The Deethylatrazine/Atrazine Ratio as an Indicator of the Onset of the Spring Flush of Herbicides into Surface Water of the Midwestern United States

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THE DEETHYLATRAZINE/ATRAZINE RATIO AS AN INDICATOR OF THE ONSET OF THE SPRING FLUSH OF HERBICIDES INTO SURFACE WATER OF THE MIDWESTERN UNITED STATES

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The ratio of deethylatrazine to atrazine (DAR) may be used to record the first major runoff of herbicides from non-point-source corn fields to surface water in the Midwestern United States. The DAR dramatically decreases from ~0.5 to < 0.1 upon application of herbicide and the first major runoff event of a basin. The DAR then gradually increases to values of approximately 0.4–0.6 during the harvest season. Furthermore, the DAR may be used in studies of surface water movement to give a temporal indicator of water moving into reservoirs for possible storage of herbicides. It is hypothesized that deethylatrazine, which accounts for only 6% of the degradation of atrazine, becomes a significant metabolite in surface water (~50% of parent compound) because of its selective removal from soil. This removal process may be an important concept for consideration in studies of herbicide contamination of rivers and reservoirs.

KEY WORDS: Atrazine, deethylatrazine, hydroxyatrazine, metabolites, surface water, and runoff

INTRODUCTION

Approximately three-fourths of all pre-emergent herbicides are applied to row crops in a 10-state area, called the "Corn Belt", where herbicides are frequently detected in surface water[1-4]. Because many herbicides and their metabolites are water soluble, they may leach into ground water[2,5-6], as well as be transported in surface runoff[7-9]. Reconnaissance studies in the Midwest have shown widespread detection of herbicides, such as atrazine and its metabolites in surface water[2,3,7-10] and in ground water[5,11,12]. Furthermore, two metabolites of atrazine, deisopropylatrazine and deethylatrazine, are also widely detected in basins throughout the Midwestern United States, with both atrazine and cyanazine as source terms[13].

It has been demonstrated that ground water is a source of atrazine to surface water[14,15]. Furthermore, the frequency of detection of the dealkylated degradation products of atrazine in surface and ground water has prompted research showing that atrazine's degradation products may be indicators of surface and ground water interaction[10]. Adams and Thurman[16] studied the movement of deethylatrazine through the unsaturated zone and found that the deethylatrazine-to-atrazine ratio (called the DAR) may indicate the slow rate of transport of atrazine to ground water; thus, the DAR may indicate nonpoint-

or point- source contamination of ground water. The concept of the DAR was applied to surface-water effects on ground water in alluvial aquifers by Thurman and others[2,10], who suggested that the DAR values found in surface water of the Midcontinent indicate ground water discharging to streams in early spring and late fall, and surface water recharging alluvial aquifers during late spring.

This paper is an extension of the idea that the DAR may be used to measure the timing of the first pulse of herbicide runoff from corn fields across the Midwest; thus, the DAR would be useful as an indicator of nonpoint source contamination of herbicides to surface water. It is hypothesized that deethylatrazine, which accounts for only 6% of the degradation of atrazine, becomes a significant metabolite in surface water (~50% of parent compound) because of its selective removal from soil. This process is discussed relative to the major metabolites of atrazine in soil and their distribution coefficients and possible transport to surface water. The objectives of this research are: (1) to apply the concept of a metabolite ratio (DAR) to surface runoff as an indicator of timing of nonpoint source pollution in the Iroquois Basin in the state of Illinois, which is representative of the central United States, (2) to examine the selective removal of atrazine metabolites from soil by consideration of sorption coefficients of the major and minor metabolites of atrazine, (3) and to give examples of how the DAR might be used to monitor or trace nonpoint source pollution into different surface water bodies with Perry Reservoir in Kansas as an example.

EXPERIMENTAL METHODS

Iroquois River.   An automatic sampler collected approximately 300 samples from the Iroquois River during the spring and summer of 1990 at Chebanese, Illinois[17]. The sampling point represents a drainage area of ~5000 km2. The automatic samplers were installed at existing U.S. Geological Survey streamflow-gaging stations. The samplers were equipped with Teflon-lined intake tubing from the pump to the stream, silicone rubber tubing in the peristaltic pump, and either 1-L or 350 mL glass sample collection bottles. Automatic samplers were capable of collecting at least 24 samples between visits and were programmed to collect a sample every other day during non-runoff periods. When runoff from precipitation occurred, samples were collected for herbicide analysis. During base-flow periods, the samplers were visited at least once, but usually twice per week to remove samples or to conduct manually activated automatic sampling. During runoff, sites were visited within 24 hours to remove samples. All water samples were collected and composited in large glass containers and filtered through glass-fiber filters (1-μm pore diameter) into baked glass bottles for shipment to the laboratory.

Perry Reservoir.   Perry Reservoir is located in northeast Kansas (U.S.A.) and is used for public water supply. The drainage area is ~2900 km^2, storage capacity is ~277 km^3, mean daily discharge of 18.9 m^3/second, and the residence time of water in the reservoir is ~170 days. The drainage area is intensively cultivated (~50%) with corn, sorghum, soybeans, and wheat. Atrazine is one of the major herbicides applied in the basin. The study ran for one year from March 1992 to March of 1993 with samplings of the reservoir both before and after herbicide application. Water samples were collected from a selection of 50 sites from the dam to the input of the Delaware River. The reservoir varied in depth from 0–18 meters and samples were collected with a Kemmerer sampler from one to four depths at each site. Equipment blanks were collected and analyzed to prevent cross contamination of sampling equipment.

Analysis. Methanol (Burdick and Jackson, Muskegon, MI), ethyl acetate, and isooctane (Fisher Scientific Springfield, NJ) were pesticide-grade solvents. Deionized water was charcoal filtered and glass distilled prior to use. Atrazine, propazine, and simazine were obtained from Supelco (Bellefonte, PA); terbuthylazine standards were obtained from the U.S. EPA (U.S. Environmental Protection Agency) Pesticide Chemical Repository (Research Triangle Park, NC); and the triazine metabolites, deethylatrazine and deisopropylatrazine, were obtained from Ciba Geigy (Greensboro NC). The C_{18} cartridges (SEP-PAK from Waters, Milford, MA) contained 360 mg of 40-mm C_{18} bonded silica. Standard solutions were prepared in methanol, and d_{10} phenanthrene (U.S. EPA, Cincinnati, OH) was used as an internal GC-MS quantitation standard.

The method of Thurman and others[18] was used for herbicide analysis, which consists of using a Waters Millilab Workstation (Milford, MA) for solid-phase extraction with C_{18} cartridges. Each 123-mL water sample was spiked with a surrogate standard, terbuthylazine (2.4 ng/mL, 100 mL) and pumped through the cartridge at a rate of 20 mL/min by the robotic probe. Analytes were eluted with ethyl acetate and spiked automatically with d_{10} phenanthrene. The extract was evaporated automatically by a Turbovap (Zymark, Palo Alto, CA) at 45°C under a nitrogen stream to 100 μL.

Automated GC-MS analyses were performed on a Hewlett Packard model 5890 GC (Palo Alto, CA) and a 5970A mass selective detector (MSD). Operating conditions were: ionization voltage, 70 electron volts; ion source temperature, 250°C; electron multiplier, 2,200 volts; direct capillary interface at 280°C, tuned daily with perfluorotributylamine; dwell time, 50 milliseconds. Separation of the herbicides was carried out using a 12-meter fused-silica capillary column, 0.2 millimeter in diameter with a methyl silicone stationary phase, 0.33 μm thick. Helium was used as the carrier gas at a flow rate of 1 mL/min and a head pressure of 35 kilopascals. The column temperature was held at 50°C for 1 minute, then increased at 6°C per minute to 250°C where it was held for 10 minutes. Injector temperature was 210°C. Quantification of the base peak of each compound was based on the response of the 188 ion of the internal standard, phenanthrene-d_{10}. Confirmation of the compound was based on the presence of the molecular ion and one to two confirming ions with a retention-time match of ± 0.2 percent relative to phenanthrene-d_{10}[18].

RESULTS AND DISCUSSION

Onset of the spring flush.   Figure 1A shows the rapid increase in concentration of atrazine that occurred in surface water of the Iroquois River after 33 days of sampling. The concentration of atrazine increased from ~0.3 μg/L to 2–10 μg/L at the onset of the spring runoff or spring flush. The sampling began on 4 April 90 prior to herbicide application and the initial onset of high concentrations occurred on 7 May 90, which is 33 days after the study began.

Herbicides were applied during this 4 week period within the basin and the first major runoff event occurred beginning on May 5th and lasting several days. During this time the discharge of the Iroquois went from 50 m³/s to 150–200 m³/s. The storm runoff that occurred, coupled with the application of herbicides resulted in this Spring flush event, a phenomenon that has been documented in numerous basin studies[7–9] and in regional studies[2,3,10].

Figure 1B shows the deethylatrazine to atrazine ratio (DAR) for this same sampling period. Note that the DAR was between ~0.3 and 0.6 during this 1 month sampling period but at 33 days the DAR decreased rapidly to < 0.1, at the same time that the first

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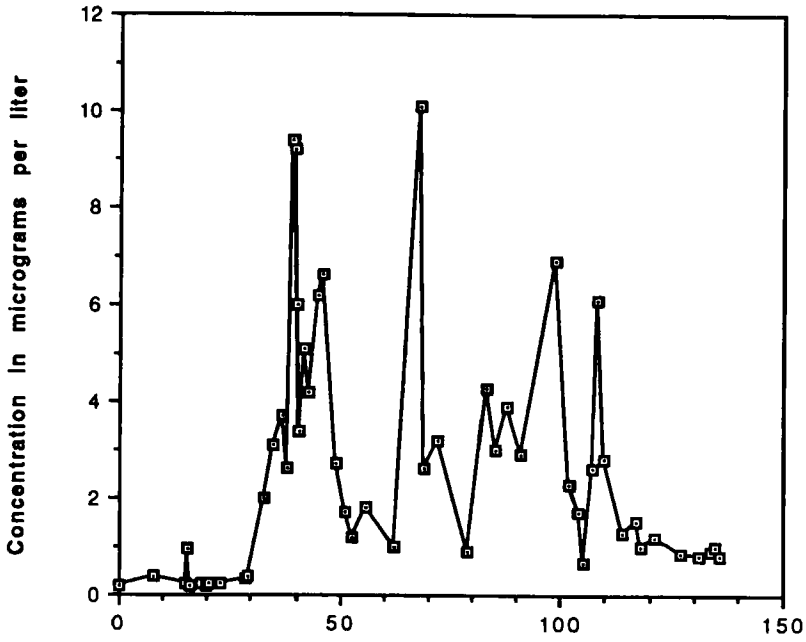
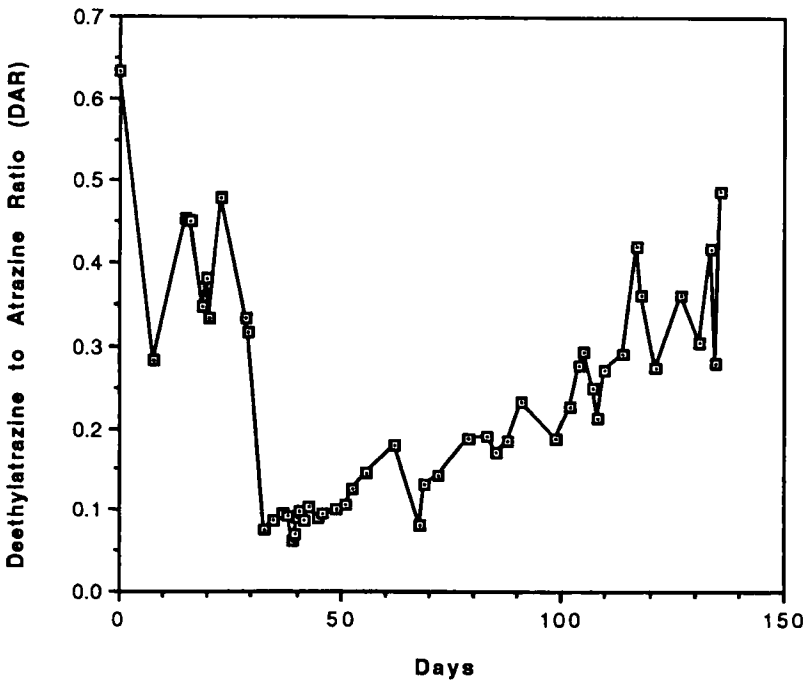**Figure 1A.   Atrazine Concentration in Iroquoris River**

Figure 1B.   DAR through Time

Figure 1   Atrazine concentrations in the Iroquois River and DAR during the same time period.

major flush of atrazine occurred from the fields into the Iroquois River. Apparently, the DAR values of 0.3–0.6 represent either surface runoff from the previous year's application of atrazine with degradation to DEA, or ground water DAR values in river alluvium, which is slowly discharged to the river[14,15].

The DAR values increase regularly from < 0.1 to values of approximately 0.4 by the end of the sampling in mid September near harvest time for the corn (140 days, Figure 1B). The DAR increases regularly with a daily value of ~0.003 per day. This regular increase in the DAR is directly reflected in the mass of metabolite that is transported by the Iroquois River compared to parent compound. For example, Figure 2 shows the transport of both atrazine and DEA in the Iroquois River. In the early season the atrazine was transported as a major peak with the first flush at 33 days. This peak represents the first major transport of atrazine at a time when the DAR is < 0.1 and the transport of DEA is less than 10% of the parent compound (the DAR is a close approximation of mass transport because molecular weight of DEA is 85% of parent compound).

By the middle to the end of the season the transport of atrazine has decreased to values of one third to one half the transport of atrazine. DEA on the other hand has the highest transport in the late season (100–120 days, Figure 2B) after time has passed for degradation of atrazine and subsequent runoff of metabolite. At this time values of transport of DEA are 75–150 mg/s. The idea of later seasonal transport of DEA has been addressed by Thurman and others[13] for several rivers in the Midwestern United States. The term of a second flush of metabolites was suggested, which was dependent on flow conditions in the basins, with wet summers more likely to increase the occurrence of a second peak of metabolites. During this period of late transport the dealkylated metabolites make an important contribution to the total transport of herbicides.

If deisopropylatrazine (DIA) is also added to the DEA, then the sum of metabolites are increased further. For example, Figure 3 shows the correlation of DIA to DEA with a correlation coefficient of 0.67 and a slope of 0.52. Thus, on the average about one half the concentration or mass of DIA is transported relative to DEA. Thus, if DIA is added to DEA then the amount of metabolite to parent that is transported increases by 50%. Thus, during the late season the amount of metabolite transported relative to parent compound is approximately 50–60% of parent compound, and this total mass makes an important contribution to health considerations, since the chlorine atom does remain on the molecule and both DEA and DIA retain some of the herbicidal activity of the parent, atrazine.

This result brings up an interesting question about why there is considerable transport of DEA and DIA relative to atrazine, when from many laboratory studies of the degradation of atrazine, these metabolites account for less than 10% of the decomposition products. A hypothesis for this result is developed in the following section.

Preferential transport of herbicide metabolites.   Atrazine degrades to a series of dealkylated and hydroxylated products in soil through both biotic and abiotic reactions, and Figure 4 shows a major metabolite pathway for atrazine elucidated over the past 30 years[8,19-28]. The pathway includes first the formation of hydroxyatrazine as a major metabolite, and DEA and DIA to a lesser degree. Hydroxyatrazine and DEA and DIA may degrade to the dealkylated hydroxmetabolites shown in Figure 4. Hydroxylation is thought to proceed abiotically by catalysis at the soil and clay mineral surfaces[21-22]. Work by Kruger and others[23,24] using C^{14} labeled compounds shows that atrazine degrades to ~3% DIA and ~6% DEA. Hydroxyatrazine, on the other hand, may account for 4% of the degradation and other bound residues up to 30% or more[23,24]. DEA and DIA may

Figure 2A.   Atrazine Transport in Iroquois River
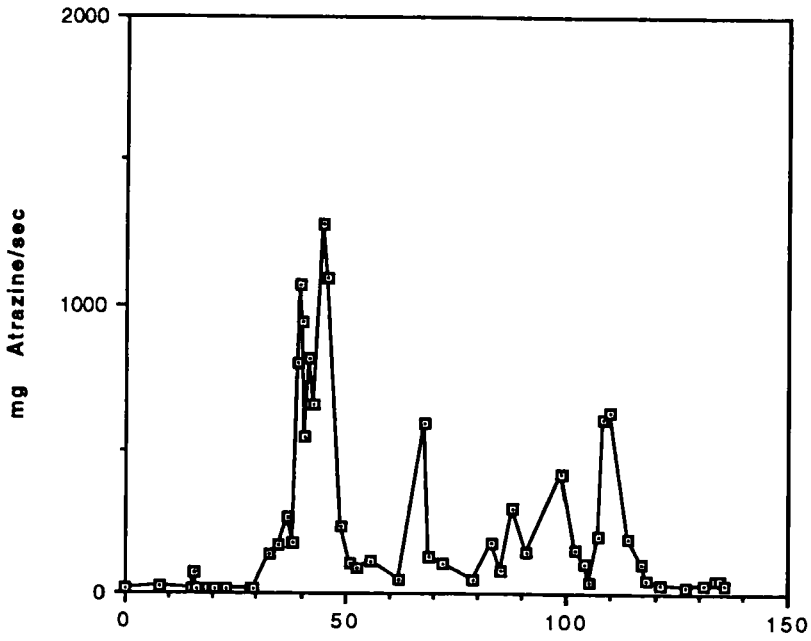
Figure 2B.   DEA Transport in Iroquois River
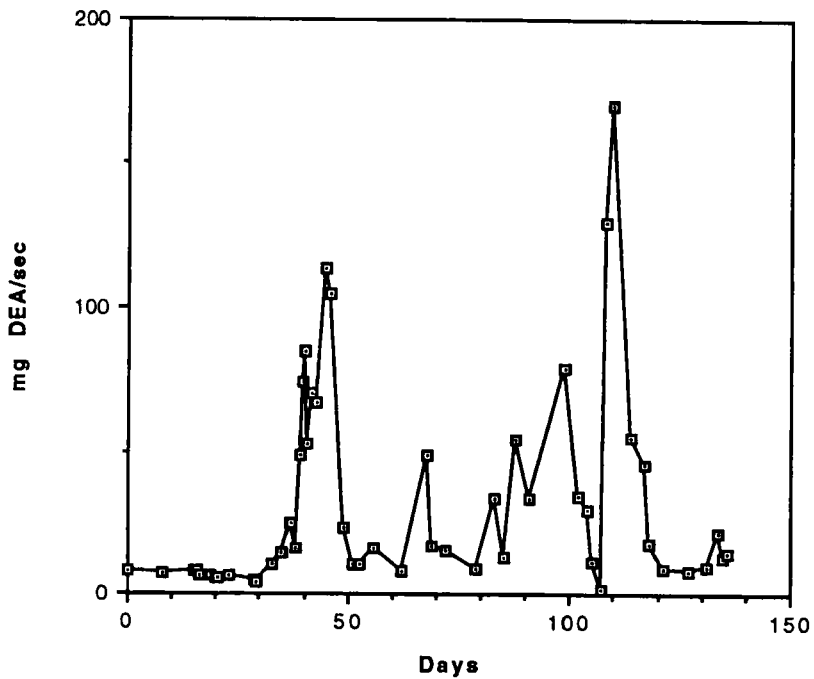
Figure 2   Transport of atrazine and deethylatrazine in the Iroquois River.
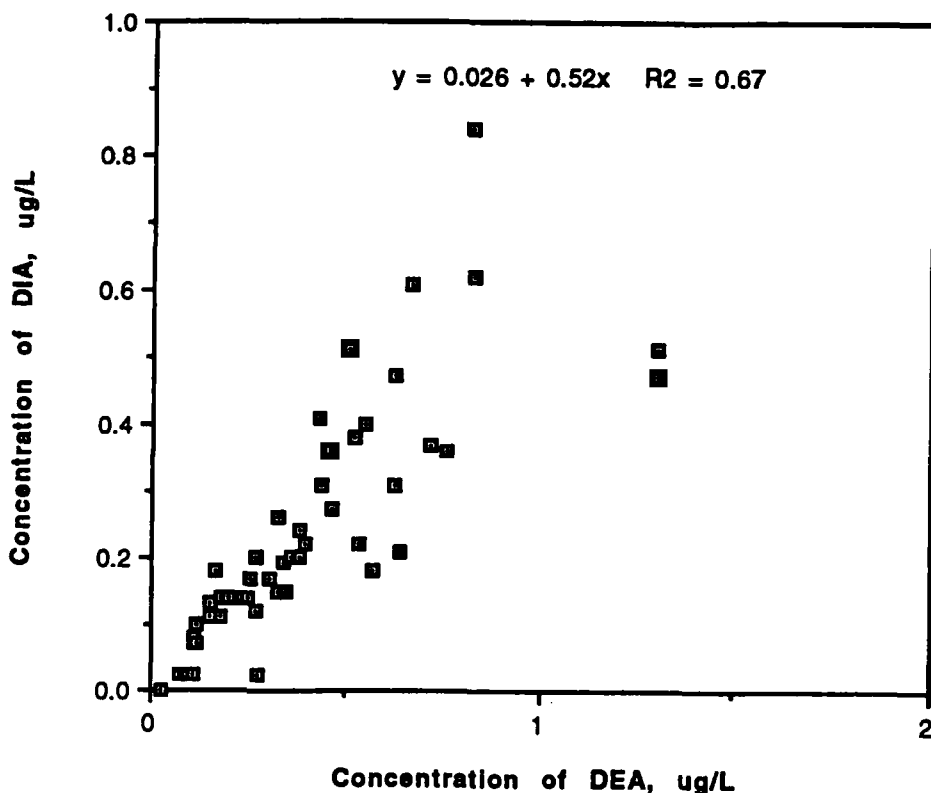
y = 0.026 + 0.52x   R2 = 0.67

Figure 3   Correlation of DIA and DEA in samples from the Iroquois River.

further dealkylate to DDA (Figure 4). Finally, there is opening of the ammeline ring and eventual mineralization to carbon dioxide and nitrogen gas.

Of the seven metabolites of atrazine that may enter the soil environment, there are several factors that contribute to surface runoff. The metabolites must be readily soluble, not degraded too quickly in the soil environment, and must not be too tightly sorbed by soil particles. Let us examine the solubility and sorption characteristics of atrazine and its metabolites for some insight into why there may be preferential transport of DEA and DIA into surface water.

Table 1 shows the solubility, estimated Koc, and pKa of atrazine and its metabolites. From the Koc values reported for the parent compound and the two metabolites, we see a marked difference with nearly 10 times more capacity for sorption of atrazine than either DEA or DIA by soil organic matter. Given that the surface soils may contain 1–2% organic carbon, Kd values could be in the 1–3 range; whereas, the metabolites of DEA and DIA are 0.1 to 0.3, which is considerably less. Thus, there is the opportunity for preferential transport of DEA and DIA relative to atrazine during runoff.

Furthermore, the type of runoff may affect preferential transport. For example, there are at least two possible flow paths for water, over the surface or leaching and lateral flow through the shallow soil. In overland flow there is considerably less interaction of the water phase with the soil particles and the ratio of water to soil is much greater. This is in effect a slurry of water and soil, which is seen as surface runoff. Thus, there would

Atrazine and Metabolites
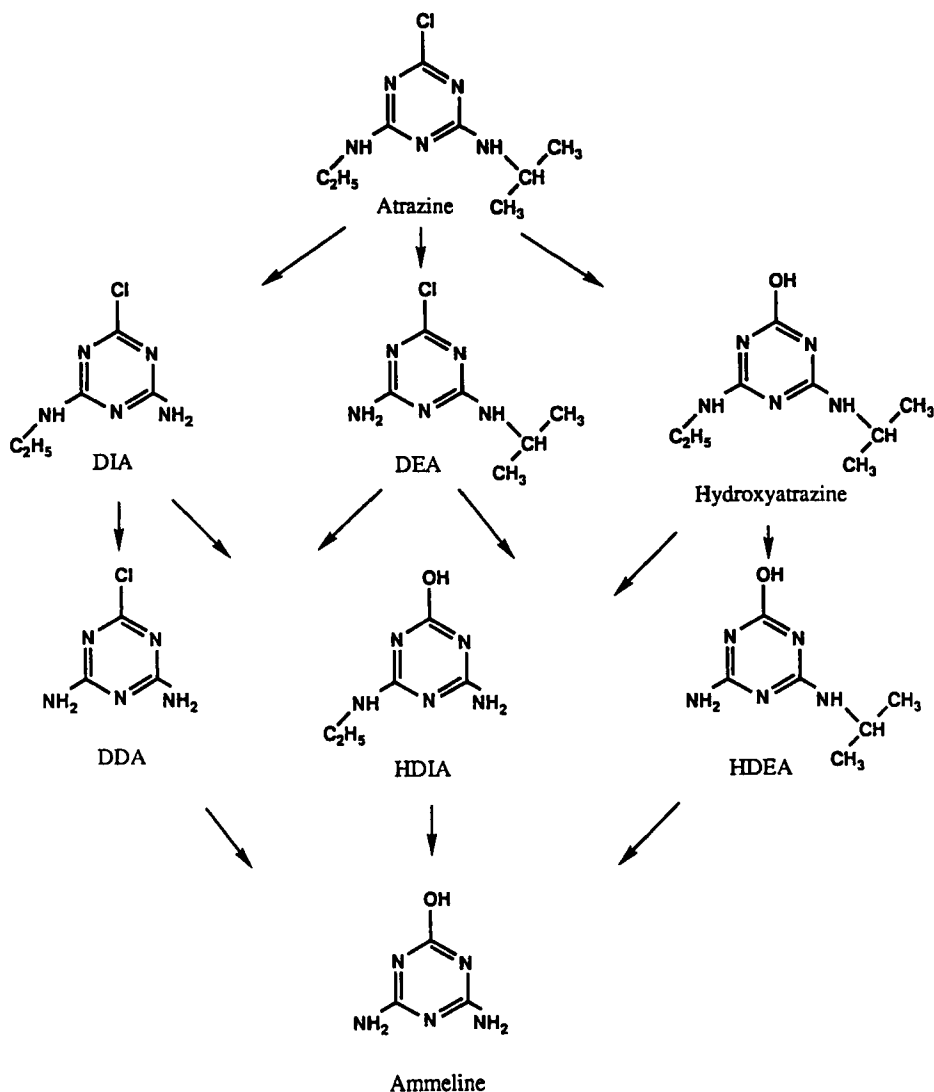
Figure 4   Degradation products of atrazine in soil.

be much less of a chromatographic effect than if flow through the soil occurs. During lateral flow the water moves through the soil moving both downward and laterally; in this case, the preferential leaching of DEA and DIA may occur given their much lower Koc values as compared to atrazine. An example of the chromatographic effect is reported by Mills and Thurman[29] for the transport of DEA relative to atrazine in the unsaturated zone; thus, this mechanism is a possible explanation for preferential movement of DEA and DIA.

Table 1   Solubility, pKa, and estimates of Koc for atrazine and its metabolites.

Herbicide or Metabolite	Koc	Pka[31]	Solubility (mg/L)
Atrazine	160	1.71	33
Deethylatrazine	16*	1.65	3200
Deisopropylatrazine	24*	1.58	670
Didealkylatazine	< 1*	No data	No data
Hydroxyatrazine	150*	5.15	227 @ pH 3
Hydroxydeethylatrazine	5*	4.57	No data
Hydroxydeisopropylatrazine	5*	4.65	No data
Ammeline	< 1*	No data	No data

* Estimated from solubility and structural information[18,29,31].

Sorption of the s-triazines and several hydroxyatrazine metabolites to clay minerals has been reported by Weber[30], who found that protonation and subsequent cation exchange and hydrogen bonding are important mechanisms for sorption by clays. The hydroxylated metabolites have a pKa of 4.57–5.15 (Table 1); thus, they may be partially protonated in soil when the pH is less than 7. The dealkylated metabolites, DEA and DIA, have a low pKa and are not affected by cation exchange, but only hydrophobic interactions. These mechanisms are carefully explained by Weber[30] and are a probable mechanism for the binding of the hydroxylated atrazine metabolites that occurs in soil. Recently, Lerch and Donald[31] took advantage of the ability of cation exchange to isolate the hydroxylated metabolites of atrazine from water. Thus, the combination of the hydrophobic effect, cation exchange, as well as the possibility for covalent binding of the hydroxylated metabolites to soil organic matter result in much less leaching of these compounds, in spite of their apparent abundance in soil decomposition studies of atrazine[23,24].

The binding of hydroxyatrazine by unsaturated zone materials is borne out by work reported by Cai and others[32], who find only trace levels of hydroxyatrazine in ground water, which indicates that leaching of hydroxyatrazine is of minor importance. Whereas, DEA and atrazine have been reported frequently in ground water[12]. Less is known about the occurrence of hydroxyatrazine in surface water. Recent work by Lerch and others[33] shows that it does occur but at concentrations considerably less than atrazine or its dealkylated metabolites, DEA or DIA. The relatively high pKa of the hydroxyatrazine (pKa 5.15) lends it to sorption by cation exchange and hydrophobic interaction.

Thus, this section has hypothesized that DEA and DIA may be transported more readily than either parent compound or hydroxylated metabolites through various sorption processes, which leads to the conclusion that although DEA represents only ~6% of the C^{14} degradation product of atrazine decomposition and DIA only ~3%, they may become important metabolites in surface water, especially later in the season when degradation and subsequent runoff have occurred. The last section will examine an example of how the DAR can be used to trace runoff events in reservoirs.
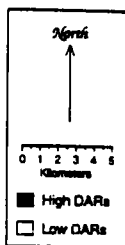
DAR as indicator of timing of runoff.   Because of the dramatic decrease in the DAR that occurs in the spring flush, the ratio might be used to trace the flow of water downstream. One application of this model is the filling of a reservoir by spring runoff. The conceptual model of how the DAR would be used to follow runoff through a reservoir is shown in Figure 5. In this model the reservoir already contains water with atrazine and deethylatrazine present from the previous year's runoff. The arrows show the direction of

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Conceptual Model

Pre-Herbicide Application   **Post Herbicide Application**

(a) High DARs enter reservoir
in pre-application inflow

(b) Low DARs enter reservoir
in post-application runoff,
pushing water with higher
DARs further downstream

North

0 1 2 3 4 5
Kilometers
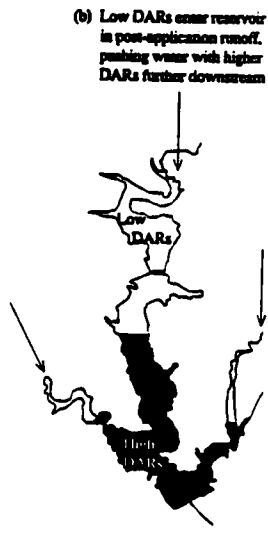
■ High DARs
□ Low DARs

Perry Reservoir Data

March 1992 Pre-Application   June 1992 Post Application
High DAR = 0.22-0.29   High DAR = Not Present
Low DAR = 0.18-0.21   Low DAR = 0.09-0.17

Figure 5   Conceptual model and values for DAR in Perry Reservoir.

flow with the dam at the bottom or south end of the figure. Near the dam the water is older in age and contains water from the previous summer, while the upstream water contain herbicides that have entered the reservoir during the fall and winter. The DAR values would be higher then on the upper end of the reservoir from the fall and winter.

In the post application scenario (b) the reservoir receives runoff water that contains the spring flush of herbicide with low DAR values. The incoming water displaces the older water in the reservoir and the higher DAR values from the previous winter and early spring are displaced to the dam end of the reservoir.

At the bottom of Figure 5 are shown the actual DAR values for Perry Reservoir during the March 1992 pre-application period. High DAR values were present from the center of the reservoir to the upstream end of the Delaware River, which flows into Perry Reservoir, with values from 0.22 to 0.29. From the dam to the center of the reservoir the values ranged from 0.18 to 0.21. After the application of atrazine to the surrounding corn fields in April and May and subsequent runoff, the reservoir was sampled in June of 1992 for the post-application period. There were no high DAR values present, with low values ranging from 0.09 to 0.17. The decrease in DAR values was accompanied by increased concentrations of atrazine in the reservoir. Calculations of water flux through the reservoir indicated that the reservoir had been flushed out and refilled in ~120 days, somewhat faster than the average residence time of 170 days. The decreased DAR values gave a similar conclusion. No doubt dilution had also occurred but atrazine concentrations had changed from 2–4 µg/L before application to 4–10 µg/L after application[34]. Thus. it appears that the concept of the DAR as an indicator of the onset of the spring flush of herbicides in the corn belt may be a useful tool as an indicator of timing of runoff and the ability to follow water movement through the reservoir.

Acknowledgements

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