Ratios of metolachlor to its metabolites in ground water, tile-drain discharge, and surface water in selected areas of New York State

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ABSTRACT

The transport and fate of the herbicide metolachlor and its principal metabolites - metolachlor ESA (ethanasulfonic acid) and metolachlor OA (oxanilic acid) - in ground water from Suffolk County, on Long Island, from tile drains in an agricultural area in central New York and in surface water from five streams in central and western New York, was evaluated in 1997-98. Comparison of (1) the ratio of metolachlor ESA to metolachlor (SAM ratio) and (2) the ratio of metolachlor ESA to metolachlor OA (SAO ratio) in well water from Suffolk County with these ratios in tile-drain runoff and in the five streams indicates that these ratios vary according to soil properties, hydrologic factors, and time since metolachlor application. Both ratios were lower in well-water samples from Suffolk County (which is dominated by coarse-grained soils), than in the tile-drain samples from central New York fields (which have finer grained soils). The lower SAM ratios for the Suffolk County well-water samples than for the tile-drain samples probably result from the more rapid transport and lesser degradation of metolachlor in the coarse soils than in the fine-grained soils. The lower SAO ratios in Suffolk County well water also result from rapid infiltration of metolachlor OA through the coarse grained soils. SAM ratios for the surface-water samples were lower than those for the well-water and tile-drain samples, probably because surface water has a shorter residence time in the soil than ground water; the shorter contact time with soil microbes and enzymes than in ground water allows less degradation of metolachlor to metolachlor ESA.

SAM and SAO ratios for samples from one of the tile drains decreased after rainstorms that followed metolachlor application. SAM ratios for this tile drain decreased from more than 500 to less than 1 during the storm, and SAO ratios decreased from about 3 to less than 2. These decreases are attributed to preferential flow that accelerated the movement of metolachlor and metolachlor OA into the subsurface during the storm. SAM ratios in the stream that receives discharge from the tile drains were lowest during stormflows in June 1998 that followed metolachlor application. These low postapplication SAM ratios are attributed to the water's short contact time with soil and, hence, minimal transformation of metolachlor to metolachlor ESA.

INTRODUCTION

The common presence of two major metabolites of metolachlor - metolachlor ethanasulfonic acid (metolachlor ESA) and metolachlor oxanilic acid (metolachlor OA) - in ground water and surface water in agricultural areas of Iowa (Kahlkhoff and others, 1998) indicates that these metabolites are readily formed in the soil and transported to ground water and to streams. In the Iowa study, more than 90 percent of the mass of acetanilide residues in ground water, and more than 80 percent of the acetanilide residues in surface water, consisted of the sulfonic and oxanilic acid
degredates. Metolachlor is transformed to metolachlor ESA by the glutathione conjugation process (Field and Thurman, 1996) and to metolachlor OA by a process that is unknown, but probably biologically mediated within the soil.

Results of previous investigations of the occurrence of metolachlor and its metabolites in tile drain discharge from agricultural fields in central New York indicate that (1) metolachlor ESA and OA can persist in agricultural soils for 3 or more years after application (P. J. Phillips, U.S. Geological Survey, written commun., 1999), (2) metolachlor ESA concentrations in tile-drain discharge exceed those of metolachlor by a factor of 200 to 1,800, and (3) metolachlor ESA concentrations in tile-drain discharge generally exceed those of metolachlor OA by a factor of 2 to 5. Results also indicate that ratios of metolachlor ESA to metolachlor (SAM ratio) in the receiving stream are lower than those in tile-drain discharge, as a result of differing flow paths. Water in tile-drain runoff (and, by extension, ground water) has a longer period of contact with the soil, and thus, more time for chemical degradation through microbial and enzyme reactions than surface water and therefore has higher SAM ratios than surface water.

The ratio of deethylatrazine concentration to atrazine concentration (DAR) has been used in many studies to indicate hydrologic pathways along which atrazine is transformed into deethylatrazine. Low DAR values in surface water have been correlated with the “spring flush” of atrazine in the midwestern United States just after planting and pesticide application (Thurman and Fallon, 1996), and high DAR values in surface water typically occur in the months before application, or in the harvesting months, when surface water flow consists mostly of ground water (Thurman and others, 1991; Thurman and others, 1994). A corresponding seasonal change in the SAM ratio would probably indicate that, like the DAR, SAM ratios in surface water are probably controlled in part by timing of metolachlor application and the proportion of surface water consisting of ground water.

This paper describes how SAM ratios in surface water differ from those in ground water from wells on Long Island and tile drains beneath cultivated fields in central New York, and how these ratios vary according to soil properties and hydrologic factors; it also compares SAM and SAO ratios among the five upstate surface-water sites to indicate the seasonal variability of these ratios in relation to the timing of metolachlor application. Results of this paper will provide information on the fate and transport of metolachlor, which is one of the most heavily used herbicides in New York State (Gail Thelin, U.S. Geological Survey, written communication, 1998).

**METHODS**

Water samples were collected from three networks - 50 wells in Suffolk County, two tile drains in Montgomery County, and five surface-water sites in Montgomery, Onondaga, Tompkins, and Livingston County (fig. 1, table 1). Most of these samples were collected as part of a cooperative effort between the U.S. Geological Survey and the New York State Department of Environmental Conservation as part of the New York State Pesticide Monitoring Program. Some samples were collected as part of the U.S. Geological Survey National Water Quality Assessment Program. Sampling Sites

Sampling Sites

The 50 Suffolk County wells tap a shallow surficial sand aquifer of glacial sand and gravel. These wells were selected on the basis of known or suspected pesticide contamination. The samples were collected by the USGS and the Suffolk County Department of Health Services (SCDHS) from April through July 1998. Each well was sampled once during the study. Well-screen depths range from 9 to 202 feet below land surface, and thickness of the unsaturated zone at wells with a detection of metolachlor or metolachlor ESA ranges from less than 5 feet to 75 feet. Of the 50 wells sampled, 22 had a detection for metolachlor or its two metabolites. Most of the wells with a detection of any of these compounds are in agricultural areas. Metolachlor, which is widely used on potatoes in Suffolk County, has been detected previously in Suffolk County ground water by the SCDHS (Baier and Trent, 1998).

The two tile drains are in the Canajoharie Creek watershed (fig. 1) and underlie fields that are in a corn-soybean rotation. The tile drains were installed in the 1980's at a depth of 3 to 4 feet below
land surface and are below the water table except in the late summer and early fall; thus, the tile-drain runoff is representative of shallow ground water beneath the fields. Parts of the fields overlying Tile Drain 4 (TD4) were treated with metolachlor in 1997 and 1998, but not during the 3 preceding years (1994-96), whereas the field overlying TD2 was treated in 1995, but not during 1996-98. The TD4 fields are underlain by an unconfined surficial aquifer that consists of as much as 20 feet of alluvial sand and gravel with some silt. The Tile Drain 2 (TD2) field is underlain by 9 to 40 feet of glaciolacustrine clay, which confines the underlying aquifer. Depth to water beneath both fields ranges from 3 to 8 feet below land surface (Hollister, 1997). Samples were collected from the tile drains once every 2 months from November 1997 through April 1998 and weekly from May through July of both years. The tile drains did not flow from mid-July through October of either year.

Samples were collected from the five upstate surface-water sites quarterly to monthly from April 1997 through May 1998, weekly during the postapplication period of June to July, and during selected storms in June and July. About 20 samples were collected at each site except Canajoharie Creek (which receives discharge from the two tile drains); 47 samples were collected at this site. Half the samples from each site were collected in June and July, the other half in the remaining months. Three of the sites (Canajoharie Creek, Fall Creek, and Canaseraga Creek) drain small (less than 350 square mile) agricultural watersheds - the other two (Seneca River and Genessee River) which drain watersheds of at least 1,500 square miles) include the Fall Creek and Canaseraga Creek watersheds,
respectively (fig. 1). These four watersheds contain substantial row-crop agriculture (table 1).

### Sample Collection and Analysis.

Samples were collected according to procedures described by Shelton (1994) and Lapham and others (1995). Sample splits were sent to two laboratories - the National Water Quality Laboratory (NWQL) in Denver, Colo., and the USGS Organic Research Laboratory (ORL) in Lawrence, Kans. The parent compound (metolachlor) was analyzed at the NWQL (Zaugg and others, 1995); the detection limit for this method is 0.002 mg/L. The two metabolites were analyzed by high-performance liquid chromatography (HPLC) with diode array detection and quantification (Ferrer and others, 1997); the detection limit for the two metabolites is 0.2 mg/L. Blank samples collected and analyzed during this study showed no detections for metolachlor or its metabolites.

### Calculation of SAM and SAO ratios

SAM ratios for samples with no detection of metolachlor were calculated as the metolachlor ESA concentrations divided by the metolachlor concentration. Six well-water samples from Suffolk County had detectable metolachlor but no detectable metolachlor ESA; the calculated SAM ratios for these samples ranged from 7 to 38. These values are generally lower than the SAM ratios for the other well-water samples. A few (less than 10 percent) of the surface-water samples had a detection of metolachlor but not metolachlor ESA. All tile-drain samples had a detection of metolachlor and metolachlor ESA.

SAO ratios were calculated only for samples with a detection for both metolachlor ESA and metolachlor OA. All well samples and tile-drain discharge samples with a detection for metolachlor ESA also had a detection for metolachlor OA. Fewer than 40 percent of the surface-water samples with a detection for metolachlor ESA had a detection for metolachlor OA.

### SAM AND SAO RATIOS IN GROUND WATER, TILE-DRAIN DISCHARGE AND SURFACE WATER

The highest median SAM ratios were in the tile-drain discharge samples, and the lowest were in the surface-water samples (fig. 2). This indicates that ratios of metolachlor ESA to metolachlor are higher in ground water (which includes tile drain and Suffolk County well water samples) than in surface water. The median SAM ratio for samples from TD2 was 950, and that for TD4 was 460; the SAM ratio for some samples from the tile drains exceeded 1,000. The median SAM ratio for the well-water samples from Suffolk County was 30 - markedly lower than the medians for the tile...
Figure 2. Ratio of metolachlor metabolite concentrations in Suffolk County ground water, tile-drain discharge, and surface water samples: A. SAM ratio (ratio of metolachlor ESA to metolachlor concentration). B. SAO ratio (ratio of metolachlor ESA to metolachlor OA concentration).
drains. Median SAM ratios for all surface-water samples were less than 10 (fig. 2a) except those from Fall Creek.

The highest median SAO ratios were in the tile-drain discharge samples - 4.4 for TD2 and 3.1 for TD4 (fig. 2B) - and the well-water samples had the lowest (1.2). The surface-water samples ratios were intermediate - from 1.8 to 2.6.

**Effects of Soil Properties**

The lower SAM and SAO ratios in Suffolk County well-water samples than in the tile-drain discharge samples (fig. 2A) are attributable to differences in soil properties. The soils overlying TD2 and TD4 are silty loam and sandy loam, respectively, and contain more clay and organic matter than the coarse-grained soils of Suffolk County. The higher SAM ratios for TD2 samples than for TD4 samples reflect the finer texture and, hence, the longer residence time of water in soils overlying TD2. Metolachlor sorption is greater in fine-grained soils than metolachlor ESA; thus the TD2 samples generally had higher SAM ratios than the TD4 samples. The low SAM ratios for the Suffolk County well-water samples reflect the poor sorption of metolachlor in these coarse soils. The coarse soils of Suffolk County also have a lower organic carbon content, which minimizes microbial or soil enzyme activity, and inhibits the transformation of metolachlor to metolachlor ESA.

The low SAO ratios of the Suffolk County well-water samples (fig. 2B) also can be attributed to the soil properties, and the lower SAO ratios for TD4 samples than for TD2 samples is attributed to preferential transport or formation of metolachlor OA in the coarser grained soils overlying TD4. Metolachlor OA is probably less stable than metolachlor ESA in the soil; therefore, the rapid infiltration of metolachlor OA through coarse soil into the aquifer would result in low SAO ratios in the underlying ground water. Once metolachlor OA has reached the aquifer, it is no longer subject to the activity of soil enzymes and microbes that cause degradation and alter the SAO ratio. The lower SAO ratios of Suffolk County well water than of tile-drain discharge are consistent with the observed difference in soil coarseness.

**Effects of Hydrologic Factors**

The lower SAM ratios in surface-water samples collected during the two postapplication months (June and July) than the other months (August-May) (fig. 3) result from the shorter residence time (contact time) of the water with soil, and soil enzymes and microbes. The median SAM ratio for Canajoharie Creek samples from June and July was 6.7, and that for the other months was 12.5. The lower SAM ratios in the two postapplication months are comparable to the low DAR values found in surface-water samples collected in the midwestern United States after pesticide application (Thurman and Fallon, 1996; Thurman and others, 1991). DAR values for the five surface-water sites (not presented here) show a similar seasonal pattern of lowest values in June and July, and highest values in other months. Metolachlor in surface water collected from August through May has had a longer contact time with the soil than surface water collected in June and July and, thus, has undergone greater degradation to metolachlor ESA.

The lower SAM ratios in upstate surface water than in tile-drain discharge or Suffolk County ground water are probably due to differences in hydrologic flowpaths. Transformation of metolachlor to metolachlor ESA is favored where water has significant contact time with the soil and soil enzymes and microbes; thus, the lower SAM ratios for surface water than for tile-drain discharge or well water is attributable to the surface water's short residence time in the soil. The anomalous high SAM ratios for Fall Creek samples (fig. 2, 3) indicate that some unknown local factor is promoting the transport or formation of metolachlor ESA in this watershed.

The few detections of metolachlor OA in surface-water samples make the SAO ratios difficult to correlate with hydrologic pathways. The median SAO ratios for surface-water samples were intermediate between those for the tile-drain discharge samples and those for Suffolk County ground water (fig. 2B). These data suggest that, in general, metolachlor OA is formed or transported more readily in ground water beneath coarse-grained soils than in surface water.
Figure 3. SAM ratios (ratio of metolachlor ESA to metolachlor concentrations) for five surface water sites, by post application months (June-July 1997-98) and other months (August-May 1997-98).
Effects of Storms

Samples collected from TD2 and Canajoharie Creek in June 1998 indicate that SAM and SAO ratios in tile-drain discharge and surface water change during storms just after metolachlor application. The SAM ratios for samples collected at TD2 before June 1998 ranged from 500 to 1,100 (fig. 4A), but the SAM ratios for samples collected after large storms in June 1998 (after metolachlor application) were less than 100. The lowest SAM ratios (less than 1) were in samples collected just after large storms on June 3 and June 15, 1998 (fig. 4A). The SAO ratios in TD2 samples also decreased in response to storms in June 1998 - the SAO ratios for non-storm samples collected from TD2 in June 1998 were similar to those for samples collected before June (fig. 4A). The SAO ratios for the two samples collected on June 3 and June 15, 1998 (less than 2) were the lowest SAO ratios obtained from this site.

The low SAM and SAO ratios for TD2 samples after the two June storms probably resulted from rapid preferential flow from the soil into the aquifer. These two samples had the lowest SAM and SAO ratios, the highest metolachlor concentrations (both greater than 7 μg/L), and the highest metolachlor OA concentrations (greater than 3 and 11 μg/L), of any samples collected at TD2. Normally, the fine-grained soils that overlie TD2 result in high SAM and SAO ratios; thus, the elevated concentrations of metolachlor and metolachlor OA in the storm samples probably are the result of preferential flow paths that allowed metolachlor and metolachlor OA to move through the soil, with minimal contact time and, thus, minimal degradation. This would indicate that heavy rain can accelerate the transport of these compounds even through fine-grained soils, which generally retard the movement of metolachlor and metolachlor OA to a greater extent than coarse-grained soils. Because the overlying field was not treated in 1998, the source of metolachlor at TD2 in 1998 is uncertain, but was probably runoff from an adjacent field.

SAM ratios in surface-water samples from Canajoharie Creek also were lowest during stormflows just after metolachlor application in late May and early June (fig. 4B). The median SAM ratio for five stormflow samples collected in June 1998 was 0.4, and the median SAM ratio for six base-flow samples collected in June 1998 was 5.2. The SAM ratios for the June 1998 stormflow samples were the lowest obtained for Canajoharie Creek during the entire 1997-98 study. SAM ratios for all Canajoharie Creek samples for June 1998, regardless of flow conditions, were lower than those for June 1997, probably because rainfall in June 1998 was greater than in June 1997. Average mean daily discharge for June 1997 was 8.36 ft³/s (cubic feet per second) - far lower than that for June 1998 (45 ft³/s). The higher flows during June 1998 resulted in a short residence time in the soil, and rapid flushing of metolachlor.

The small number of samples with detections for metolachlor OA at Canajoharie Creek make the relation between SAO ratios and stormflow difficult to assess, yet some generalizations can be made. Stormflow samples had lower SAO ratios than base-flow samples, and SAO ratios of stormflow samples (those collected just after metolachlor application and some at other times) ranged from 1.9 to 1.4, whereas those for base-flow samples ranged from 2.2 to 3.0 (fig. 5). The low SAO ratios in storm-flow samples is consistent with the hypothesis that transport of metolachlor OA during storms results in less degradation than during dry conditions.

SUMMARY

Data collected from 50 wells in Suffolk County, from 2 tile drains beneath agricultural fields in Montgomery County, and from 5 streams in western New York indicate that SAM and SAO ratios for surface water differ from those for ground water. Differences in these ratios are related to soil texture, amount of time since metolachlor application, hydrologic flow paths, and storms. The median SAM ratio for samples from the two tile drains and from Suffolk County wells also were lowest during stormflows just after metolachlor application in late May and early June (fig. 4B). The median SAM ratio for five stormflow samples collected in June 1998 was 0.4, and the median SAM ratio for six base-flow samples collected in June 1998 was 5.2. The SAM ratios for the June 1998 stormflow samples were the lowest obtained for Canajoharie Creek during the entire 1997-98 study. SAM ratios for all Canajoharie Creek samples for June 1998, regardless of flow conditions, were lower than those for June 1997, probably because rainfall in June 1998 was greater than in June 1997. Average mean daily discharge for June 1997 was 8.36 ft³/s (cubic feet per second) - far lower than that for June 1998 (45 ft³/s). The higher flows during June 1998 resulted in a short residence time in the soil, and rapid flushing of metolachlor.

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Figure 4. Ratios of SAM ratio (metolachlor ESA to metolachlor concentrations) and SAO ratio (metolachlor ESA to metolachlor OA concentrations) for samples collected from A. Tile Drain 2 between April 1997 and July 1998, and B. Canajoharie Creek between April 1997 and September 1998. SAO ratio values are not joined for Canajoharie Creek samples because few samples had SAO ratios.
correspond to high median SAM ratios. The high SAM ratios for samples from the tile drain overlain by fine-grained soils probably reflect greater sorption of metolachlor in these soils. The coarse soils in Suffolk County allow rapid infiltration, and the low organic carbon content probably inhibits the transformation of metolachlor to metolachlor ESA. These characteristics also result in lower SAO ratios for well water than for tile-drain discharge.

The lowest SAM ratios in tile-drain discharge were in samples collected during storms just after metolachlor application. SAM ratios for TD2 generally were 500 or more, but decreased to less than 100 in response to storms of June 1998. SAO ratios for TD2 also decreased just after storms in June 1998 despite the fine-grained overlying soil that normally retards the movement of metolachlor and metolachlor OA. The low SAM and SAO ratios in TD2 samples in June 1998 were probably the result of rapid infiltration along preferential flow paths. SAM ratios for surface-water samples were lower for samples collected in the 2 months just after application (June and July) than in those from other months, when the contact time with soil and enzymes was longer. The lowest SAM and SAO ratios were in Canajoharie Creek samples collected just after storms.

![Figure 5. SAO ratio (metolachlor ESA to metolachlor OA concentration) for storm and baseflow samples collected from Canajoharie Creek from April 1997 through August 1998.](image-url)
REFERENCES


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