



## Holistic assessment of occurrence and fate of metolachlor within environmental compartments of agricultural watersheds



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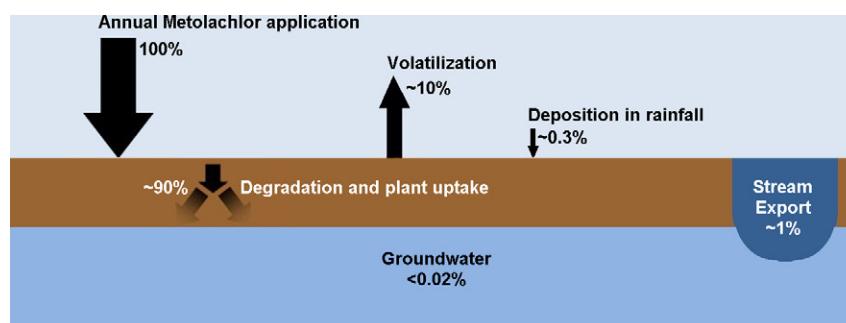
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### HIGHLIGHTS

- Metolachlor is frequently detected in surface and groundwater in the United States
- Metolachlor and two degradates were observed in multiple environmental compartments.
- Ratios of parent and degradates systematically change across environmental compartments.
- Degradates are used to understand the environmental fate and transport of metolachlor.

### GRAPHICAL ABSTRACT



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### ABSTRACT

**Background:** Metolachlor [(RS)-2-Chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-2-yl)acetamide] and two degradates (metolachlor ethane-sulfonic acid and metolachlor oxanilic acid) are commonly observed in surface and groundwater. The behavior and fate of these compounds were examined over a 12-year period in seven agricultural watersheds in the United States. They were quantified in air, rain, streams, overland flow, groundwater, soil water, subsurface drain water, and water at the stream/groundwater interface. The compounds were frequently detected in surface and groundwater associated with agricultural areas. A mass budget approach, based on all available data from the study and literature, was used to determine a percentage-wise generalized distribution and fate of applied parent metolachlor in typical agricultural environments.

**Results:** In these watersheds, about 90% of applied metolachlor was taken up by plants or degraded, 10% volatilized, and 0.3% returned as rainfall. One percent was transported to surface water, while an equal amount infiltrated into the unsaturated zone soil water. <0.02% reached the groundwater. Subsurface flow paths resulted in greater degradation of metolachlor because degradation reactions had more time to proceed.

**Conclusions:** An understanding of the residence times of water in the different environmental compartments, and the important processes affecting metolachlor as it is transported along flowpaths among the environmental compartments allows for a degree of predictability of metolachlor's fate. Degradates with long half-lives can be used (in a limited capacity) as tracers of metolachlor, because of their persistence and widespread occurrence in the environment.

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**Abbreviations:** (MET), metolachlor; (ESA), ethane sulfonic acid; (OXA), oxanilic acid; (MESA), metolachlor ESA; (MOXA), metolachlor OXA; (Koc), organic carbon normalized sorption coefficient; (CA), California; (IN), Indiana; (IA), Iowa; (MD), Maryland; (MS), Mississippi; (WA), Washington; (NE), Nebraska; ( $K_{ow}$ ), octanol-water partitioning coefficient; ( $K_{oc}$ ), soil organic carbon-water partitioning coefficient.

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## 1. Introduction

The use of pesticides for weed and pest control is a key component of large-scale agricultural production, which provides food, fuel, and fiber to an ever-increasing world population (Food and Agriculture Organization (FAO) of the United Nations, 2008). While improving crop yields, the use of pesticides has also resulted in their widespread occurrence in the surface waters and groundwaters of agricultural areas (Scribner et al., 2004; Capel et al., 2008). Detection frequency of pesticides in the environment is related to three factors: (1) the pesticide's amount of use, (2) its mobility, and (3) its persistence (Gilliom et al., 2006). A recent study reported that metolachlor [(RS)-2-Chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-2-yl)acetamide] is the most frequently detected agricultural pesticide in surface and groundwater in the United States (Gilliom et al., 2006).

Metolachlor, an herbicide, has been used extensively throughout the country for over three decades. Usually applied to the soil surface before planting, metolachlor requires rainfall or irrigation to move it into the soil to make it available for uptake by plants. Even with the best available methods to estimate application amount and to apply metolachlor efficiently, a fraction of the herbicide may not reach its target and most will be degraded into other short- and long-lived chemicals (degradates). A fraction of the excess metolachlor or its degradates can leach from the field and be transported to other environmental compartments such as groundwater, surface water, or the atmosphere. In 2002, the U.S. Geological Survey studied pesticides in 51 streams within 9 states in the Midwestern United States; 73% of the samples contained detectable metolachlor and over 95% contained detectable degradates (Scribner et al., 2003). More recent studies showed that metolachlor and its degradates were commonly observed in many hydrologic compartments (McCarty et al., 2014; Milan et al., 2015; Stone et al., 2014).

Metolachlor was developed in 1970, first registered for use with the U.S. Environmental Protection Agency in 1976, and became widely used for agriculture by 1978 as a broad spectrum, pre-emergent herbicide on corn, soybeans, sorghum, cotton, peanuts, beans, potatoes, tomatoes, and other crops to control broadleaf and annual grassy weeds. Agricultural use of metolachlor in the United States was >30,000 Megagrams per year (Mg/yr) in the mid-1990s (GfK Kynetec, Inc., modified from Thelin and Stone, 2013). Originally formulated as a racemic mixture, metolachlor was reformulated in 1993–1994, as the original patents expired, to include only the phyto-active enantiomer of metolachlor, producing S-metolachlor (United States Environmental Protection Agency, 1998). S-metolachlor allowed a 35% reduction in the application rate to achieve the same weed control compared to racemic metolachlor. In the early 2000s, there was a decline in the amount of metolachlor applied because of the rising cultivation of glyphosphate-resistant, genetically modified crops (Supplemental Fig. S1). By the mid-2000s, the use of metolachlor stabilized at about half the mass applied annually in the mid-1990s (United States Environmental Protection Agency, 1998; Thelin and Stone, 2013; Desai, 2009; Corbin and Hetrick, 2002).

Metolachlor reacts to form numerous degradates through both abiotic and biotic processes (Field and Thurman, 1996; Graham et al., 1999; Zemolin et al., 2014). Two of these degradates, metolachlor ethane-sulfonic acid (MESA) (2-([2-ethyl-6-methylphenyl][2-methoxy-1-methylethyl]amino)-2-oxoethanesulfonic acid), and metolachlor oxanilic acid (MOXA) (2-([2-ethyl-6-methylphenyl][2-methoxy-1-methylethyl]amino)-2-oxoacetic acid), are biologically-degraded through the glutathione-S-transferase enzyme pathway (Supplemental Fig. S2) (Field and Thurman, 1996; Graham et al., 1999). MESA and MOXA differ in their formation, chemical properties and environmental persistence (Table 1), which affects their frequencies of detection in the environment (Capel et al., 2008; Rivard, 2003; Bayless et al., 2008). The water solubility of MESA is three orders of magnitude higher than MOXA and metolachlor, which is the least water soluble. However, both degradates are persistent, can accumulate

in the environment, and are commonly detected along with metolachlor in surface and groundwater (Gilliom et al., 2006). Although the behavior and fate of metolachlor depends upon many factors, the presence of aerobic microbial colonies in the soil column is critical to the formation of MESA and MOXA.

Degradation pathways of metolachlor provide some insight into the subsequent ratios of metolachlor and its two degradates, as well as the environmental compartment from which a water sample is collected. As water containing metolachlor moves through each environmental compartment, the opportunity for degradation will depend on the flowpath the water follows (slow or fast), its residence time in the soil column, redox conditions, the microbiological community, and soil type. For example, overland flow runoff or subsurface drains are water pathways that support little to no exposure with the soil column, microbiological communities, or anaerobic conditions, which generally results in minimal degradation of metolachlor (Graham et al., 1999). Long exposures of parent metolachlor to microorganisms (such as what occurs in downward movement of water through the soil unsaturated zone) create a greater potential for the degradation to MESA and/or MOXA.

This paper summarizes the behavior and fate of metolachlor and its two main biotic degradates (MESA and MOXA) in seven diverse agricultural areas in the United States (California (CA), Indiana (IN), Iowa (IA), Maryland (MD), Mississippi (MS), Nebraska (NE), and Washington (WA); Fig. 1) across multiple environmental compartments (rain, surface water, soil water (unsaturated zone), overland flow runoff, subsurface drain water, shallow groundwater, and the interface between groundwater and surface water). The result is a broad-based field perspective of degradation processes in diverse environments for metolachlor. A generalized mass budget approach is used to describe the fate of parent metolachlor. Some of the data used here have been reported elsewhere to describe metolachlor behavior in single environmental compartments (Bayless et al., 2008; Baker et al., 2006; Fredrick et al., 2006; Gronberg and Kratzer, 2006; Hancock et al., 2008; Kalkhoff et al., 2012; McCarthy et al., 2011; Steele et al., 2008; Vogel et al., 2008; Webb et al., 2008). In this study, the concentration and ratios of the three chemicals are used as tracers of environmental processes and are shown to yield consistent patterns across many different hydrologic settings.

## 2. Materials and methods

### 2.1. Study area and hydrologic setting

Each of the seven study areas was located in river basins where the land use was predominantly agriculture (Fig. 1; Table 2) (Capel et al., 2008; Fredrick et al., 2006; Gronberg and Kratzer, 2006; Thelin and Stone, 2013; Hancock and Brayton, 2006; Lathrop, 2006; Payne et al., 2007; McCarthy et al., 2012). The WA site, located in the Granger Drain basin, a subbasin of the Yakima River in south central Washington was the smallest drainage area. The Nebraska site was located in Maple Creek watershed, a 955-square-kilometer area in eastern Nebraska. The Maryland site was located in Morgan Creek basin, a 31-square-kilometer watershed in Kent County, Maryland on the Delmarva Peninsula. The California site was located in the San Joaquin–Tulare basin, specifically the lower Merced River basin, a diversified agricultural region requiring spring to fall irrigation. The Iowa site was located in the South Fork Iowa River basin, where corn and soybeans are the predominant crops and a large percentage of the cultivated land is underlain by artificial drainage. The Mississippi site was located in the Bogue Phalia basin, an area of corn, soybean, cotton, and rice cropping in the humid, subtropical southeastern United States. The Indiana site was located in the Leary Weber Ditch and Sugar Creek basins, an area of moderate temperatures and well-defined winter and summer seasons. The study areas' hydrologic settings are described in detail in Capel et al. (2008).

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