

# ENVIRONMENTAL FATE OF S-METOLACHLOR - A REVIEW -

## *Dinâmica Ambiental do Herbicida S-metolachlor - Revisão -*

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**ABSTRACT** - S-metolachlor is a preemergent herbicide used for the control of annual grasses and small-seeded broadleaf weeds in more than 70 agricultural crops worldwide. Recently, S-metolachlor has been used to control imidazolinone-resistant red rice in rice-soybean rotation in lowland environments of the Southern Brazil. However, limited information concerning the environmental fate of S-metolachlor in lowland soil is available in the literature. Thus, this review was designed to describe the major transport and dissipation processes of S-metolachlor in attempting to improve weed management programs used in rice-soybean rotation and mitigate environmental contamination of lowland areas.

**Keywords:** chloroacetamide, degradation, dissipation, transport, retention.

*RESUMO* - S-metolachlor é um herbicida pré-emergente utilizado mundialmente para controle de plantas daninhas em mais de 70 culturas agrícolas. Nos últimos anos, esse herbicida vem sendo usado para controlar arroz-vermelho resistente às imidazolinonas em áreas de rotação soja-arroz irrigado, em terras baixas no Sul do Brasil. No entanto, existem poucas informações consistentes sobre a dinâmica ambiental de S-metolachlor em terras baixas. Nesse contexto, esta revisão teve por objetivo descrever os principais processos de transporte e dissipação de S-metolachlor, visando otimizar o manejo de plantas daninhas na rotação soja-arroz irrigado e mitigar a contaminação ambiental de terras baixas.

**Palavras-chave:** cloroacetamida, degradação, dissipação, transporte, retenção.

## INTRODUCTION

Agricultural systems comprising integrated weed management practices are required to either slow and/or prevent the development of herbicide resistance in weed populations. Recently, rice-soybean rotation has been the most effective method used by rice producers to control imidazolinone-resistant red rice in lowland environments of Southern Brazil. In this system, S-metolachlor has been widely applied due to its alternative mode of action and soil residual activity, providing soybean establishment free of weed interference.

Although S-metolachlor has been applied worldwide for weed control in upland crops, its use in rice-soybean rotation is still recent

in lowland areas of Rio Grande do Sul. Moreover, limited information concerning the environmental fate of S-metolachlor in lowland soil is currently available in the literature. Thus, this review was designed to describe the major transport and dissipation processes of S-metolachlor in attempting to improve weed management programs in rice-soybean rotation and mitigate environmental contamination of lowland areas.

## S-metolachlor

S-metolachlor {2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-[(1*S*)-2-methoxy-1-methylethyl] acetamide} is a nonionic compound belonging to the chloroacetamide herbicides resulting from a proprietary breakthrough in the catalyst system of the

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manufacturing process for metolachlor, which is comprised of 50% *R*- and 50% *S*- isomers (Shaner et al., 2006; Senseman, 2007). *S*-metolachlor is physically and chemically equivalent to metolachlor, but it was enriched with the *S*-isomer that increases its herbicidal activity in susceptible plants (Blaser & Spindler, 1997; Spindler et al., 1998; Senseman, 2007). This enrichment resulted in a substantial reduction of risks to applicators, consumers and the environment since application rates in agricultural crops were reduced by 35% (Shaner et al., 2006).

In Brazil, *S*-metolachlor (Dual Gold® 960 g a.i. L<sup>-1</sup>) was first commercialized in 1998 for the control of annual grasses and some broadleaf weeds in soybean, sugarcane, corn, cotton and dry bean (Rodrigues & Almeida, 2011; Brasil, 2013). This herbicide inhibits very-long-chain fatty acids (VLCFAs) that have more than 18 carbon atoms, impairing cell division and shoot development in susceptible plants (Götz & Böger, 2004; Senseman, 2007). In annual grasses, *S*-metolachlor is absorbed by shoot tissues as they grow through the treated soil (Lebaron et al., 1988) and general symptoms are characterized by malformed and twisted seedlings where leaves are tightly rolled in the whorl and cannot unroll properly (Senseman, 2007). In broadleaf weeds, root absorption is an important pathway for herbicide uptake (Lebaron et al., 1988) and symptoms are typically crinkled leaves with heart shaped appearance (Senseman, 2007).

Depending on crop and variety, *S*-metolachlor can be applied in preplant incorporated (PPI), preemergence (PRE) or early postemergence (EPOST) of tolerant plant species with minimal crop injury under certain conditions (Parker et al., 2005; Senseman, 2007; Bollman et al., 2008). Crop tolerance has been attributed to the ability of plants to rapidly metabolize *S*-metolachlor by detoxification reactions, preventing accumulation at phytotoxic levels in plant cells (Liebl, 1995). This occurs by the cleavage of methyl ether group followed by conjugation with glucose or conjugation of the chloroacetyl group with glutathione (GSH) or homoglutathione in certain legumes (Senseman, 2007).

## Sorption

Adsorption and desorption are key processes controlling herbicide efficacy and dissipation in soil as well as the potential to contaminate air and water (Laabs & Amelung, 2005). Nonionic herbicides such as *S*-metolachlor can be sorbed to soil particles by Van der Waals forces, hydrophobic partitioning, charge-transfer complexes, ligand exchange and covalent bonding or a combination of these interactions (Berry & Boyd 1985; Dec & Bollag 1997).

Sorption of *S*-metolachlor in soil has been positively correlated to organic matter and clay content (Weber et al., 2003; Gannon et al., 2013). A variation in organic matter content from 0.9 to 5.7% increased the sorption coefficient ( $K_d$ ) of metolachlor by approximately 6-fold (Weber et al., 2003). Another study demonstrated that  $K_d$  values of *S*-metolachlor were 1.08 and 9.32 L kg<sup>-1</sup> in soils with 1.2 and 4.5% organic matter content, respectively (Gannon et al., 2013). In addition, as organic matter content gradually decreases with depth in the soil profile, an increase on herbicide retention in the topsoil layer is expected (Alletto et al., 2010). This was reported by Bedmar et al. (2011) who found 1.78-fold higher adsorption of *S*-metolachlor in soil surface (0-5 cm) with 4.4% of organic carbon than in subsurface soil (>81 cm) with 0.2% of organic carbon content.

Organic matter and clay content also influence desorption process of *S*-metolachlor. In general, metolachlor exhibits hysteresis in soils with high organic matter and clay content (Youbin et al., 2009). This process occurs due to the existence of irreversible binding interaction with the soil constituents or slowly reversible chemical sorption that causes a decrease in the desorbed amount of the herbicide (Zhu & Selim, 2000; Youbin et al., 2009). Metolachlor hysteresis has been demonstrated by Pignatello & Huang (1991), Zhu & Selim (2000) and Youbin et al. (2009).

## TRANSPORT

Herbicide transport is characterized by the movement *in* and *out* of the soil matrix as well as the way herbicides reach ground and

surface water and/or the atmosphere. S-metolachlor can be transported to different environmental compartments by runoff, volatilization and leaching.

### Runoff

The agricultural runoff is the primary process that contributes to herbicide contamination of surface water (Krutz et al., 2005). In this process, herbicides are transported dissolved in water or adsorbed to eroded soil particles by rainfall or irrigation from a treated area (Leonard, 1990; Arora et al., 2003). Water-monitoring studies have confirmed contamination of reservoirs (Thurman et al., 1996), lakes (Thurman et al., 2000), streams (Scribner et al., 2000) and rivers (Grutzmacher et al., 2008; Silva et al., 2009; Marchesan et al., 2010) by several pesticides. S-metolachlor has been one of the most commonly detected herbicide (Thurman et al., 1996, 2000; Scribner et al., 2000) due to its moderate water solubility ( $488 \text{ mg L}^{-1}$ ) and sorption to the soil particles ( $K_{oc}$  of  $200 \text{ mL g}^{-1}$ ) (Senseman, 2007).

Several factors may affect S-metolachlor runoff in agricultural fields. For example, researches showed that the first rainfall event after herbicide application is highly correlated to herbicide export *out* of treated area. It has been also reported that the shorter the interval between rainfall event and the S-metolachlor application, the greater is the herbicide export (Rector et al., 2003; Southwick et al., 2009; Caron et al., 2012). Application method is another important factor affecting S-metolachlor runoff. Runoff losses were reduced by 69% when S-metolachlor was applied in preplant incorporated instead of soil-surface applications (Rector et al., 2003). According to the authors, mechanical incorporation of S-metolachlor in soil also reduced runoff by decreasing the herbicide amount present in the mixing zone, the layer where rainfall and runoff interacts (Baker & Laflen, 1979; Hall et al., 1983; Rector et al., 2003). At the same study, S-metolachlor applications at  $0.7 \text{ kg ha}^{-1}$  decreased in 58% runoff compared to similar application at  $1.4 \text{ kg ha}^{-1}$  (Rector et al., 2003).

S-metolachlor runoff is a major concern in many watersheds because intensive

agriculture may be adjacent to sensitive ecosystems. Vegetative filter strip (VFS) is an effective approach used along field edges and water bodies to reduce herbicide runoff from cultivated fields (Otto et al., 2012). VFS allows reducing runoff flux, volume and herbicide concentration in the runoff water by increasing herbicide retention to organic matter and soil sediments. S-metolachlor concentration in runoff water from a 6-m VFS was significantly reduced when compared to a non-VFS area at the first rainfall event after herbicide application (Milan et al., 2013). Also, 3-m long grass VFS resulted in 77% less runoff when simulated rainfall was applied 14 days after herbicide application (Pätzold et al., 2007). Under field conditions, an average of 54.4% of the total metolachlor applied was retained by VFS (Arora et al., 2003).

### Volatilization

Herbicide transport into the atmosphere involves the movement of molecules from soil or vegetated surfaces and dispersion into the boundary layer of the atmosphere by diffusion and turbulent mixing (Taylor, 1995). In other words, volatilization represents the sum of all the processes required to transfer chemical molecules from soil or plant surface to atmosphere (Bedos et al., 2002). As S-metolachlor exhibits relatively low Henry's Law constant ( $2.4 \times 10^8 \text{ atm m}^3/\text{mole}$  at  $25 \text{ }^\circ\text{C}$ ) and vapor pressure ( $1.73 \times 10^{-3} \text{ Pa}$  at  $20 \text{ }^\circ\text{C}$ ) (Table 1), volatilization losses are considered minimal but they still occur under certain environmental conditions. These losses appear to be highly variable occurring during the day and night periods in response to varying and complicated interactions involving meteorological, soil and chemical factors (Prueger et al., 2005). Among these factors, soil moisture content plays a major role on S-metolachlor volatilization. A study conducted over three-consecutive years demonstrated that volatilization losses of metolachlor increased significantly in soil surface with increment of the moisture content (Gish et al., 2009). Interacting with moisture content, soil and air temperatures variations also affect metolachlor losses by volatilization (Jury et al., 1987). In four of the five years evaluated, the total daytime volatilization was greater



Table 1 - S-metolachlor physicochemical properties

Density (g mL <sup>-1</sup> at 20 °C) <sup>1/</sup>	1.12
Molecular weight (g mol <sup>-1</sup> ) <sup>1/</sup>	283.8
Water solubility (mg L <sup>-1</sup> at 20 °C) <sup>1/</sup>	488
K <sub>ow</sub> <sup>2/</sup> (at 20 °C)	794
K <sub>H</sub> <sup>3/</sup> (atm m <sup>3</sup> /mole at 25 °C)	2.4x10 <sup>-8</sup>
K <sub>OC</sub> <sup>4/</sup> (average, mLg <sup>-1</sup> ) <sup>5/</sup>	200
P <sub>VP</sub> <sup>6/</sup> (Pa at 20 °C)	1.73x10 <sup>-3</sup>
Ionizability (pKa) <sup>1/</sup>	Non-ionizable

<sup>1/</sup> Senseman, 2007. <sup>2/</sup> Octanol-water partition coefficient. <sup>3/</sup> Henry's law constant. <sup>4/</sup> Soil organic carbon sorption coefficient. <sup>5/</sup> Wauchope et al. (1992). <sup>6/</sup> Vapor pressure.

(60-86%) than the nighttime period (14-57%) and largest losses of metolachlor occurred under warm and wet soil conditions while minimal losses were observed under cool and dry soil (Prueger et al., 2005).

### Leaching

According to water solubility and sorption properties (Table 1), metolachlor exhibits weak (Rodrigues & Almeida, 2011) to moderate leaching potential in soil (Keller et al., 1998). Research showed greater S-metolachlor leaching in quartz-sand soils with 20 g kg<sup>-1</sup> of organic matter and 140 g kg<sup>-1</sup> of clay content compared to soils with higher organic matter (Procópio et al., 2001). Indeed, it was also reported that other soil physical properties such as porosity, soil density and aggregate size affect S-metolachlor leaching (Procópio et al., 2001).

Rainfall volume is positively correlated to S-metolachlor leaching potential. According to Inoue et al. (2010), S-metolachlor leaching was found down to 15-cm depth when rainfall was 60 mm while herbicide leaching was greater than 20-cm depth when rainfall increased to 80 mm. In addition, the elapsed interval between S-metolachlor application and rainfall or irrigation directly affected herbicide leaching. There was a trend to move the herbicide to deeper soil layers when rainfall occurred shortly after application. When a rainfall event occurs shortly after herbicide application, there may not be enough time for the herbicide to reach the adsorption equilibrium with soil (Procópio et al., 2001).

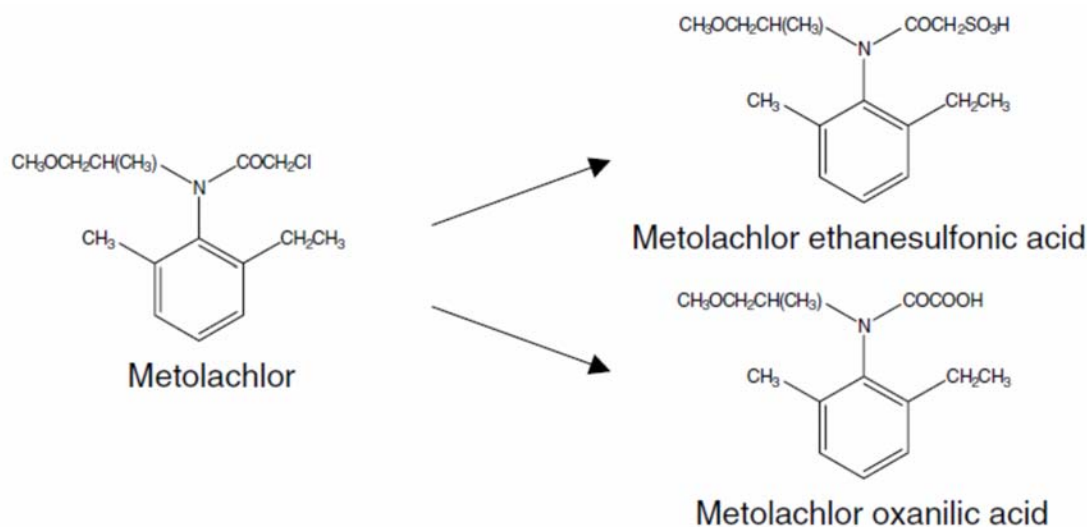
### TRANSFORMATION

Microbial degradation and photolysis are common pathways for S-metolachlor transformation in soil. These processes lead to the formation of metabolites that are typically less toxic and more easily degraded than the parent compound.

#### Microbial degradation

Microbial degradation is considered the major pathway for metolachlor transformation in soil (Accinelli et al., 2001; Ma et al., 2006). This occurs by a cometabolic process (Liu et al., 1991) in which the herbicide molecule is degraded by several metabolic reactions, but it does not serve as energy source for growth of microorganisms (Childs, 2007). On the other hand, a study demonstrated that some microorganisms were able to mineralize metolachlor by using the herbicide as source of carbon (Munoz et al., 2011). The major metabolites resulting from metolachlor degradation are ethanesulfonic acid (ESA) and oxanillic acid (OA) (Figure 1), which are formed through the dechlorination process and subsequent addition of the functional group (Postle et al., 2004).

Microbes, fungi and bacteria have been reported to degrade S-metolachlor. Fungal metabolism of metolachlor using resting cells of *Chaetomium globosum* was first reported by McGahen & Tiedje (1978) who found 45% disappearance of this herbicide after 144 hours of incubation. Microorganisms such as *Rhizopus*, *Actinomyces* and *Streptomyces* isolated from a soil treated with metolachlor for five years mineralised 18.4% of the initial <sup>14</sup>C metolachlor applied (Liu et al., 1988). In addition, *Bacillus circulans*, *B. megaterium*, *Fusarium* sp., *Mucor racemosus*, *Phanerochaete chrysosporium*, *Rhizoctonia praticola*, *Syncephalastrum racemosum* and actinomycete have also been found to degrade metolachlor (Saxena et al., 1987; Liu et al., 1991, Liu et al., 1995; Libra et al., 1996; Sanyal & Kulshrestha, 2002). A mixed culture of *Bacillus luciferensis*, *Stenotrophomonas acidaminiphila* and *Pseudomonas* sp. degraded 39% of the initial metolachlor concentration applied in soil after 21 days of incubation (Xu et al., 2008). In a related study, *Candida xestobii* showed



Adapted from Krutz et al. (2006).

**Figure 1** - Chemical structure of metolachlor and its ethanesulfonic acid (ESA) and oxanilic acid (OA) metabolites.

high capability to break down and mineralize metolachlor converting up to 25% of the <sup>14</sup>C-metolachlor to CO<sub>2</sub> after 10 days of microbial growth (Munoz et al., 2011).

### Photolysis

Photodegradation contributes to S-metolachlor dissipation in soil under prolonged drought periods when the herbicide remains near to the soil surface (Senseman, 2007). Studies evaluating metolachlor photodegradation in water found monochloroacetic acid (MCA) as the main photoproduct (Kochany & Maguire, 1994; Wilson & Mabury, 2000). Although photodegradation has been shown to occur, metolachlor is considered relatively resistant to photolytic decomposition (Kochany & Maguire, 1994).

### Field Persistence

Soil-applied herbicides are typically used in agricultural systems to achieve season-long weed control. However under certain conditions, herbicides can remain in soil for long periods of time, injuring sensitive crops used in succession/rotation systems. The length of time that an herbicide remains in soil is referred as "persistence" and is measured by the dissipation time (DT50), which express the time required to dissipate

50% of the initial concentration applied (Silva et al., 2007). Herbicide persistence in soil is influenced by sorption, volatilization, leaching and degradation processes that control herbicide concentration and movement in the soil solution (Loux et al., 1989). Metolachlor half-life in soil ranges from 2.5 to 289 days (Sanyal & Kulshrestha, 1999; Wu et al., 2011) according to soil management, edaphic factors and environmental conditions (Table 2).

Soil management practices affect soil properties and therefore influence S-metolachlor dissipation in soil. For example, conservation tillage techniques tend to increase the accumulation of organic residues and organic matter near the soil surface (Alletto et al., 2010) providing greater S-metolachlor adsorption in the first centimeters of the soil profile (Youbin et al., 2009). This fact reduces herbicide bioavailability to microbial degradation, increasing S-metolachlor persistence in soil (Alletto et al., 2013). On the other hand, an increase in organic matter content near to the soil surface may also enhance microbial biomass and activity. Several studies have been shown shorter metolachlor half-life in soil with higher organic matter content (Rice et al., 2002; Wu et al., 2011). Similar results were observed in VFS systems described above. In VFS areas, a litter layer from decaying



above-ground vegetation and a massive network of roots can alter the pattern of organic matter accumulation and consequently, stimulate the microbial population decreasing metolachlor half-life (Staddon et al., 2001).

Environmental conditions influencing microbial activity also affect S-metolachlor persistence in soil. In particular, temperature variations directly influence the kinetics of microbial activity (Pietikäinen et al., 2005). This was supported by a mineralization study of metolachlor where the half-life was reduced from 100 days at 5 °C to 5.7 days at 35 °C (Dinelli et al., 2000). Moisture content is another important environmental condition affecting S-metolachlor persistence in soil (Stamper & Touvinen, 1998). In saturated soil, Rice et al. (2002) observed a greater amount of metolachlor dissolved in soil solution and consequently, greater herbicide degradation. In this study, metolachlor half-life decreased from 81 days in unsaturated soil to 50 days in saturated soil.

In addition, it has been postulated that associations with other herbicides can impact S-metolachlor persistence. The half-life of S-metolachlor was 34 and 28 days when the herbicide was applied with paraquat and glyphosate, respectively (Nunes & Vidal, 2008). According to the authors, glyphosate increased S-metolachlor degradation because microorganisms used glyphosate as an energy source, stimulating their biomass and activity. Also, repeated applications of S-metolachlor over consecutive years in the same area may select for microorganisms adapted to degrading this herbicide. Enhanced degradation was observed by Sanyal & Kulshrestha (1999) who found shorter metolachlor half-life in areas with previous metolachlor applications.

In conclusion, S-metolachlor exhibits moderate to long persistence in soil with potential to contaminate ground and surface water. Under certain conditions, carryover effects might be observed in sensitive crops

**Table 2** - Persistence of S-metolachlor and metolachlor in soil influenced by soil management practices, edaphic factors and environmental conditions

Local	Condition	Half-life (days)	Reference
China	Soil (3.94-1.22% O.M <sup>1/</sup> - 20 °C)	37.9 - 49.5	Wu et al., 2011 <sup>2/</sup>
Italy	Soil (1.72% O.M - 21 °C)	17.4	Fava et al., 2000 <sup>2/</sup>
Romania	Soil (2.2% O.M)	69.3	Coroi et al., 2011 <sup>3/</sup>
Italy	Field capacity (35 °C)	5.7	Dinelli et al., 2000 <sup>2/</sup>
Italy	Field capacity (20 °C)	12.2	Dinelli et al., 2000 <sup>2/</sup>
Italy	Field capacity (5 °C)	100.7	Dinelli et al., 2000 <sup>2/</sup>
USA	Field capacity (0-30 cm depth)	81	Rice et al., 2002 <sup>2/</sup>
USA	Field capacity (90-120 cm depth)	289	Rice et al., 2002 <sup>2/</sup>
USA	Saturated soil (0-30 cm depth)	50	Rice et al., 2002 <sup>2/</sup>
USA	Saturated soil (90-120 cm depth)	94	Rice et al., 2002 <sup>2/</sup>
China	Sterilized soil (20 °C)	126 - 135.9	Wu et al., 2011 <sup>2/</sup>
China	Unsterilized soil (20 °C)	37.9 - 49.5	Wu et al., 2011 <sup>2/</sup>
USA	Sterilized soil (24±5 °C)	210	Rice et al., 2002 <sup>2/</sup>
USA	Unsterilized soil (24±5 °C)	81	Rice et al., 2002 <sup>2/</sup>
USA	Soil from VFS <sup>5/</sup> area	6.0	Mersie et al., 2004 <sup>4/</sup>
USA	Soil from non- VFS area	9.6	Mersie et al., 2004 <sup>4/</sup>
USA	Soil from VFS area	10	Staddon et al., 2001 <sup>4/</sup>
USA	Soil from non-VFS area	23	Staddon et al., 2001 <sup>4/</sup>
India	History application	2.5	Sanyal & Kulshrestha, 1999 <sup>3/</sup>
India	No history application	18	Sanyal & Kulshrestha, 1999 <sup>3/</sup>
Brazil	Tank mixture with paraquat	34	Nunes & Vidal, 2008 <sup>3/</sup>
Brazil	Tank mixture with glyphosate	28	Nunes & Vidal, 2008 <sup>3/</sup>
France	Deep tillage	127	Alletto et al., 2013 <sup>2/</sup>
France	No tillage	106	Alletto et al., 2013 <sup>2/</sup>
France	Reduced tillage	97	Alletto et al., 2013 <sup>2/</sup>

<sup>1/</sup> Organic matter content. <sup>2/</sup> Laboratory study. <sup>3/</sup> Field study. <sup>4/</sup> Greenhouse study. <sup>5/</sup> Vegetative filter strips.

used in succession/rotation systems after S-metolachlor applications. However, studies suggest that carryover associated with saturated soil conditions found in rice production could shorten rather than prolong the persistence of the herbicide. Sorption of S-metolachlor in soil is positively correlated to organic matter and clay content. This process controls herbicide availability for runoff, volatilization, leaching, photolysis and microbial degradation processes, affecting its efficacy on weed control and persistence in soil. Microbial degradation appears to be the major pathway for S-metolachlor dissipation in soil.

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