

# Herbicide transport and transformations in the unsaturated zone of two small agricultural basins with corn and soybean row crops

## Introduction

In the United States, herbicides are among the most significant nonpoint-source pollutants and were applied to 95% of all fields in corn production and 97% of all fields in soybean production in 2003 and 2004.

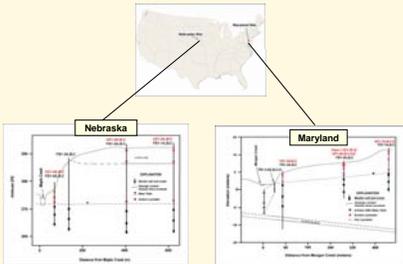


Spatial and temporal variability in the transport and fate of herbicides in the unsaturated zone is complex and poorly understood.

Leaching through soil has been identified as a major cause for the occurrence of pesticides in ground water, however, there is limited understanding of the fate and transport overall.

## Study Design

The United States Geological Survey (USGS), National Water Quality Assessment (NAWQA) Program conducted a study on select herbicides in the unsaturated zone of two sites in predominantly agricultural basins: Morgan Creek (Maryland) and Maple Creek (Nebraska).



In 2004, the Maryland fields were in soybeans and the Nebraska fields were in corn. The Nebraska fields were irrigated, whereas those in Maryland were not.

Samples of unsaturated-zone water were obtained with soil-suction and pan lysimeters, which were installed at several locations in agricultural fields and depths below land surface. Lysimeters were sampled throughout the agricultural growing season of 2004.



Solid core, wet deposition (rain), and ground-water samples were also collected as part of a larger study by the USGS.

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## Conceptual Model

In the unsaturated zone, reactions occur and degradates form in the root zone where there are active microbial communities and substrates. Recharge events rinse out this reactive reservoir over time moving degradates and unreacted parent compounds to deeper parts of the unsaturated zone. Below the root zone, transformations may continue, but transformation rates could potentially be much slower depending on environmental conditions.

### Question

Which factors affect the occurrence, fate, and transport of pesticides in the unsaturated zone?

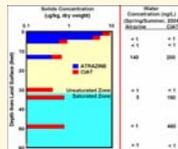
- Agricultural management practices
- Physical-chemical properties of compounds
- Natural features, such as soils and geology
- Hydrology/Climatic conditions

## Results and Discussion

The occurrence of herbicides and their degradates in the unsaturated zone of these basins reflects application practices over the past several of years. Among these compounds, those that were detected most frequently were the pre-emergent triazines and acetanilides -- specifically atrazine, metolachlor, acetochlor, and alachlor -- and their degradates.

Agricultural Characteristics - 2004		
State	Maryland Site	Nebraska Site
Crop	Soybeans	Corn
Herbicides	Glyphosate, Paraquat	None
Agricultural Characteristics - Prior to 2004		
Typical crop	2-yr. Corn, Soybeans, except 2003 was in soybeans	2-yr. Corn, Soybeans
Herbicides	Glyphosate, Atrazine, Metolachlor, Simazine, Paraquat, 2,4-D, Dinoseb	Glyphosate, Atrazine, Acetochlor, Metolachlor

Few herbicides were detected on solid core samples from select unsaturated-zone sites of these basins. An exception was found at a Maryland site in an upland recharge area with sandier soils. Here, atrazine concentrations were highest in the near surface solids and decreased with depth.



In the unsaturated-zone water of the Maryland site, parent triazine and acetanilide herbicides were detected and only at the site in the upland recharge area at relatively low concentrations at depths greater than 13 feet (4 meters), probably because these compounds had not been applied for several years. These results indicate that if transported out of the root zone, some of the parent compounds can persist in the deeper unsaturated zone for much longer than in the root zone, where half-lives for these compounds are assumed to be weeks to months.

## Results and Discussion (continued)

At the Maryland site, acetanilide degradates of metolachlor, acetochlor, and alachlor were frequently detected in the unsaturated-zone water. In general, concentrations of both metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OXA) increase over time, but relatively more metolachlor ESA is present (the fraction of metolachlor ESA relative to the total mass of parent and degradates was higher than the fraction of metolachlor OXA). A similar trend was also observed for the acetochlor and alachlor degradates. The fraction of metolachlor ESA also increased with depth and over time at several individual sampling locations. This trend was not observed for acetochlor and alachlor degradates.

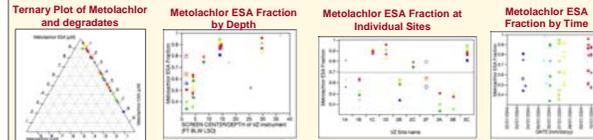
### Degradate Fraction (Yield):

$$\text{Degradate}(i) \text{ Yield} = \frac{[\text{Degradate}(i)]}{\sum [\text{Degradates}] + [\text{Parent}]}$$

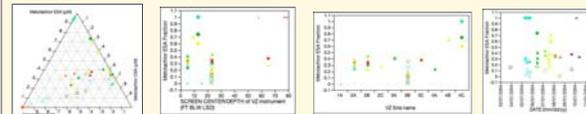
Concentrations are in moles/L  
Fraction = 1: all Degradate i  
Fraction = 0: no Degradate i

At the Nebraska site, parent compounds atrazine, metolachlor, acetochlor, and alachlor were detected, typically at concentrations higher than their degradates. No trend was observed with depth and over time. In general, metolachlor OXA fractions were slightly higher than ESA.

### Maryland



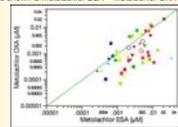
### Nebraska



There may be preferential degradation, sorption, and/or transport of certain compounds below the root zone. At the Maryland site, the metolachlor ESA fraction increases relative to metolachlor OXA with depth and over time. In addition, Maryland has relatively more ESA than OXA compared to Nebraska. At the Maryland site, is ESA retained and more stable and/or is OXA degraded or transported faster? The Koc for ESA is roughly four times larger than the value estimated for OXA. ESA should be more sorptive than OXA and OXA should be more mobile than ESA.

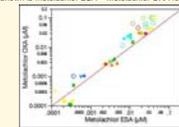
### Maryland

Metolachlor OXA by Metolachlor ESA  
Line shows is metolachlor ESA = Metolachlor OXA for reference



### Nebraska

Metolachlor OXA by Metolachlor ESA  
Line shows is metolachlor ESA = Metolachlor OXA for reference



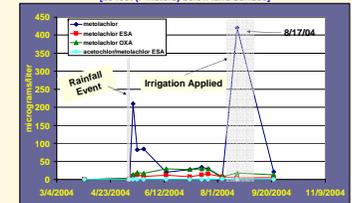
## Results and Discussion (continued)

Hydrologic events (irrigation or rain) that occur soon after herbicide application, and that are of significant magnitude, may cause water containing parent compounds (and/or degradates) to pass through the root zone quickly preventing further degradation of compound.

The timing of these events allows parent herbicides (and less degraded compounds) to reach deeper depths within the unsaturated zone.

At the Nebraska VZ1-3B site, located in the down slope end rows of the field, runoff from large hydrologic events caused ponding on the land surface. Subsequently, focused recharge led to significant washing out of the root zone, thereby decreasing the residence time for parents and transformation opportunities.

### Metolachlor at Nebraska Site VZ1-3B (23 feet (7 meters) below land surface)



Similar results were observed for acetochlor, atrazine, and their degradates at site VZ1-3B, where a transition in soil hydraulic properties (resulting from loess to sand) slowed the movement of water and compounds to deeper depths in the unsaturated zone.

Even at deeper depths in unsaturated zone, parent herbicides may become bound to solid surfaces. Again, large scale recharge events may thoroughly rinse out the deeper unsaturated zone, drawing solutes of solids and into mobile water initially increasing aqueous concentrations. However, concentrations would likely decrease over time (most likely related to a physical movement, rather than degradation) until the next large scale recharge event.

## Summary

Several factors/processes affect the occurrence, fate, and transport of pesticides in the unsaturated zone

- Agricultural management practices including herbicide applications over several years
- Physical-chemical properties of compounds leading to preferential degradation, sorption, transport
- Environmental setting and hydraulic properties of soil
- Hydrology including focused recharge from irrigation and precipitation

## For further information

Please contact thancock@usgs.gov or jrvoegel@usgs.gov. More information on this and related projects can be obtained at <http://pubs.usgs.gov/fs/2004/3098/>.

