10	-	7.3	5.7	2.1	-	-	
Sulfentrazon	NT		280	30.6	6.6*	0.9	1.2	30	(Reddy and Locke, 1998)
	CT		250	17.8	6.4*	0.8	1.0	47	
	NT		330	46.0	6.2*	3.2	3.4	71	
	CT	0-7.5	260	19.2	4.5*	2.9	2.6	153	
	NT		230	21.4	5.2*	2.3	3.3	96	
	CT		210	16.0	5.3*	1.5	1.8	106	
2,4-Dichlorophenol	NT (9)	0-3	188	27.0	6.6*	4.2	-	155	(Düring et al., 2002)
	NT	3-10	177	16.7	6.6*	2.2	-	132	
	NT	10-25	168	10.3	6.4*	1.3	-	122	
	CT	0-3	132	11.3	6.1*	1.7	-	150	
	CT	3-10	155	11.6	6.1*	1.6	-	140	
	CT	10-25	143	11.3	6.2*	1.4	-	126	

¹ Codes of tillage practices are reported in Table I.² Adv: weed residues; B: wheat residues; Rg: ray-grass residues; S: rye residues; V: vetch residues.³ Numbers in parenthesis indicate the age in years of the tillage system.* pH CaCl₂.

and, hence, its reactivity, are also affected by tillage (Ding et al., 2002a; Sleutel et al., 2007; Tatzber et al., 2008) and by the nature of crop residues (Ding et al., 2006). In soil organic matter collected under a no-tillage system, Preston et al. (1994) found a higher number of reactive functional groups compared with that collected under a conventional tillage system. Ding et al. (2002a) found that humic acids and humin from conservation tillage contained more aliphatic carbon and less aromatic carbon than under conventional tillage. A larger amount of amino acids were also linked to these humic acids under no-tillage, whereas they were more linked to fulvic acids under conventional tillage (Szajdak et al., 2003). Moreover, reactive/recalcitrant peak ratios indicated that humic acids in the topsoil (0–5 cm-depth) were more biologically active under conservation tillage than under conventional tillage. With depth, the soil organic matter composition changes. Humification processes are more advanced in deeper soil layers and lead to an increase in aromaticity with the development of polycondensed rings (Ding et al., 2002a). The reactivity of organic matter fractions may also affect pesticide desorption. As an example, desorption of metolachlor from conventional tillage humic acids was less significant than from conservation tillage humic acids (Ding et al., 2002b). The hysteresis index (which is the ratio of Freundlich exponents for desorption and sorption) was lower for humic acids under conventional tillage, indicating that sorbed metolachlor molecules were more difficult to desorb. This may be caused by higher aromatic carbon contents in conventional tillage humic acids (Ding et al., 2002b; Xing, 2001).

The nature of crop residues also influences the composition of soil organic matter. For example, rye residues tend to form more aromatic and less aliphatic humic acids than a mix of vetch/rye residues (Ding et al., 2006), which could potentially affect pesticide behaviour and efficacy in soil (Ding et al., 2002a; Nanny and Maza, 2001). However, to our current knowledge, little work has been published on the effects of these changes in soil organic matter composition due to tillage on pesticide sorption. Ding et al. (2002b) highlighted a stronger sorption of metolachlor by humin than by humic acids, and humin content was found to be higher under no-tillage systems (Stearman et al., 1989). For humin, which is a highly condensed form of soil organic matter, several studies showed that sorption was more variable and that sorption isotherms were less linear (Xing and Pignatello, 1997; Yuan and Xing, 1999). In contrast, Stearman et al. (1989) observed a higher sorption of metribuzin and oxyfluorfen on fulvic and humic acids, which are abundant in conventional tillage, than on humin, which is abundant in conservation tillage. Dissolved organic carbon content is most often higher under conservation tillage and is mainly composed of small molecules, with a size similar to that of fulvic acids (Suba and Essington, 1999). In some studies, sorption of pesticides on dissolved organic carbon was found to be an efficient way to increase the mobility of some pesticides in soils, e.g. atrazine and 2,4D, leading to a significant transport of these chemicals through the soil profile (Chin et al., 1990; Gao et al., 1998; Lafrance et al., 1994; Li et al., 2005). In another study, sorption of fluometuron and norflurazon on the dissolved organic carbon formed

under conservation tillage did not lead to a higher leaching of these molecules (Suba and Essington, 1999).

2.3. Soil pH effect

Soil pH may be differently modified by tillage techniques: conservation tillage leads to an increase in pH (Reddy and Locke, 1998), no change (Comia et al., 1994; Rasmussen, 1991) or, more often, to a decrease in pH, especially in surface soil due to the accumulation of organic matter and fertilisers (Arshad et al., 1999; Doran, 1980; Levanon et al., 1994). For many pesticides, sorption is strongly influenced by soil pH and tends to increase when soil pH decreases (Barriuso and Calvet, 1992; Barriuso et al., 1992; Grey et al., 1997). In sandy soils, it has been found that, for similar organic carbon contents between tillage treatments, acidification in conservation techniques could significantly increase the sorption of several molecules according to their pKa (Shang and Arshad, 1998). For s-triazines (weak bases), the decrease in pH causes their protonation, promoting sorption on organic matter (Senesi and Testini, 1982) and decreasing their herbicide activity.

2.4. Other effects

Tillage techniques modify other soil properties (Fig. 4) whose effects on retention mechanisms are still poorly understood. Due to the presence of a mulch, water content in conservation techniques is generally higher than in conventional techniques (Drury et al., 1999; Shelton et al., 1998). This increase in soil water content led, in some cases, to a decrease in pesticide retention (Dao and Lavy, 1991; Walker, 1971). In other cases, it led to an increase in adsorption that could be explained by a decrease in the hydrophobicity of the organic compounds and an access to sorption sites facilitated by the presence of water (Berglof et al., 2000; Ochsner et al., 2006). Soil temperature is also modified by the mulch under conservation tillage. The mulch intercepts light energy, thus reducing temperature at the soil surface in conservation techniques, from 1 to 5 °C (Bragagnolo and Mielniczuk, 1990; Grant et al., 1990; Gupta et al., 1988). However, to our current knowledge, there is no published data about the consequences of soil water content and temperature modifications by tillage management on pesticide retention.

2.5. Sorption of metabolites

Little information is available on tillage effects on metabolite retention. According to their molecular composition, metabolites can have lower sorption capacities, e.g. cyanazine metabolites (Reddy et al., 1997a), or higher sorption capacities, e.g. atrazine and bentazon metabolites (Clay and Koskinen, 1990; Gaston et al., 1996) than the parent compound. For cyanazine metabolites, as observed for the parent compound, sorption was higher under conservation tillage than under conventional tillage.

2.6. Summary and recommendations

Regarding pesticide retention processes, most studies highlighted the role of the mulch in conservation tillage systems which intercepted the molecules. In a general way, tillage systems act on pesticide retention mainly through their effect on the distribution of organic matter in soil. Recent works on the characterisation of organic matter fractions and their reactivity towards pesticides show significant influences of the type of tillage and nature of crop residues. Using recent analytical technologies, these studies on the characterisation of organic compounds found in soils or crop residues are a significant advance in the qualitative evaluation of the effects of agricultural practices on pesticide retention. To progress in this direction, further research should not be focused on tillage management only, but rather on the whole cropping systems. As a matter of fact, other management options such as crop rotation, cover crops and manure application play important roles in the dynamics of soil organic matter. Regarding conservation tillage systems, research efforts should be made to clarify the indirect effects of the mulch via modifications of pH, water and temperature dynamics in the underlying soil.

3. DEGRADATION

Understanding pesticide degradation in soils is a key step for assessing their persistence and their risks of transfer in the environment. Degradation studies can be carried out in the field, thus integrating a set of non-controlled phenomena such as fluctuations in temperature, soil water content or radiation (Tab. IV), or in the laboratory, where soil samples are kept under controlled conditions (Tab. V). In all cases, degradation is conditioned by a combination of factors, i.e. microflora, organic matter, water content, temperature and pH, which are directly influenced by tillage (Fig. 4). Biotic degradation of pesticides is most often seen as quantitatively more important than abiotic degradation. In conservation tillage, the total microbial biomass is generally larger than in conventional tillage (Biederbeck et al., 1997; Dalal et al., 1991; Doran, 1980), but it remains strongly dependent on soil conditions. Fungi populations, which were found to be efficient in pesticide degradation (Barr and Aust, 1994), are generally larger in conservation tillage and their biomass increases as degree of tillage is reduced (Drijber et al., 2000; Kabir, 2005). These biological differences due to tillage have effects, sometimes contradictory, on the degradation of pesticides in the mulch and in the soil.

3.1. Pesticide degradation in the mulch

The interception by the mulch in conservation techniques can modify the persistence of the applied pesticides. These effects are sometimes negligible (Banks and Robinson, 1982), but more often they significantly affect the fate of pesticides in soil. Crop residues may have higher microbial activity and

degradation capacity than the soil, thus reducing the concentrations of pesticide that reach the soil surface (Locke et al., 2005; Zablotowicz et al., 1998). Moreover, depending on the nature of the pesticide, interception by the mulch may generate photodegradation, thus reducing the persistence of the molecules (Selim et al., 2003). In other works, crop residues increased the residence time of pesticides because of the competition between retention and degradation processes, and a gradual release of the molecules by desorption was observed (Mazzoncini et al., 1998). By acting as a physical protector of the soil surface, crop residues may also limit the air flow between the soil and the atmosphere and within the soil, thus slowing down the activity of degrading microorganisms (Sorenson et al., 1991).

Depending on the nature of crop residues, the degradation of molecules can be affected by the presence of a mulch, but in contrasted ways. For example, in no-tillage, vetch residues accelerated the degradation of metolachlor by from 1.5 to 3 times, but had no effect on the degradation of atrazine (Teasdale et al., 2003). On the contrary, according to laboratory studies, vetch residues seemed to slow down fluometuron degradation compared with soil samples without vetch residues (Brown et al., 1994; Zablotowicz et al., 1998) or other types of residues such as wheat residues (Gaston et al., 2001), rye residues (Zablotowicz et al., 1998), or ray grass residues (Locke et al., 1995). This slowdown could be due to the abundance of nitrogen in legumes (Fabaceae). This nitrogen would be preferentially used by the microorganisms to the detriment of the N sources contained in pesticides. In the same way, Gan et al. (1996) observed a lower degradation rate of atrazine after an addition of nitrogen. However, experiments on undisturbed soil columns with simulated rainfall, that allowed nitrogen leaching and thus reduced the amount bioavailable in the soil column, relativised these results and no negative effect of vetch residues on fluometuron degradation was found (Gaston et al., 2003). This experiment provided an explanation of the difference between the results obtained in laboratory incubations where leaching of nitrogen is not possible (Gaston et al., 2001) and those obtained in the field where N can leach out through the soil (Brown et al., 1996).

3.2. Pesticide degradation in soil

Tillage practices were found to modify significantly pesticide degradation in soil, but in contrasted ways according to studies. Degradation of several pesticides was indeed found to be slower (Brown et al., 1994; Gaston and Locke, 2000; Otto et al., 1997; Ulbrich et al., 2005), equivalent (Gaynor et al., 1998; Locke et al., 1996, 2005; Monks and Banks, 1993; Reddy et al., 1995b; Renner et al., 1998), or faster (Gaston et al., 2001, 2003; Lavorenti et al., 2003; Levanon et al., 1994; Sadeghi and Isensee, 1997) under conservation tillage than under conventional tillage. Several reasons could explain these differences. To explain a lower degradation under conservation tillage, the most commonly mentioned phenomenon is the competition between retention and degradation. In conservation tillage, pesticide adsorption to the soil solid phase is

Table IV. Field studies of pesticide degradation under different tillage practices.

Pesticide	Tillage ¹	Depth cm	Soil properties			DT ₅₀ d	Reference
			Clay	Organic carbon g kg ⁻¹	pH		
Alachlor	NT	0-30	-	-	-	< 1	(Weed et al., 1998)
	CT	0-30	-	-	-	< 1	
Alachlor encapsulated alachlor	NT	0-110	-	-	-	8-41	(Gish et al., 1994)
	CT	0-110	-	-	-	8-41	
	NT	0-110	-	-	-	4-20	
	CT	0-110	-	-	-	4-20	
Atrazine	NT	0-10	-	-	-	50	(Ghadiri et al., 1984)
	CT	0-10	-	-	-	42	
Atrazine	NT	0-50	-	-	-	71	(Gish et al., 1991)
	CT	0-70	-	-	-	73	
Atrazine encapsulated atrazine	NT	0-110	-	-	-	36	(Gish et al., 1994)
	CT	0-110	-	-	-	36	
	NT	0-110	-	-	-	110	
	CT	0-110	-	-	-	110	
Atrazine	NT	0-10	390	14.5	5.4	45, 36, 56 ⁴	(Gaynor et al., 2000)
	NT+Rg ³	0-10				40, 33, 54	
	CT	0-10				46, 34, 54	
	CT+Rg	0-10				35, 59, 24	
Atrazine	NT	0-10	-	-	-	43, 56, 43, 35	(Gaynor et al., 1998)
	RT top		-	-	-	33, 75, 53, 36	
	RT furrow		-	-	-	31, 47, 53, 35	
	CT		-	-	-	33, 62, 58, 47	
Atrazine	NT	0-50	17-26	11.0	6-6.5	35, 25, 12, 23	(Isensee and Sadeghi, 1994)
	CT		16-24	7.0	4.8-5	37, 21, 29, 18	
Atrazine	NT	0-150	55-166	0.1-9.7	5.3-6.1	149	(Heatwole et al., 1997)
	CT		59-179	1.2-4.4	5.5-6.7	215	
Atrazine	NT (7) ⁵	0-50	-	-	-	12	(Sadeghi and Isensee, 1996)
	CT		-	-	-	22	
	CT → NT		-	-	-	-, 21, 32	
	NT		-	-	-	-, 17, 23	
	(7) → CT		-	-	-	-	
Clomazon	RT	0-10	230	23.2	6.0	52, 91	(Curran et al., 1992)
	CT		-	-	-	58, 83	
Chlorimuron	NT	-	260	10.4	7.8	32, 14, 22	(Baughman et al., 1996)
	CT	-	260	10.4	7.8	44, 13, 18	
	NT	-	220	8.7	6.3	17, 82	
	CT	-	220	8.7	6.3	14, 22	
Cyanazine	NT	-0-50	-	-	-	13	(Gish et al., 1991)
	CT	0-70	-	-	-	13	
Fluometuron	NT, NT+Rg CT, CT+Rg	0-2	-	-	-	7-15	(Locke et al., 2005)
Fluometuron	NT	0-8	150	8.7	5.2	30, 23	(Brown et al., 1996)
	NT+V ²		150	10.4	4.8	38, 19	
	CT		130	7.6	5.6	24, 26	
	CT+V		140	8.7	5.0	30, 25	
Imazapic	NT (3)	0-10	780	20.3	4.7	66	(Ulbrich et al., 2005)
	CT	0-10				45	
	NT	0-10	280	27.3	5.8	35	
	CT	0-10				32	
Imazapyr	NT (3)	0-10	780	20.3	4.7	53	(Ulbrich et al., 2005)
	CT	0-10				50	
	NT	0-10	280	27.3	5.8	43	
	CT	0-10				45	
Imazaquin	RT	0-10	230	23.2	6.0	39, 144	(Curran et al., 1992)
	CT					41, 117	

Table IV. Continued.

Pesticide	Tillage ¹	Depth cm	Soil properties			DT ₅₀ ² d	Reference
			Clay	Organic carbon g kg ⁻¹	pH		
Imazaquin	NT CT	0-20	- -	16.9, 19.8	5.9, 6.4	27, 33 53, 22	(Mills and Witt, 1991)
Imazethapyr	RT CT	0-10	230	23.2	6.0	82, 53 122, 56	(Curran et al., 1992)
Imazethapyr	NT CT	0-20	- -	16.9, 19.8	5.9, 6.4	36, 40 40, 12	(Mills and Witt, 1991)
Isoproturon	NT	0-30	170	6.1	-	12	(Otto et al., 1997)
	RT	0-30	170	5.8	-	8	
	CT	0-30	170	4.5	-	15	
Metolachlor	NT	0-30	170	6.1	-	9	(Otto et al., 1997)
	RT	0-30	170	5.8	-	26	
	CT	0-30	170	4.5	-	29	
Metolachlor	NT	0-150	55-166	0.1-9.7	5.3-6.1	45	(Heatwole et al., 1997)
	CT		59-179	1.2-4.4	5.5-6.7	34	
Metolachlor	NT	0-10	-	-	-	40, 65, 37, 30	(Gaynor et al., 1998)
	RT top		-	-	-	23, 87, 41, 35	
	RT furrow		-	-	-	28, 42, 40, 28	
	CT		-	-	-	32, 68, 43, 40	
Metolachlor	NT	0-10	390	14.5	5.4	46, 42, 72	(Gaynor et al., 2000)
	NT+Rg	0-10				42, 40, 69	
	CT	0-10				42, 45, 79	
	CT+Rg	0-10				44, 44, 97	
Metribuzin	NT	0-10	390	14.5	5.4	24, 27, 34	(Gaynor et al., 2000)
	NT+Rg	0-10				24, 26, 36	
	CT	0-10				23, 29, 32	
	CT+Rg	0-10				24, 29, 37	
Metribuzin	NT	0-5	-	13.3	5.7	12, 11	(Sorenson et al., 1991)
	CT	0-5	-			5, 17	
	NT	0-5	-	18.0	5.1	15, 15	
	CT	0-5	-			13, 11	
Terbuthylazine	NT	0-30	170	6.1		25	(Otto et al., 1997)
	RT	0-30	170	5.8		32	
	CT	0-30	170	4.5		22	

¹ Codes of tillage practices are reported in Table I.² DT₅₀: pesticide half-life.³ Rg: ray-grass residues; V: vetch residues.⁴ Commas are used to separate different years of study.⁵ Numbers in parenthesis indicate the age in years of the tillage system.

generally increased and may lead to a decrease in the availability of the molecules for biological degradation (Zablotowicz et al., 2000). In some cases, microbiological activity in soil can be affected by a lower temperature (Sorenson et al., 1991) or higher soil acidity (Brown et al., 1994) under conservation tillage. Both of these consequences were found to increase sorption of pesticides and thus to reduce their bioavailability. For some authors, repeated fertiliser inputs (Gaynor et al., 1998; Ghadiri et al., 1984), the use of legumes as cover crops (Brown et al., 1994) and the absence of lime could lead to soil acidification and thus mask the effects of tillage practices, particularly for molecules of the s-triazine family whose sorption

is highly sensitive to acidity. Other pesticides such as sulfonyl-ureas have their chemical stability reduced by acidification, leading to a faster degradation of these compounds under conservation techniques (Chapman and Cole, 1982). Global soil microbial activity can be correlated with mineralisation of the molecules (Lavorenti et al., 2003), but not systematically (Reddy and Locke, 1998). The increase in soil microbial activity under conservation techniques did not always mean that specific microbial populations involved in the degradation of a molecule were more abundant (Gaston and Locke, 2000). In some cases, crop residues on the soil surface under conservation tillage seemed to disrupt microorganisms' activity

Table V. Laboratory studies of pesticide degradation under different tillage practices.

Pesticide	Tillage ¹	Depth cm	Soil properties			Water content g g ⁻¹	Temperature °C	Incubation duration d	DT ₅₀ ² d	CO ₂ ² % applied dose	NER ² % applied dose	Reference
			Clay	Organic carbon	pH							
				g kg ⁻¹								
Acifluorfen	NT	0-10	-	10.2	5.6*	0.35	25	49	108	5	9	(Gaston and Locke, 2000)
	NT	20-30	-	4.4	5.7*				165	4	5	
	CT	0-10	-	8.7	5.8*				74	6	12	
	CT	20-30	-	4.9	5.8*				169	5	3	
Alachlor	NT (7) ³	0-5	-	22.0	5.3*	0.35	25	54	6.5	13	54	(Locke et al., 1996)
	CT	0-5	-	11.6	5.1*				6.5	7	43	
Alachlor	NT	0-30	-	-	-	-	-	-	≈ 3	-	-	(Weed et al., 1998)
	CT	0-30	-	-	-	-	-	-	≈ 3	-	-	
Bentazon	NT	0-10	-	10.2	5.6*	0.30	25	22	50	2	15	(Gaston et al., 1996)
	NT	20-30	-	4.4	5.7*				87	2	8	
	CT	0-10	-	8.7	5.8*				39	3	20	
	CT	20-30	-	4.9	5.8*				77	2	9	
Bentazon (soil columns)	NT	0-10	-	-	-	-	-	-	17-23 ⁴	0.1	15-17	(Gaston and Locke, 1996)
	NT	10-20	-	-	-	-	-	-	69	0.1	8-12	
	CT	0-10	-	-	-	-	-	-	12-14			
	CT	10-20	-	-	-	-	-	-	23-35			
Bentazon	NT (9)	0-7.5	-	15.3	5.4*	0.33	25	48	7	12	63	(Wagner et al., 1996)
	CT		-	13.1	5.7*				9	17	65	
	NT (16)		-	48.0	6.3*				9	18	60	
	CT		-	18.9	4.5*				15	14	53	
	NT (18)		-	30.6	6.8*				9	14	61	
	CT		-	17.8	6.4*				8	14	62	
	NT (4)		-	20.4	6.3*				11	15	59	
	CT		-	17.7	5.0*				11	14	59	
Chlorimuron	NT (3)	0-7.5	-	10.2	5.6*	0.31	-	63	50	2	15	(Reddy et al., 1995b)
	CT		-	8.7	5.8*				39	3	20	
	NT		280	30.6	6.6*				-	10	22	
	CT		250	17.8	6.4*				-	12	18	
	NT		330	46.0	6.2*				-	11	24	
	CT		260	19.2	4.5*				-	14	15	
	NT		-	15.3	5.4*				-	16	24	
	CT		-	13.1	5.7*				-	16	24	
Diclosulam	NT	0-10	355	19.9	5.0*	60	25	119	67	14	29	(Lavorenti et al., 2003)
	CT	0-10	341	12.8	4.4*				87	11	24	
Fluometuron	NT (11)	0-2	-	30.1	-	0.33	28	25	20	-	24	(Zablotowicz et al., 2000)
	NT	2-5	-	11.8	-				19	-	25	
	NT	5-10	-	5.9	-				48	-	13	
	NT	10-25	-	3.3	-				50	-	9	
	CT	0-2	-	20.3	-				9	-	43	
	CT	2-5	-	11.2	-				11	-	31	
	CT	5-10	-	6.9	-				25	-	23	
	CT	10-25	-	4.4	-				94	-	7	
Fluometuron	NT+Adv ⁶	0-3	-	7.2	5.2	33 kPa ⁷	25	60	6	-	-	(Gaston et al., 2001)
	NT+V ⁶	0-3	-	9.1	5.5				44	-	-	
	NT+B ⁶	0-3	-	9.2	6.1				9	-	-	
	CT+Adv	0-3	-	3.4	5.7				44	-	-	
	CT+V	0-3	-	4.6	5.5				74	-	-	
	CT+B	0-3	-	4.9	5.8				23	-	-	
Fluometuron	NT+Adv	0-7.5	-	13.9	5.2	PS	25	109	9	-	-	(Gaston et al., 2003)
	NT+V	0-7.5	-	15.6	5.5				9	-	-	
	NT+B	0-7.5	-	11.2	6.1				9	-	-	
	CT+Adv	0-7.5	-	7.4	5.7				19	-	-	
	CT+V	0-7.5	-	7.4	5.5				12	-	-	
	CT+B	0-7.5	-	7.8	5.8				9	-	-	

Table V. Continued.

Pesticide	Tillage ¹	Depth cm	Soil properties			Water content g g ⁻¹	Temperature °C	Incubation duration d	DT ₅₀ ² d	CO ₂ ² % applied dose	NER ² % applied dose	Reference
			Clay	Organic carbon	pH							
				g kg ⁻¹								
Fluometuron	NT (11)	0-4	150	20.0	5.1	0.25	30	84	57	-	-	(Brown et al., 1994)
	NT	4-8	150	10.0	5.5				79	-	-	
	NT	8-15	160	9.0	6.5				49	-	-	
	CT	0-4	130	13.0	5.5				49	-	-	
	CT	4-8	140	13.0	5.7				55	-	-	
	CT	8-15	150	11.0	6.3				52	-	-	
	NT+V (11)	0-4	150	25.0	4.7				78	-	-	
	NT+V	4-8	150	11.0	4.9				90	-	-	
	NT+V	8-15	150	9.0	5.7				83	-	-	
	CT+V	0-4	140	15.0	5.0				71	-	-	
	CT+V	4-8	150	15.0	5.0				68	-	-	
	CT+V	8-15	150	11.0	5.6				52	-	-	
Imazaquin	SS (3)	-	660	16.9	6.4	0.25-0.30	30-25	6	12-16	-	-	(Seifert et al., 2001a)
	CT	-							-	-	-	
Sulfentrazone	NT	0-7.5	230	21.4	-	0.30	-	77	-	2	27	(Reddy and Locke, 1998)
	CT		210	16.0	-				-	2	23	

¹ Codes of tillage practices are reported in Table I.

² DT₅₀: pesticide half-life; CO₂: mineralisation; NER: non-extractable residues.

³ Numbers in parenthesis indicate the age in years of the tillage system.

⁴ Hyphens are used to indicate the range of variation of values.

⁵ Water content expressed in % of the water-holding capacity (WHC).

⁶ Adv: weed residues; B: wheat residues; V: vetch residues.

⁷ Water content expressed with the corresponding matric potential (kPa).

* pH CaCl₂.

(Locke and Harper, 1991b; Sorenson et al., 1991), and, compared with conventional tillage, lag phases in the activation of mineralisation may occur (Seifert et al., 2001b). In addition, a greater availability of carbon under conservation tillage compared with conventional tillage can defer the use of pesticides as a source of carbon and thus their degradation in soil (Locke and Harper, 1991b).

Mineralisation is considered as the last step of pesticide degradation, leading to its complete removal from the soil. The mineralisation results are highly contrasted according to pesticides, location sites and incubation conditions (Tab. V) and do not allow any conclusion on an increase or a limitation of mineralisation in conservation tillage. In the same way, non-extractable residue fractions vary widely depending on pesticides, techniques and soils. However, the formation of non-extractable residues is often correlated with the degradation half-life of the molecules (Gaston and Locke, 2000; Lavoretti et al., 2003; Zablotowicz et al., 2000). Locke and Harper (1991b) have also shown that the difference in non-extractable residues of metribuzin between conventional tillage and conservation tillage was mainly due to the coarse fraction of organic matter.

Moreover, although little information is generally mentioned in the literature, the age of the tillage system seems to be a major source of differences in pesticide degradation

(Wagner et al., 1996). Sadeghi and Isensee (1996) have evaluated the effect of reversing the tillage of 7-year-old no-tillage and conventional tillage field plots on atrazine degradation. Their results suggested that, after reversing a well-established tillage, time for the new tillage to fully develop its particular effects on atrazine degradation may be shorter for a new conventional tillage than for a new no-tillage. Another major source of degradation variability in field studies is the inter-annual variability of climatic conditions. It can hide or completely cancel the effects of tillage and it can lead to opposite conclusions depending on the year (Baughman et al., 1996; Mills and Witt, 1991; Sorenson et al., 1991).

In most cases, pesticide degradation forms one or several degradation products. In the same manner as for mother compounds, their degradation can be modified by tillage practices. For example, under a no-tillage system, an accumulation of polar metabolites formed by the degradation of metribuzin was observed, while they were degraded under conventional tillage (Locke and Harper, 1991a, b). On the contrary, the formation of alachlor metabolites was faster but their degradation was slower under conventional tillage than under conservation tillage (Locke et al., 1996). Similarly, the accumulation of a fluometuron metabolite, trifluoromethylphenylurea (TFMPU), occurred mainly under conventional tillage (Zablotowicz et al., 2000), and another of its metabolites, dimethylfluometuron,

seemed to be formed mainly when the air flow conditions, due notably to tillage operations, were favourable (Locke et al., 2005).

Pesticide formulation also appeared to have important consequences on their persistence. For example, whatever the tillage system, starch encapsulation of atrazine and alachlor tended to increase their field persistence (Gish et al., 1994).

Spatial variability of local conditions seems to be an important source of pesticide degradation variation. In their study, Gaynor et al. (1987) observed that the ridge tops retained more herbicide than the furrows, resulting in differences in pesticide persistence. Recently, Alletto et al. (2008) have examined the degradation of the diketonitrile metabolite of isoxaflutole under two tillage systems. Under conventional tillage, the herbicide persistence was found to be highly variable vertically and laterally according to soil sample location within the tilled horizon. The main source of variation in this case was the tillage operation with the mouldboard plough. Under mulch tillage with disk harrowing, MT_{Dk} (Tab. I), the effect of tillage was minimised but variations in diketonitrile persistence were associated with the vertical distribution of organic carbon. Both of these studies highlight the importance of the soil sampling strategy in order to provide accurate assessment of environmental impacts of agricultural practices. Last, the mulch can reduce water content and temperature variations (Bragagnolo and Mielniczuk, 1990; Unger, 1987), leading to a lower variability of degradation under conservation tillage compared with conventional tillage (Mills and Witt, 1991).

3.3. Summary and recommendations

Results about tillage effects on pesticide degradation are highly contrasted. Studies of the effects of management practices on soil properties and microorganism activity have to deal with complex interactions between soil physics, physico-chemistry and microbiology which control the microbial activities involved in pesticide breakdown. Particularly the strong coupling between retention and degradation processes highly depends on soil physical and hydrodynamic properties, ensuring the access of microbes to water, substrates and the movement of solutes such as pesticides to sorption and degradation sites. Degradation studies should therefore pay great attention to the soil conditions (dynamics of temperature, water content, pH, N content, etc.), which have been shown to be largely modified by the presence of the mulch at the soil surface. In the same way, studies focusing on the understanding and prediction of pesticide degradation in soil should use dynamic experimental systems where soil solution is allowed to move and be renewed (e.g. soil columns) rather than static (batch) experimental systems. Improving knowledge and quantitative prediction of pesticide degradation in soils also implies an accurate estimation of the spatial distribution and temporal dynamics of active degradative populations. Research efforts should thus be oriented at (a) improving field study for a better understanding of the in situ dynamics of these microorganisms and their location ('hot-spots'), and (b) establishing a comprehensive link between this dynamics and agricultural

operations. Particular attention should be paid to the soil sampling strategy in this regard.

4. TRANSFER OF PESTICIDES

Depending on their mobility and their persistence, pesticides can migrate within and outside the soil and contaminate other compartments of the environment, such as water and air. The three main transfer processes are volatilisation, leaching and runoff. The relative importance of each of these processes depends on the application conditions, the pesticide properties, the climatic conditions and the soil properties partly governed by agricultural practices.

4.1. Volatilisation

Volatilisation is an important pathway for the loss of pesticide that is controlled by the pesticide properties (such as saturated vapour pressure, Henry constant, K_{OC}), the soil properties (temperature, water content, organic carbon content), the farming operations (mode of application, soil roughness, presence of a mulch) and the climatic conditions (wind, solar radiation, temperature) (Bedos et al., 2002). Although volatilisation is often mentioned in the literature to explain differences in the pesticide persistence due to tillage operations (Banks and Robinson, 1982; Curran et al., 1992; Gaynor et al., 2000), this phenomenon remains poorly studied. Whang et al. (1993) highlighted a higher volatilisation in conservation tillage than in conventional tillage that was attributed to the presence of a mulch. In their study, four days after treatment, transfer by volatilisation accounted for 48 and 18% of applied fonofos, 23 and 7% of applied chlorpyrifos and 0.9 and 0.7% of applied atrazine under no-tillage and conventional tillage, respectively. Wienhold and Gish (1994) also observed a larger volatilisation of alachlor and atrazine under conservation tillage, but only until the first rainfall occurred (5 days after treatment). Following this rainfall, volatilisation in conservation tillage was strongly slowed down, which could be explained by the migration of the pesticides from the mulch to the soil. After 35 days, the cumulative loss accounted for 9 and 14% of applied alachlor and 4 and 9% of applied atrazine under conservation tillage and conventional tillage, respectively. In addition, this study showed a significant effect of pesticide formulation on volatilisation. Starch-encapsulated alachlor was less volatilised under conservation tillage than the commercial formulation, and a similar effect was measured for atrazine under both conservation tillage and conventional tillage systems. Volatilisation directly depends on environmental conditions and is favoured first by high temperatures (Glotfelty, 1987; Weber et al., 2002) and also by wet soils that keep the molecules available in water solution. Weber et al. (2006) observed during a year of monitoring that volatilisation reached 22 and 32% of applied metolachlor in conservation tillage and conventional tillage, respectively. Due to the mulch, soil surface water content was higher under conservation tillage, which slowed down the soil warming and thus reduced the amount of herbicide lost.

4.2. Leaching

Pesticide properties play a decisive role in the modifications of the leaching risk by tillage. First, retention properties determine the mobility of the molecules (Singh N. et al., 2002) and directly influence their transfer to groundwater. Masse et al. (1998) reported that leaching of atrazine and deethylatrazine was more significant under conservation tillage, whereas metolachlor leaching, that has a stronger sorption capacity, was not affected by tillage. Water solubility of pesticides also influences their leaching. As an example, alachlor and cyanazine leaching was related to the interaction between tillage and water solubility (Sadeghi and Isensee, 1997). Under no-tillage, the migration depth of alachlor in soil was lower than that of cyanazine, whereas the opposite was observed under conventional tillage. The highest solubility of alachlor compared with that of cyanazine allowed a migration through the soil matrix, thus increasing the possibilities of adsorption, while cyanazine rather circulated via macropores under conservation tillage. Water solubility of the molecules may be modified by soil pH, which could increase leaching risk (Li et al., 2003). For sulfentrazone, solubility in water was, for example, multiplied by a factor of 16 when soil pH rose from 6 to 7.5 (Reddy and Locke, 1998). Other studies have shown a positive correlation between the half-life of several molecules (alachlor, atrazine, cyanazine, metolachlor, metribuzin and simazine) and their concentrations measured in drains without any tillage effect on these transfers (Logan et al., 1994; Ritter et al., 1996).

Formulation, by modifying solubility in water, persistence and retention in soils of pesticides, also influences their transport. Micro-encapsulation of alachlor increased its solubility in water and its transport through the soil matrix (Sadeghi et al., 1998). Starch-encapsulation of atrazine limited its losses by leaching in both no-tillage and conventional tillage (Gish et al., 1994, 1995). Hall et al. (1998) also observed a good efficiency of starch-encapsulation of atrazine, allowing a reduction of the leaching losses by a factor of 2 to 4 compared with the commercial formulation, depending on the year and on the application rate. Likewise, coating of metolachlor with a polyurea polymer helped reduce losses by a factor of 2 compared with the commercial formulation (Hall et al., 1998). According to these results, an efficient control of leaching seems achievable via adequate pesticide formulations.

Pesticide leaching depends on soil physical properties, such as the hydraulic conductivity, which is directly influenced by the soil structure created by tillage. Many studies on pesticide leaching have been conducted under field conditions, on plots equipped with ceramic cups, lysimeters or drains (Tab. VI), and under laboratory conditions, on undisturbed soil columns with simulated rainfalls (Tab. VII). Although most of these works showed greater losses under conservation tillage (Isensee and Sadeghi, 1997; Isensee et al., 1990; Masse et al., 1998; Singh et al., 2002; Weber et al., 2006), results are contrasted, some of them indicating no effect of tillage (Clay et al., 1998; Fomsgaard et al., 2003; Gaynor et al., 2000; Granovsky et al., 1993; Weed et al., 1995), or even greater losses under

conventional tillage (Düring and Hummel, 1993; Gish et al., 1995; Levanon et al., 1993).

On one hand, mulch on the soil surface absorbs rainfall energy, thus avoiding the formation of soil crust (Baumhardt and Lascano, 1996; Blevins and Frye, 1993) and pore sealing (Ela et al., 1992). On the other hand, the continued deposition of crop residues on the soil surface appears to contribute to macropore development by stimulating earthworm activity (Bouché, 1972; Edwards et al., 1988; Rovira et al., 1987; Satchell, 1983). Under conservation tillage, and more particularly under no-tillage, the macropore network formed by earthworm burrows, root channels and cracks is not disrupted by tillage and thus may allow downward flows of water and solutes at a higher rate than if movements occurred only through the soil matrix. Because of this bypass of the soil matrix, this type of water and solute movement is called 'preferential flow through macroporosity'. It occurs mainly during saturated conditions. In the soil matrix, solutes move by convection-dispersion and, due to significant contact between the liquid and solid phases, opportunities for pesticide retention are greater than in macropores (Shipitalo and Edwards, 1996). Ogden et al. (1999) showed that soil tillage destroyed the connectivity of the macropores and thus increased fluxes through the soil matrix.

Proportionally to their quantity, crop residues can limit losses due to leaching. By reducing the infiltration rate at the soil surface, i.e. at the crop residues/soil interface, the mulch promotes pesticide fluxes within the soil matrix, thus avoiding preferential flows through macropores (Sigua et al., 1993). On the other hand, at the residues/soil interface or when residues and soil are mixed, the presence of these two compartments that have different water-holding capacities and hydraulic conductivities can also generate preferential flow (Kasteel et al., 2007; Ma and Selim, 2005).

There is no direct relationship between the number of macropores and the intensity of preferential flow, since some macropores do not participate in the conduction of water (Shipitalo et al., 1990). Preferential flow activation seems to depend, in particular, on the initial soil water content, but in contrasted ways according to studies (Granovsky et al., 1993; Shipitalo and Edwards, 1996). Although preferential flows through macropores occur in both conservation and conventional tillage (Andreini and Steenhuis, 1990; Essington et al., 1995; Gish et al., 1991; Granovsky et al., 1993), this dependency on initial water content was found to be greater under conservation tillage (Flury et al., 1995; Sigua et al., 1995). At low initial water content, the hydrophobicity of organic materials at the soil surface under conservation tillage could limit the entry of water into the soil matrix, creating locally and temporarily saturation conditions, thus favouring macropore fluxes (Edwards et al., 1989, 1992a; Phillips et al., 1989; Shipitalo et al., 1990). Despite earthworm burrows being found to have high pesticide sorption capacities due to high amounts of organic compounds in burrow linings (Edwards et al., 1992b; Stehouwer et al., 1993), water and pesticide transfer rates through macropores are generally higher than for the soil matrix (Shipitalo and Edwards, 1996). Other studies showed a higher leaching of atrazine (Kitchen et al., 1998;

Table VI. Field studies of pesticide leaching (% of applied dose) under different tillage practices.

Pesticide	Dose	Tillage ¹	Depth	Water sampling system	Soil properties			Leaching	Reference
					Clay	Organic carbon	pH		
	kg a.i. ha ⁻¹		cm			g kg ⁻¹		% applied dose	
Alachlor	2.2	NT	0-120	-	-	17.3-21.4	5.7-7.0	0.0002-0.10 ²	(Weed et al., 1995)
		RT		-	-	17.6-20.8	5.9-6.7		
		MT _{Ch}		-	-	18.6-21.3	5.7-6.8		
		CT		-	-	19.7-20.4	6.3-6.6		
Atrazine Desethylatrazine	2.2, 1.5, 1.8, 1.9 ³	NT	0-100	-	-	-	-	0.09, 0.08, 0.15, 0.05 ³	(Masse et al., 1996)
		CT		D ⁴	-	-	-		
		NT		-	-	-	-		
		CT		-	-	-	-		
Atrazine	2.8	NT	0-120	-	-	17.3-21.4	5.7-7.0	0.02-0.35	(Weed et al., 1995)
		RT		-	-	17.6-20.8	5.9-6.7		
		MT _{Ch}		-	-	18.6-21.3	5.7-6.8		
		CT		-	-	19.7-20.4	6.3-6.6		
Atrazine	1.3	MT _{Ch}	-	-	120-300	15.4-24.2	5.4-4.9	0.07-0.11, 0.08-0.22	(Fortin et al., 2002)
		CT	-	-	120-300	15.7-23.5	5.3-5.8	0.03-0.07, 0.11-0.12	
Atrazine	1.7	NT	0-120	L ⁴	324-421	2.0-12.0	5.5-6.7	0.15-0.86, 0.21-9.60	(Hall et al., 1989)
		CT						< 0.01 – 0.19, 0.75 – 0.85	
Atrazine, Cyanazine Simazine	1.7, 2.2, 1.7	MT mulch	0-120	L	-	-	-	3.0-5.1	(Watts and Hall, 1996)
		CT						0.69-0.93	
Cyanazine	2.2	NT	0-120	L	324-421	2.0-12.0	5.5-6.7	0.03-0.23, <0.10-4.73	(Hall et al., 1989)
		CT						< 0.01 – 0.15, 0.32 – 0.56	
Dicamba	0.56	NT	-	-	-	2.0-12.0	5.5-6.7	1.99, 0.39, 5.56, 1.05, 2.45	(Hall and Mumma, 1994)
		CT	-	-	-	-	-	< 0.01, 0.20, 0.20, 0.0, 0.58	
Fluometuron	1.6	NT	0-90	L	130	1.3-17.7	5.61	29.9-37.4, 37.9-50.8, 0-10.3, 0.8-54.7	(Essington et al., 1995)
		CT				1.1-10.2	5.85	11.9-69.3, 30.0-79.5, 6.1-28.7, 3.4-73.3	
Glyphosate AMPA Glyphosate AMPA	0.8	NT (20) ⁵	0-110	L	134-227	1.1-19.2	5.9-7.6	0.022	(Fomsgaard et al., 2003)
		NT						0.018	
		CT			83-268	0.5-11.3	6.4-8.7	0.0305	
		CT						0.0205	
Metolachlor	2.6, 2.6, 2.6, 2.4	NT	0-100	D	-	-	-	0.00, 0.02, 0.02, 0.04	(Masse et al., 1996)
		CT						0.00, 0.00, 0.02, 0.01	
Metolachlor	2.2	MT mulch	0-120	L	-	-	-	2.46	(Watts and Hall, 1996)
		CT						0.37	
Metolachlor	2.5	MT _{Ch}	-	-	120-300	15.4-24.2	5.4-4.9	0.02-0.04, 0.06-0.12	(Fortin et al., 2002)
		CT	-	-	120-300	15.7-23.5	5.3-5.8	0.01-0.03, 0.07-0.10	
Metolachlor	4.48	NT (10)	0-97	L	60-290	3.0-6.4	4.4-6.1	1.4, 6.7	(Weber et al., 2006)
		CT						0.7, 4.4	
Metolachlor	2.2	NT	0-120	L	324-421	2.0-12.0	5.5-6.7	0.01-0.47, <0.10-4.19	(Hall et al., 1989)
		CT						< 0.01 – 0.10, 0.25 – 0.61	
Metribuzine	0.45	NT	0-120	-	-	17.3-21.4	5.7-7.0	0.14-0.87	(Weed et al., 1995)
		RT		-	-	17.6-20.8	5.9-6.7		
		MT _{Ch}		-	-	18.6-21.3	5.7-6.8		
		CT		-	-	19.7-20.4	6.3-6.6		
Simazine	1.7	NT	0-120	L	324-421	2.0-12.0	5.5-6.7	0.06-1.76, 0.18-8.36	(Hall et al., 1989)
		CT						0.01-0.18, 1.50-1.63	

¹ Codes of tillage practices are reported in Table I.² Hyphens are used to indicate the range of variation of values.³ Commas are used to separate different years of study.⁴ D: water sampling in drains; L: water sampling in lysimeters.⁵ Numbers in parenthesis indicate the age in years of the tillage system.

Table VII. Laboratory studies on pesticide leaching (% of applied dose) under different tillage practices.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Depth cm	Soil properties			Rainfall intensity mm h ⁻¹	Leaching % applied dose	Reference
				Clay	Organic carbon g kg ⁻¹	pH			
Alachlor	2.2	NT (16) ² CT	0-30	- -	- -	- -	50	1.6 0.4	(Weed et al., 1998)
Alachlor	3.3	NT (8) CT	0-10	- -	- -	- -	50	29.7 14.4	(Clay et al., 1991)
Atrazine	2.8	NT	0-18	170	10.2-15.3 ³	6.4-5.9	-	14.7	(Levanon et al., 1993)
		CT			11.8-12.6	6.4-6.7	-	19.3	
		NT			10.2-15.3	6.4-5.9	-	12.9	
		CT			11.8-12.6	6.4-6.7	-	20.4	
Atrazine	1.3	NT	0-10	-	NT: 7.5 - 24.4	-	9	58.4	(Sigua et al., 1995)
		CT		-		-	9	42.7	
		NT		-		-	9	47.2	
		CT		-		-	9	33.2	
		NT		-	CT: 7.0	-	9	31.6	
		CT		-		-	9	29.4	
		NT		-		-	9	26.7	
		CT		-		-	9	20.1	
Atrazine	1.3	NT	0-10	-	NT: 24.4 – 7.5	-	9	50.7	(Sigua et al., 1995)
		NT		-		-	9	35.7	
		NT		-		-	9	34.9	
		NT		-		-	9	35.9	
		CT		-	CT: 7.0	-	9	40.3	
		CT		-		-	9	40.1	
		CT		-		-	9	38.2	
		CT		-		-	9	37.0	
Carbofuran	1.9	NT	0-18	170	10.2-15.3	6.4-5.9	-	4.5	(Levanon et al., 1993)
		CT			11.8-12.6	6.4-6.7	-	18.7	
		NT			10.2-15.3	6.4-5.9	-	4.2	
		CT			11.8-12.6	6.4-6.7	-	7.7	
Diazinon	2.5	NT	0-18	170	10.2-15.3	6.4-5.9	-	0.25	(Levanon et al., 1993)
		CT			11.8-12.6	6.4-6.7	-	0.35	
		NT			10.2-15.3	6.4-5.9	-	0.0	
		CT			11.8-12.6	6.4-6.7	-	0.0	
Metamitron	4	NT (20)	0-30/40	112-210	9.0-18.0	-	0.16, 0.38, 0.46	0.03, 3.0, 10.1	(Düring and Hummel, 1999)
		CT		151-217	9.0-1.0	-		0.3, 5.0, 12.2	
Metolachlor	2.25	NT	0-18	170	10.2-15.3	6.4-5.9	-	8.2	(Levanon et al., 1993)
		CT			11.8-12.6	6.4-6.7	-	10.2	
		NT			10.2-15.3	6.4-5.9	-	6.5	
		CT			11.8-12.6	6.4-6.7	-	9.3	
Metolachlor	10	NT (20)	0-30/40	112-210	9.0-18.0	-	0.25, 0.42	1.8, 5.7	(Düring and Hummel, 1999)
		CT		151-217	9.0-1.0	-		3.6, 12.4	
Metolachlor	20	NT	0-15	280	19.0	7.3	saturation	38	(Singh N. et al., 2002)
		CT						27	
Terbuthylazine	5	NT (20)	0-30/40	112-210	9.0-18.0	-	0.25, 0.42	3.5, 9.7	(Düring and Hummel, 1999)
		CT		151-217	9.0-1.0	-		5.2, 12.2	
Terbuthylazine	10	NT	0-15	280	19.0	7.3	saturation	11	(Singh N. et al., 2002)
		CT						6	

¹ Codes of tillage practices are reported in Table I.² Numbers in parenthesis indicate the age in years the tillage system.³ Hyphens are used to indicate the range of variation of values.

Seyfried and Rao, 1987; Sigua et al., 1995) and fluometuron (Essington et al., 1995) under wet soil initial conditions. A better understanding of the effect of the initial water content on the dynamics of macropore flow is thus needed to improve the control of pesticide leaching and to complement modelling efforts. An illustration is given by Sigua et al. (1995), who observed under laboratory conditions that a decrease in soil matric potential from -1 kPa (near saturation) to -33 kPa led to a decrease of 15% in atrazine leaching.

In addition, the temporal dynamics of preferential flow through macropores needs to be taken into account. During wetting, the number of macropores hydraulically active tends to increase, thus increasing the possibilities of preferential flow (Jaynes et al., 2001; Kung et al., 2000; Malone et al., 2001). However, under unsaturated conditions, macropores are inactive but still the observed movements of solutes through the soil matrix may be faster than those estimated by the convection-dispersion equation.

To describe solute movements in the soil matrix better, the Mobile-Immobile water Model (MIM) has been developed (Coats and Smith, 1964). This model considers that the water-filled pore space is partitioned into two domains: a mobile domain where water can move and solute transport is due to convection and dispersion, and an immobile domain where water is stagnant and solutes move only by diffusion (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). In this model, it is possible to distinguish different degradation and retention kinetics between the two domains (van Genuchten and Wagenet, 1989), allowing a better description of preferential fluxes under unsaturated conditions (Gaston and Locke, 1996; Gaston and Locke, 2000; Pot et al., 2005). This type of preferential flow has been identified for pesticides under both conventional and conservation tillage (Gaston and Locke, 1996; Gaston and Locke, 2000; Singh N. et al., 2002), but laboratory studies on undisturbed soil columns showed that immobile water fractions were higher under conservation tillage than under conventional tillage, with 56 vs. 49% (Singh and Kanwar, 1991) and 56 vs. 35% (Singh N. et al., 2002), respectively. As for macropore fluxes, preferential flows within the soil matrix also seem to increase under wet soil conditions (Shipitalo and Edwards, 1996). Despite its strong impact on solute transfers, little data about the impact of tillage on MIM-type preferential flow has been published and thus further experimental studies are needed.

Intensity and timing of rainfall after treatment are major factors affecting pesticide leaching (Granovsky et al., 1993; Heatwole et al., 1997; Isensee and Sadeghi, 1994; Masse et al., 1996). Their effects may be greater than those generated by tillage (Gaynor et al., 1995; Granovsky et al., 1993; Otto et al., 1997). During small, low-intensity rainfalls, pesticides intercepted by the mulch can be washed off and then can penetrate slowly into the soil matrix where sorption processes can reduce their leaching (Shipitalo et al., 1990). On the contrary, during high-intensity rainfalls, wash-off is significant and the hydrophobicity of organic residues can slow down infiltration and activate preferential flow in macropores (Isensee and Sadeghi, 1994). By removing the mulch under conservation tillage, Sadeghi and Isensee (1997) observed that leach-

ing was reduced and finally, lower losses under conservation tillage than under conventional tillage were measured. Furthermore, high-intensity rainfall generally leads to greater water and solute fluxes than low-intensity rainfall (Quisenberry et al., 1994; Trojan and Linden, 1992), with most pesticide leaching occurring during the first 2 or 3 rains (Fortin et al., 2002). For atrazine, Sigua et al. (1993) showed on undisturbed soil columns collected under no-tillage plots that the intensity of rainfall determines the percentage of losses: 33% of the applied dose for an intensity of 3 mm h^{-1} and 52% at 9 mm h^{-1} . In addition, if a small and low-intensity rainfall (1.5 mm for Sadeghi and Isensee, 1997, or 5 mm for Shipitalo et al., 1990) preceded a leaching event, then pesticide transport could be reduced by 50% compared with treatments that did not receive this preliminary rain. Moreover, these studies also showed that allowing time for sorption and diffusion in the soil matrix to occur can reduce pesticide movements in soils.

Some questions remain about how rapidly soil hydraulic properties change and preferential flow paths develop when tillage is modified. Very few data have been published on this aspect. In their study, Isensee and Sadeghi (1996) reversed the tillage of 7-year-old no-tillage and conventional tillage plots on which preferential flows had been previously observed (Isensee and Sadeghi, 1994; Isensee et al., 1990; Sadeghi and Isensee, 1992). They found that, immediately after ploughing, preferential flows under the new conventional tillage had disappeared and that sufficient macropore pathways were developed under the new no-tillage in only one year without tillage, leading to significant leaching differences. However, it seemed that two years were required before preferential transport systems became well established. Moreover, in the new conventional tillage, the macropore network inherited from 7 years of no-tillage and situated below the newly ploughed horizon appeared to be functional and preferential flow could still occur (Isensee and Sadeghi, 1997). Soil structural stability, which depends on soil texture, also greatly influences the dynamics of preferential flow (Singh et al., 2002). For example, in four soils of various textures under no-tillage, clay content enhanced macropore stability, leading to a leaching of atrazine 40% higher than for a sandy soil (Sadeghi et al., 2000).

Most of the studies about the effects of tillage on leaching compare contrasted techniques such as ploughing and no-tillage. Other conservation techniques such as mulch tillage or ridge tillage are still poorly studied in terms of pesticide leaching. In some studies of mulch tillage systems, greater leaching of atrazine, cyanazine, simazine and metolachlor was measured compared with conventional tillage (Watts and Hall, 1996). To the contrary, other studies did not find any differences in atrazine and metolachlor leaching between mulch tillage and conventional tillage, concluding that the differentiation between these systems was too weak (Fortin et al., 2002). Between mulch tillage and ridge tillage systems, differences in the migration of atrazine were also poorly marked (Kitchen et al., 1998). However, localisation of the herbicide in seed rows under ridge tillage allowed a decrease by a factor of 3 in the applied doses and could significantly reduce losses by leaching (Lamb et al., 1998; Lowery et al., 1998). In their study comparing three different tillage systems, Mazzoncini et al.

(1998) observed a deeper migration of diclofop-methyl after a heavy rainfall under no-tillage, while the pesticide was found mainly in the seedbed layer (0–5-cm depth) under mulch and conventional tillage.

4.3. Runoff

Agricultural runoff is the primary mechanism contributing to pesticide contamination of surface waters. The main objective of conservation tillage is to reduce runoff and soil erosion (Gebhardt et al., 1985).

Runoff is also affected by pesticide properties. Sorption properties directly act on the dominant mode of transport. For pesticides that have a high sorption capacity on organo-mineral particles, such as glyphosate, trifluralin, paraquat or organochlorine pesticides, surface transport is associated with erosion and soil particle transport (Wauchope, 1978). Potter et al. (2004) indicated that 55% of pendimethalin ($K_{OC} = 5000 \text{ L kg}^{-1}$) losses were bound to sediment. However, for most pesticides, transport to surface water is realised in solution in water runoff (Wauchope, 1978). Losses in solution represented from 88 to 97% of total losses of alachlor and cyanazine (Hansen et al., 2001), 99.8% of atrazine losses (Basta et al., 1997) and, according to tillage practices, from 89 to 98% of fluometuron losses (Potter et al., 2004). For herbicides transported only in solution, such as chlorimuron and nicosulfuron, the interest of conservation techniques, especially no-tillage used to control erosion, is very limited (Afyuni et al., 1997). For some authors, however, pesticide transport in solution may be overestimated due to desorption from suspended sediments during runoff or sample storage and thus the importance of the solid phase as a source of pesticides in runoff would be underestimated (Hansen et al., 2001).

Logan et al. (1994) compared the effects of conventional tillage and no-tillage on the transport of atrazine, alachlor, metolachlor and metribuzin by runoff. No difference between tillage systems was found but runoff losses were positively correlated with the half-lives of the molecules. In other studies, water solubility directly determines the loss by runoff and explains differences in behaviour between alachlor and cyanazine (Hansen et al., 2001) or between atrazine and metribuzin (Gaynor et al., 2001). Isoxaflutole has a low solubility in water but its hydrolysis forms a diketonitrile metabolite (active ingredient) which is 50 times more soluble and thus transported by runoff (Rector et al., 2003). However, mainly because of analytical costs, metabolite monitoring in runoff is not systematic even in research studies. For fluometuron, Potter et al. (2004) indicated that 50% of the herbicide losses occurred as desmethylfluometuron metabolite. Results of runoff losses for some molecules, such as atrazine or fluometuron, are often contrasted under conservation tillage despite similar water solubility and retention by organic compounds. Potter et al. (2003) suggested a relationship to predict the mode of transport of pesticides (in solution or adsorbed) based on their K_{OC} and their solubility.

Pesticide solubility may vary according to formulation. For example, micro-encapsulation of alachlor increases its solubility, allowing a faster migration within the soil matrix and a decrease in its runoff compared with the commercial formulation (Isensee and Sadeghi, 1993). Metolachlor solubility is higher than that of atrazine but it may be reduced by its formulation, which may then limit its runoff compared with atrazine (Sadeghi and Isensee, 2001).

Concerning soil properties, increasing soil organic matter content in topsoil improves soil aggregate stability and cohesion, leading to a significant decrease in soil loss (Rhoton et al., 2002). It appears, however, that tillage effects on pesticide transfer by runoff or erosion are, as for leaching, mixed (Tab. VIII). Many works highlighted a decrease in pesticide losses by runoff under conservation tillage due to a decrease in water runoff volume as the degree of tillage is reduced (Seta et al., 1993; Tebrügge and During, 1999; Watts and Hall, 1996; Webster and Shaw, 1996). However, in some studies, pesticide concentrations in runoff from conservation tillage plots, especially no-tillage plots, were higher than in runoff from conventional tillage plots. As a consequence, conservation tillage plots may generate greater pesticide losses despite a lower water runoff volume (Heatwole et al., 1997; Kenimer et al., 1987; Shipitalo and Owens, 2006; Webster and Shaw, 1996). In other studies, water runoff volume was higher under conservation tillage (Gaynor et al., 1995; Myers et al., 1995). A review of tillage effects by Fawcett et al. (1994) concluded that, under natural rainfall, conservation tillage was efficient in controlling runoff, erosion and pesticide losses. Under simulated rainfall, the amount and intensities of water applied shortly after treatment resulted in very mixed results in conservation tillage. For Fawcett et al. (1994), intensive rainfall was more an indicator of the limits of the efficiency of conservation tillage to control runoff rather than an accurate representation of their effects under real field conditions. Modelling was used to identify and classify the most suitable practices to control atrazine runoff in a watershed (Harman et al., 2004). In this study, conservation tillage was found to be marginally effective. The most effective practices were: sediment retention ponds, grass filter strips, atrazine application at planting time in bands and wetlands construction. According to these contradictory results, it seems necessary to clarify the main conditions and mechanisms involved in pesticide transfer by runoff that may lead to an efficient or inefficient control of losses by conservation tillage.

Rainfall is the most important parameter controlling water runoff, soil erosion and pesticide loss. Depending on its arrival time after treatment, its intensity and the interval between two rainfall events, rainfall can lead to very contradictory results for the same study site, the same molecule or even the same practice (Baker and Johnson, 1979). Pesticide transport in soils directly depends on the interval between treatment and the first rainfall (Baker and Johnson, 1979; Potter et al., 2004; Shipitalo and Owens, 2003). Several studies indicated that conservation tillage was inefficient in controlling runoff when heavy rainfall occurs quickly after pesticide application (Rector et al., 2003; Shipitalo and Owens, 2003; Shipitalo and Owens, 2006). Moreover, most pesticide loss by

Table VIII. Field studies of water and pesticide runoff under simulated (S) or natural (N) rainfall under different tillage practices.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Soil properties		Slope %	Rainfalls		Runoff		Reference
			Clay	Organic carbon (OC) g kg ⁻¹		mm	Type	water % applied dose	pesticide % applied dose	
Alachlor	2.24	NT	-	-	-	-	-	13, 4, 12, 8 ³	7.1, 0.45, 1.8, 0.1 ³	(Baker and Johnson, 1979)
		RT	-	5.8-17.4 ²	-	12-18 ²	N ⁴	17, 4, 8, 8	8.0, 0.8, 0.45, <0.1	
		CT	-	-	-	657, 487, 463, 425 ³	-	17, 8, 18, 9	14.3, 0.7, 4.1, 0.2	
Alachlor	2.80	NT	-	-	-	-	-	34, 41	0.32, 4.8	(Sauer and Daniel, 1987)
		MT _{Ch}	220	17.4	6	136	N	28, 54	0.25, 2.1	
		RT	-	-	-	-	-	35, 54	0.36, 6.0	
Alachlor	1.79	CT	-	-	-	-	-	44, 48	0.29, 3.0	(Isensee and Sadeghi, 1993)
		NT	-	7.4-23.7	3-5	-	-	4-6, 3-4 ¹	0.22-0.24, 0.15-0.24	
		CT	-	6.6-6.9	-	-	-	5-6, 3-5	0.48-0.57, 0.15-0.28	
Alachlor	3.36	NT C ⁵	-	-	-	67	-	19	0.06	(Felsot et al., 1990)
		NT U/D ⁵	-	12.8	-	66	S ⁴	34	0.08	
		CT C	-	-	7-11	67	-	27	0.1	
Alachlor	3.36	CT U/D	-	-	-	56	-	58	0.2	(Felsot et al., 1990)
		NT C ⁵	-	-	8	63	-	6	0.09	
		NT U/D ⁵	-	-	8	64	-	23	2.1	
Alachlor	3.36	ST C	-	-	9	64	-	4	0.06	(Felsot et al., 1990)
		ST U/D	-	-	9	63	-	10	0.6	
		RT C	-	12.8	10	64	S	24	0.75	
Alachlor	3.36	RT U/D	-	-	10	63	-	29	1.3	(Felsot et al., 1990)
		MT _{Ch} C	-	-	8	64	-	33	1.7	
		MT _{Ch} U/D	-	-	8	64	-	32	1.2	
Alachlor	3.36	CT C	-	-	10	63	-	33	2.3	(Felsot et al., 1990)
		CT U/D	-	-	10	64	-	43	6.5	
Alachlor	2.24-3.36	NT 1	-	-	11	629-1012	-	1-10	Tr-0.23	(Shipitalo et al., 1997)
		NT 2	-	-	10	686-1025	N	2-14	0.01-0.19	
		MT _{Ch} 1	-	-	13	609-981	-	< 0.01 - 1	Tr-<0.01	
Alachlor	2.2	MT _{Ch} 2	-	-	7	663-1007	-	1-15	Tr-0.22	(Hansen et al., 2001)
		MT _{Ch}	-	14.0	7.1	-	-	-	0.4, 0.2	
		RT	-	17.4	8-10	-	-	-	0.1, 0.1	
Alachlor	2.2	CT	-	13.4	-	240, 480	N	-	1.0, 0.6	(Hansen et al., 2001)
		MT _{Ch}	-	14.0	-	-	-	-	0.1, 0.06	
		RT	-	17.4	-	-	-	-	0.1, 0.06	
Alachlor ⁷	1.68	CT	-	13.4	-	-	-	-	0.2, 0.06	(Shipitalo and Owens, 2006)
		NT	-	-	10-11	976	-	8	0.28	
		MT _{Ch}	-	-	7-13	953	N	7	0.11	
Atrazine	1.7	MT _{Dk}	-	-	6-9	960	-	11	0.12	(Watts and Hall, 1996)
		NT	-	-	-	-	-	-	0.06, -	
		MT mulch	-	-	3-5	-	-	-	-, 0.28	
Atrazine	1.68	CT	-	-	-	-	-	-	0.18, 0.77	(Heatwole et al., 1997)
		NT	67	9.7	5.64	-	-	-	0.7	
		CT	59	4.4	5.91	-	-	-	1.5	

Table VIII. Continued.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Soil properties		Slope pH	Rainfalls mm	Runoff		Reference
			Clay	Organic carbon (OC) g kg ⁻¹			Type	% applied dose water	
Atrazine (+ DEA + DIA)	2.24	NT 1	-	-	- 13	-	-	4-7	0.027-0.82
	2.24	NT 2	-	-	- 7	-	-	6-15	0.049-4.95
	2.24	MT _{Ch} 1	-	-	- 11	-	-	0.1-2	Tr-0.011
	2.24	MT _{Ch} 2	-	-	- 10	-	-	9-18	0.0045-2.62
	1.12	MT _{Dk} 3	-	-	- 6	-	-	7-17	0.034-0.64
	1.12	MT _{Dk} 4	-	-	- 7	-	-	4-8	0.0010-0.59
	1.12	MT _{Dk} 5	-	-	- 9	-	-	10-22	0.0043-6.37
Atrazine	2.24	NT	-	5.8-17.4	- 12-18	657, 487	N	13, 4	7.1, 0.75
		RT	-					17, 4	19.2, 1.8
Atrazine		CT	-					18, 8	20.1, 0.09
		NT							
	2.80	MT _{Ch}	220	17.4	- 6	136	-	34, 41	0.32, 7.3
Atrazine		RT						28, 54	0.21, 3.0
		CT						35, 54	0.34, 8.7
		CT						44, 48	0.25, 4.3
Atrazine	2.24	NT	-	-	- -	941, 1158, 824, 926, 1029, 860	-	5, 6, 7, 18, -, 1	2.5, 1.9, 1.0, 5.1, -, 2.0
		MT	-	-	- -		-	1, 4, 7, 18, 18, 1	1.1, 0.3, 0.6, 1.5, 4.0, 2.1
Atrazine	1.34	NT	-	7.4-23.7	3-5	-	-	4-6, 3-4	1.39-1.51, 0.56-0.90
		CT	-	6.6-6.9	-	-	-	5-6, 3-5	0.81-0.97, 0.21-0.47
Atrazine	1.7	NT	-	12.0	6.7	-	-	-, 0.1, <0.01, 0.02	-, 0.10, <0.01, <0.01
		CT	-		3-4	-	-	0.3, 0.3, 0.03, 0.04	0.36, 0.33, 0.02, <0.01
Atrazine		NT	-	-	-			6	0.7
	2.24	MT	-	-	- 9	132	S	22	1.3
		CT	-	-	-			34	1.8
Atrazine	2.24	NT	232	21.5	- 10.3	100	S	0.2	0.28
		CT			- 10.6			3	2.85
Atrazine	0.56	NT (1) ⁸	-	9.5	4.9	80	S		7.9
		MT _{Ch}	-						10.5
Atrazine		MT _{Dk}	-						7.5
		NT 1	-	-	- 11	629-1012		1-10	< 0.01 - 0.08
	2.24	NT 2	-	-	- 10	686-1025	N	2-14	< 0.01 - 1.10
		MT _{Ch} 1	-	-	- 13	609-981		< 0.01 - 1	< 0.01
Atrazine		MT _{Ch} 2	-	-	- 7	663-1007		1-15	< 0.01 - 0.91
		NT (2) - M. ⁹						31-50, 35-38	2.2-9.4, 2.1-4.7
Atrazine	1.6	NT - Sil. ⁸	210	9.1	5.9	31.7-50.8	S	31-56, 35-48	1.7-8.1, 1.9-2.5
		CT						16-24, 34-47	0.5-1.6, 1.7-3.0
Atrazine	0.9	NT (4)	-	-	-			-	4.99 / 10.51
	0.9 Inc. ¹⁰	CT	-	13.4	6.0		N / N+S	-	1.26 / 2.73
	0.9	CT	-		-			-	2.48 / 7.72
	1.8	NT (4)	-		-			-	2.64 / 7.52
Atrazine	0.55	MT _{Ch} + Cov. ¹¹						8, 7	0.1, 1.8
		MT _{Ch}	-	14.5	- < 1	995, 688	N	14, 9	0.4, 1.5
		CT + Cov.C						8, 6	0.4, 0.7
		CT						12, 7	0.6, 1.8
Atrazine ⁷		NT	-	-	- 10-11	976	N	8	1.29
	2.24	MT _{Ch}	-	-	- 7-13	953		7	0.66
		MT _{Dk}	-	-	- 6-9	960		11	0.92

Table VIII. Continued.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Soil properties		Slope pH	Rainfalls mm	Runoff		Reference
			Clay	Organic carbon (OC) g kg ⁻¹			Type	% applied dose	
Carbofuran	1.12	NT C	-	-	-	67	19	0.2	(Felsot et al., 1990)
		NT U/D	-	12.8	-	66	34	0.6	
		CT C	-	-	7-11	67	27	0.1	
		CT U/D	-	-	-	56	58	1.21	
Chlorimuron	0.014	NT	80	5.3	5.9	0-1	-	2.0	(Afyuni et al., 1997)
		CT	-	-	-	-	-	1.3	
Chlorpyrifos	1.34	NT	-	-	-	-	34, 41	0.04, 0.10	(Sauer and Daniel, 1987)
		MT _{Ch}	220	17.4	-	136	28, 54	0.05, 0.29	
		RT	-	-	6	-	35, 54	0.06, 0.28	
		CT	-	-	-	-	44, 48	0.08, 0.20	
Cyanazine	2.24	NT	-	-	-	-	12, 8	4.5, 0.2	(Baker and Johnson, 1979)
		CT	-	5.8-17.4	-	463, 425	8, 8	2.0, 0.1	
Cyanazine	1.34	NT	-	7.4-23.7	-	-	4-6, 3-4	1.30-1.91, 0.50-0.68	(Isensee and Sadeghi, 1993)
		CT	-	6.6-6.9	-	-	5-6, 3-5	0.52-0.84, 0.15-0.27	
Cyanazine	2.2	NT	-	12.0	6.7	-	-	-	(Hall et al., 1991)
		CT	-	-	3-4	-	-	-	
Cyanazine	2.1	MT _{Ch}	-	14.0	-	-	-	2.0, 0.9	(Hansen et al., 2001)
		RT	-	17.4	-	-	-	0.38, 0.8	
		CT	-	13.4	7.1	8-10	-	4.4, 1.0	
		MT _{Ch}	-	14.0	-	240, 480	-	0.8, 0.2	
Cyanazine	0.7 Loc ⁶	RT	-	17.4	-	-	-	0.6, 0.2	(Watts and Hall, 1996)
		CT	-	13.4	-	-	-	0.8, 0.2	
Cyanazine	2.2	NT	-	-	-	-	-	0.02, -	(Watts and Hall, 1996)
		CT	-	-	3-5	-	-	-	
Dicamba	0.56	NT	-	12.0	6.7	-	-	-	(Hall and Mumma, 1994)
		CT	-	-	3-4	-	-	-	
Dimethipin	0.35	ST (1)	32	5.1	6.5	-	23	5.0	(Potter et al., 2003)
		CT	-	-	3-4	-	23	1.6	
Fluometuron	1.7	NT	-	-	-	-	6	8.0, 5.3	(Baughman et al., 2001)
		CT	-	18.6	6.4	376, 480	5	8.2, 3.2	
Fluometuron	2.0	ST	-	-	-	63.8	20	1.4	(Potter et al., 2006)
		ST	32	5.1	6.5	64.3	23	1.9	
		CT	-	-	3-4	62.7	45	0.8	
		CT	-	-	-	60.0	50	0.6	
Fonofos	1.12	NT	-	5.8-17.4	-	-	4, 12, 8	0.18, 1.3, 0.05	(Baker and Johnson, 1979)
		CT	-	-	12-18	487, 463, 425	4, 8, 8	0.09, 0.25, nd	
Imazaquin	0.14	SS (3)	660	16.9	6.4	NA	-	1.22, 3.39	(Seifert et al., 2001b)
		CT	-	-	-	-	-	1.53, 3.63	
Isoxaflutole/ diketonitrile	0.11	NT (4)	-	-	-	-	-	2.82 / 9.24	(Rector et al., 2003)
		CT	-	-	-	-	-	0.93 / 3.35	
		CT	-	13.4	6.0	1-2	-	1.63 / 6.75	
		NT (4)	-	-	-	-	-	2.35 / 6.84	

Table VIII. Continued.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Soil properties		Slope pH	Rainfalls mm	Type	Runoff		Reference
			Clay	Organic carbon (OC) g kg ⁻¹				water % applied dose	pesticide % applied dose	
Linuron	1.12	NT 1	-	-	- 11	629-1012		1-10	< 0.01 - 0.01	(Shiptalo et al., 1997)
		NT 2	-	-	- 10	686-1025	N	2-14	< 0.01 - 1.04	
		MT _{Ch} 1	-	-	- 13	609-981		< 0.01 - 1	< 0.01	
		MT _{Ch} 2	-	-	- 7	663-1007		1-15	< 0.01 - 0.46	
Linuron ⁶	1.12	NT	-	-	- 10-11	976	N	8	0.70	(Shiptalo and Owens, 2006)
		MT _{Ch}	-	-	- 7-13	953		7	0.29	
		MT _{Dk}	-	-	- 6-9	960		11	0.21	
Metolachlor	3.4	NT - S/W ¹³	-	-	-			8, 7, 9	0.4, 0.2, 0.6	(Webster and Shaw, 1996)
		NT - Soy ¹³	-	18.6	6.4 3	213, 191, 188	N+S	~ 14, 18	~ 1.4, 0.3	
		CT - S/W	-	-	-			9, 9, 15	0.8, 1.1, 0.6	
		CT - Soy	-	-	-			9, 5, 10	0.4, 0.5, 0.8	
Metolachlor	1.9	NT (2) - M. ⁹	-	-	-			31-50, 35-38	1.2-9.0, 0.9-4.3	(Myers et al., 1995)
		NT - Sil. ⁹	210	9.1	5.9 2-6	31.7-50.8	S	31-56, 35-48	1.4-8.0, 0.8-1.8	
Metolachlor	2.2	CT	-	12.0	6.7 3-5	-	-	16-24, 34-47	0.4-1.5, 1.1-2.7	(Hall et al., 1991)
		CT	-	-	- 3-4	-	-	~ 0.1, < 0.01, 0.02	~ 0.06, < 0.01, < 0.01	
Metolachlor	2.2	NT	-	-	-			0.3, 0.3, 0.03, 0.04	0.16, 0.25, 0.01, < 0.01	(Watts and Hall, 1996)
		MT mulch	-	-	- 3-5	585, 748, 486, 562	N	-	0.03, -	
Metolachlor	2.24	CT	-	-	-			-	~ 0.22	(Heatwole et al., 1997)
		CT	67	9.7	5.64 2	-	-	-	0.29, 0.55	
Metolachlor	1.12-1.87	NT	-	-	-			0.5	1.2	(Chidey et al., 2005)
		CT	59	4.4	5.91	-	-	-	1.2	
		NT	-	-	-	941, 1158, 824, 926, 1029, 860	N	5, 6, 7, 18, ~ 1	5.5, 1.0, 0.9, 2.1, ~ 0.3	
		MT	-	-	-	-		1, 4, 7, 18, 18, 1	2.0, 0.4, 1.2, 1.6, 5.4, 0.4	
Metolachlor	0.84	MT _{Ch} + Cov.C ¹¹	-	-	-			8, 7	0.06, 0.8	(Gaynor et al., 2001)
		MT _{Ch}	-	14.5	- < 1	995, 688	N	14, 9	0.2, 1.0	
		CT + Cov.C	-	-	-			8, 6	0.3, 0.5	
		CT	-	-	-			12, 7	0.4, 1.4	
Metolachlor	0.7	NT (4)	-	-	-			-	4.22/8.28	(Rector et al., 2003)
		CT	-	13.4	6.0 1-2	-	N/N+S	-	1.01 / 1.97	
		CT	-	-	-			-	2.22 / 5.98	
		NT (4)	-	-	-			-	2.44 / 6.01	
Metribuzin	0.38	NT 1	-	-	- 11	629-1012		1-10	< 0.01 - 0.79	(Shiptalo et al., 1997)
		NT 2	-	-	- 10	686-1025	N	2-14	0.08-0.22	
		MT _{Ch} 1	-	-	- 13	609-981		< 0.01 - 1	< 0.01 - 0.02	
		MT _{Ch} 2	-	-	- 7	663-1007		1-15	< 0.01 - 0.01	
Metribuzin ⁷	0.38	NT	-	-	- 10-11	976	N	8	0.83	(Shiptalo and Owens, 2006)
		MT _{Ch}	-	-	- 7-13	953		7	0.04	
		MT _{Dk}	-	-	- 6-9	960		11	0.55	
Metribuzin	0.25	MT _{Ch} + Cov.C ¹¹	-	-	-			8, 7	0.04, 1.1	(Gaynor et al., 2001)
		MT _{Ch}	-	14.5	- < 1	995, 688	N	14, 9	0.3, 1.4	
		CT + Cov.C	-	-	-			8, 6	0.3, 0.6	
		CT	-	-	-			12, 7	0.3, 1.7	
Metribuzin	0.4	NT - S/W ¹³	-	-	-			8, 7, 9	0.7, 0.5, 0.7	(Webster and Shaw, 1996)
		NT - Soy ¹³	-	18.6	6.4 3	213, 191, 188	N+S	~ 14, 18	~ 1.9, 0.6	
		CT - S/W	-	-	-			9, 9, 15	1.7, 1.6, 0.9	
		CT - Soy	-	-	-			9, 5, 10	0.9, 0.8, 1.4	
Metribuzin	0.816	NT	120	13.0	- 10	294	N	0.2	0.01	(Malone et al., 1996)
		CT	-	-	-			15	0.64	

Table VIII. Continued.

Pesticide	Dose kg a.i. ha ⁻¹	Tillage ¹	Soil properties		Slope		Rainfalls		Runoff		Reference
			Clay	Organic carbon (OC)	pH	%	mm	Type	water % applied dose	pesticide % applied dose	
Nicosulfuron	0.014	NT	80	5.3	5.9	0-1	-	-	-	2.3	(Afyuni et al., 1997)
		CT						-	-	1.1	
Norflurazon	1.7	NT						6		4.2, 4.2	(Baughman et al., 2001)
		CT	-	18.6	6.4	3	376, 480	N+S	5	4.2, 2.5	
Pendimethalin	1.0	ST					63.8	S - I _{Var} ¹²	20	4.8, 3.6	
		ST					64.3	S - I _{cons}	23	0.4	
		CT	32	5.1	6.5	3-4	62.7	S - I _{Var}	45	5.0	(Potter et al., 2006)
		CT					60.0	S - I _{cons}	50	4.1	
Simazine	1.7	NT	-	12.0	6.7	3-5	-	-	0.1, <0.01, 0.02	0.18, <0.01, <0.01	(Hall et al., 1991)
		CT				3-4		-	0.3, 0.3, 0.03, 0.04	0.62, 0.51, 0.03, <0.01	
Simazine	1.7	NT						-	-	0.02, -	
		CT	-	-	-	3-5	-	-	-	0.13	(Watts and Hall, 1996)
Terbufos + Terbufos metabolites	1.12	NT C				8	63	6		0.03	
		NT U/D				8	64	23		0.3	
		ST C				9	64	4		0.03	
		ST U/D				9	63	10		0.2	
		RT C				10	64	24		0.4	
		RT U/D	-	12.8	-	10	63	29		2.3	(Felsot et al., 1990)
		MT _{Ch} C				8	64	33		1.4	
		MT _{Ch} U/D				8	64	32		1.3	
		CT C				10	63	33		1.6	
		CT U/D				10	64	43		7.5	
		ST (1) ⁸	32	5.1	6.5	3-4	-	S	23	13.7	(Potter et al., 2003)
		CT							23	12.2	
Tribufos	0.30	ST (1)	32	5.1	6.5	3-4	-	S	23	12.8	(Potter et al., 2003)
		CT							23	14.5	
2,4-D	0.56	NT	232	21.5		10	100	S	0.2	0.02	(Kenimer et al., 1987)
		CT				11			3	0.27	

¹ Codes of tillage practices are reported in Table I.² Hyphens are used to indicate the range of variation of values.³ Commas are used to separate different years of study.⁴ N: natural rainfall; S: simulated rainfall.⁵ C: contoured slope; U/D: up-and-down slope.⁶ Loc: seed row localisation of the pesticide treatment.⁷ Average results for 9 years of study.⁸ Numbers in parenthesis indicate the age in years of the soil tillage.⁹ M.: maize = residues restituted; Sil.: silage = no crop residues.¹⁰ Inc.: preplant soil incorporation of herbicide.¹¹ Cov.C: cover crop.¹² I_{Var}: variable rainfall intensity; I_{cons}: constant rainfall intensity.¹³ Soy: continuous soybean; S/W: soybean/wheat rotation.

runoff occurred during the first few runoff events after application (Seifert et al., 2001a; Shipitalo and Owens, 2006). In a 9-year-study comparing three types of conservation tillage (NT, MT_{Ch} and MT_{Dk}), Shipitalo and Owens (2006) indicated that 60 to 99% of herbicide (alachlor, atrazine, linuron, and metribuzin) losses were due to the five largest transport events. After a rainfall representing 3% of annual rainfall and occurring 2 days after treatment, atrazine losses reached 4.7% of the applied dose (Shipitalo and Owens, 2003). Triplett et al. (1978) proposed a linear relationship to predict atrazine concentrations in runoff ($[\text{atrazine}]_{\text{runoff}}$) based on the number of days after treatment ($\ln([\text{atrazine}]_{\text{runoff}}) = a + b \cdot \ln(\text{number of days after treatment})$). This relationship has been tested and used for several pesticides such as alachlor (Shipitalo et al., 1997), atrazine and its metabolites (deethylatrazine and deisopropylatrazine) (Gaynor et al., 1995; Shipitalo and Owens, 2003; Shipitalo et al., 1997), cyanazine (Franti et al., 1998), linuron (Shipitalo et al., 1997), dimethipin (Potter et al., 2003), metolachlor (Gaynor et al., 1995; Ghidry et al., 2005; Webster and Shaw, 1996), metribuzin (Shipitalo et al., 1997), thidiazuron and tribufos (Potter et al., 2003). However, Hansen et al. (2001) indicated that the relationship between $\ln[\text{pesticide}]_{\text{runoff}}$ and $\ln(\text{number of days after treatment})$ was sensitive to annual variability in weather and may not be a good variable for simple estimates of herbicide concentration in runoff. They recommended the use of cumulative rainfall as a variable for estimating concentration in runoff: $\ln[\text{pesticide}]_{\text{runoff}} = a + b \cdot \ln(\text{cumulative rainfall})$. The intensity of the first rainfall also influences the fate of the applied molecules. A small, low-intensity rainfall occurring a few days after treatment allows the incorporation of pesticide within the topsoil horizon, thus reducing losses during subsequent runoff events (Afyuni et al., 1997; Gaynor et al., 1995; Olson et al., 1998).

As for leaching, the initial soil water content is also a key factor controlling runoff. Runoff due to exceedance of infiltration capacity was found to occur earlier under no-tillage than under conventional tillage (Isensee and Sadeghi, 1993; Rector et al., 2003; Sadeghi and Isensee, 2001). In hydromorphic soils, saturation occurred more rapidly under no-tillage and runoff was more significant than under conventional tillage (Ghidry et al., 2005). Soil tillage, even superficial, increases soil infiltration capacity and drainage, which can limit runoff (Olson et al., 1998). The time interval between two rainfalls may significantly affect runoff volumes under no-tillage. Isensee and Sadeghi (1993) indicated that, for a time interval lower than 7 days between two rainfalls, the high soil water content remaining under no-tillage, favoured by the mulch, led to a significantly higher runoff than under conventional tillage.

The mulch increases soil surface roughness, thus reducing runoff (Isensee and Sadeghi, 1993; Selim et al., 2003). However, the mulch effectiveness in controlling runoff and erosion depends on the nature and quantity of plant residues. For example, Olson et al. (1998) observed that after a soybean crop, the abundance of residues under no-tillage was not sufficient to limit (water and atrazine) runoff and higher runoff volumes than under mulch tillage were measured. For quantities of residues increasing from 0 to 1.5 t ha⁻¹ either remaining on

the soil surface in no-tillage or mixed in the ploughed horizon in conventional tillage, runoff was reduced by 96 and 40%, respectively (Kenimer et al., 1987).

Strip tillage is a conservation tillage well-developed in the US which is starting to be used for spring productions by farmers in Europe. On one hand, strip tillage was found to reduce runoff compared with conventional tillage but, on the other hand, to increase lateral subsurface flow (Bosch et al., 2005). Potter et al. (2003) indicated that, after only one year of strip tillage, no effect on runoff volumes was measured compared with conventional tillage but erosion rates were lower. On the same study site, a few years later, runoff volumes were decreased by a factor of 4 compared with conventional tillage (Potter et al., 2004). Concerning pesticide losses, flumeturon losses were 2 to 3 times higher and pendimethalin losses were 12 times lower under strip tillage than under conventional tillage (Potter et al., 2006). Under strip tillage, herbicide treatments are applied only on the seed row representing only 1/3 of the field surface. In inter-row positions, the soil surface is most often covered by a cover crop, which reduces the risk of runoff (Hansen et al., 2001). Ridge tillage can also be used to reduce runoff but, in some cases, pesticides could migrate from the ridge tops to the furrows and then be transferred by runoff (Gaynor et al., 1987; Olson et al., 1998). Very few studies reported results on the effects of sub-soiling on runoff. Seifert et al. (2001a) did not observe any effect of this tillage practice on runoff and pesticide loss compared with conventional tillage. Pesticide incorporation into soil through superficial tillage was found to significantly reduce losses by runoff (Franti et al., 1998; Olson et al., 1998; Rector et al., 2003) but this technique is not suitable for no-tillage systems and may lead to an increase in losses by leaching. Finally, whatever the tillage system, soil tillage along isotopographic lines rather than up-and-down slope was efficient in reducing transfers by runoff (Felsot et al., 1990).

4.4. Summary and recommendations

Concerning pesticide transfer, it clearly appears that initial soil conditions (water content and temperature) and climatic conditions (rainfall intensity, interval between treatment and the first rainfall) play a large role in the dynamics of water and solutes and may explain the contrasted effects of tillage on pesticide transfers. Improving the understanding of pesticide transport related to tillage operations implies clarifying the temporal and spatial dynamics of solute flows, especially preferential flows, which are in this case particularly relevant. Most of the studies mentioned in this review highlighted the transient and local nature of transport mechanisms, making them difficult to characterise. In the same order of ideas, the lack of efficient and robust ways to quantify soil structure and its dynamics is an impediment to the prediction of pesticide fate and transport, especially in topsoil layers.

The significant effect of rainfall characteristics on pesticide transfers suggests that tillage effects are highly dependent on the type of climate, and its eventual modifications to come. Regional studies should be of great help in developing

generic models for more robust predictions. Tillage is certainly a relevant means of controlling agricultural pesticide impacts on the environment. Pesticide fate in soil implies numerous processes in complex interactions. If one is to improve tillage systems to mitigate these impacts, one needs first to understand how the various tillage practices modify the functional characteristics of soil (water retention, hydraulic conductivity, solute transport, etc.) through detailed, comprehensive studies. Such studies should consider the diversity of tillage systems, which are currently insufficiently explored and documented. Such research efforts would imply long-term studies (> 10 years) to allow significant and well-established differentiation between the cropping systems being compared and would thus involve stability in funding research programmes.

5. CONCLUSION

This review article outlines the four main following points.

1. Pesticide interception is enhanced under conservation tillage practices. The intensity of this process depends on (a) the amount and nature of crop residues which have sorption capacities 10 to 60 times higher than soil, and (b) the climatic conditions, such as the timing between pesticide treatment and the first rainfall and its intensity.
2. Pesticide retention, which is generally positively correlated with organic carbon content, is increased in the top-soil layer under conservation tillage. Desorption of pesticides is also affected by tillage and greater proportions of pesticides remained sorbed on soil particles and on mulch under conservation tillage.
3. As a consequence of points 1 and 2, a lower fraction of pesticide remains available for biological degradation under conservation tillage and, in several cases, pesticide persistence in soils increases. In addition to this lower bio-availability due to retention processes, the presence of crop residues, a lower temperature and a higher acidity under conservation tillage can disrupt or slow down microorganisms' activity. Moreover, a greater availability of carbon under conservation tillage can defer the use of pesticides as a source of carbon.
4. Transport of pesticides is affected by tillage management and by its interactions with climatic conditions – more particularly by the intensity of rainfall, its arrival time after treatment, the interval between two rainfall events – and pesticide properties – e.g. water solubility, retention, half-life and formulation. In a general way, conservation tillage is more efficient in reducing runoff than leaching. Indeed, a higher soil surface roughness due to the presence of crop residues and a greater aggregate stability lead to a significant decrease in pesticide loss in water runoff or bound to eroded sediment, while reducing tillage intensity maintains a well-connected macropore network through which leaching of pesticides is enhanced.

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