

## Influence of a Riparian Wetland on Nitrate and Herbicides Exported from an Agricultural Field

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Agrochemicals are a major source of nonpoint pollution. Forested corridors along stream channels (riparian zones) are thought to be potential sites for removal of agricultural contaminants from ground and surface waters. First-order riparian wetlands are reputed to be especially effective at groundwater remediation. The study site is a fairly typical (for eastern Maryland) small, first-order stream in an agricultural watershed. Preferential flow supplies most of the stream water within the riparian headwater wetland. This upstream area also contains the highest average stream N and pesticide loads in the entire first-order riparian system. Zones of active groundwater emergence onto the surface display high concentrations of nitrate throughout the soil profile and in the exfiltrating water, whereas inactive areas (where there is no visible upwelling) show rapid attenuation of nitrate with decreasing depths. Atrazine degradation products appear to penetrate more readily through the most active upwelling zones, and there is a correlation between zones of high nitrate and high atrazine metabolite levels. Deethylatrazine/atrazine ratios (DAR) seem to indicate that stream flow is dominated by ground water and that much of the ground water may have reached the stream via preferential flow. Remediative processes appear to be very complex, heterogeneous, and variable in these systems, so additional research is needed before effective formulation and application of riparian zone initiatives and guidelines can be accomplished.

**KEYWORDS:** Nitrate; atrazine; ground water; stream flux; upwelling zone; DAR

### INTRODUCTION

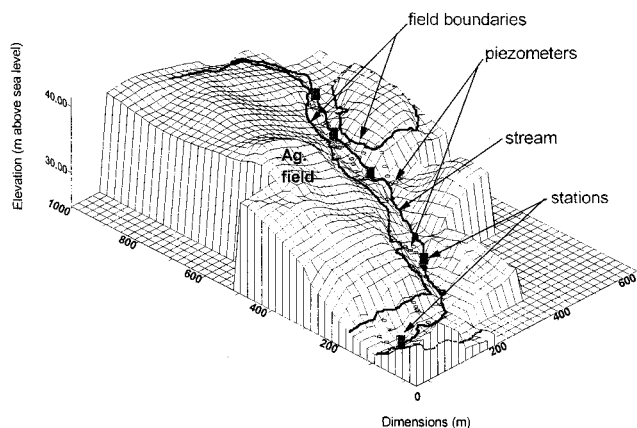
Field-applied agricultural chemicals, particularly nutrients (nitrogen and phosphorus) and pesticides, are a major form of non-point-source pollution. Excess nutrients in surface waters can lead to eutrophication (1, 2), outbreaks of water-borne bacteria and other microorganisms (such as *Pfeisteria piscicida*) (3), and contamination of drinking water supplies (1). Nitrogen is primarily transported through ground water (1, 4), whereas phosphorus is mostly transported via surface runoff (5, 6). Pesticides, and pesticide degradation products, are also detected in surface waters, often exceeding U.S. EPA maximum contaminant levels (MCL) (7). Vegetated riparian corridors are frequently cited as areas where agrochemicals can potentially be sequestered or removed (8, 9). First-order streams are considered to be particularly effective at nutrient removal (10). However, the capacity for first-order riparian systems to mitigate agricultural contaminants is highly variable (both spatially and temporally) and is largely dependent on external environmental conditions. Moisture and temperature conditions, and local hydrology, may exert strong influences on riparian buffer

function and behavior and, consequently, affect the contaminant-removing capabilities of a site.

Nitrogen applied to agricultural fields may enter the ground water and end up discharged into surface waters, particularly if oxic conditions prevail in the subsurface (11). However, anaerobic conditions combined with high organic carbon levels can provide mechanisms (principally, denitrification) by which significant amounts of groundwater nitrate-N can be removed (12). Riparian buffer zones often present these favorable conditions, with the added benefit of potential nitrogen uptake by the typically abundant vegetation found at these locales. Nevertheless, nitrogen is sometimes detected in surface water regardless of the presence of a riparian buffer strip. Preferential groundwater flow, resulting in rapid movement of ground water through a riparian system, may be responsible for much of the agricultural nitrogen that ends up in streams (13).

Residues of pesticides applied to agricultural fields can enter surface waters either via surface runoff or groundwater discharge. In the case of atrazine, a commonly used herbicide, the parent compound is more likely found in surface runoff, whereas certain degradation products, deethylatrazine (CIAT) and deisopropylatrazine (CEAT), are more soluble and more commonly found in ground water. The ratio between CIAT and atrazine (deethylatrazine/atrazine ratio, or DAR) is often used

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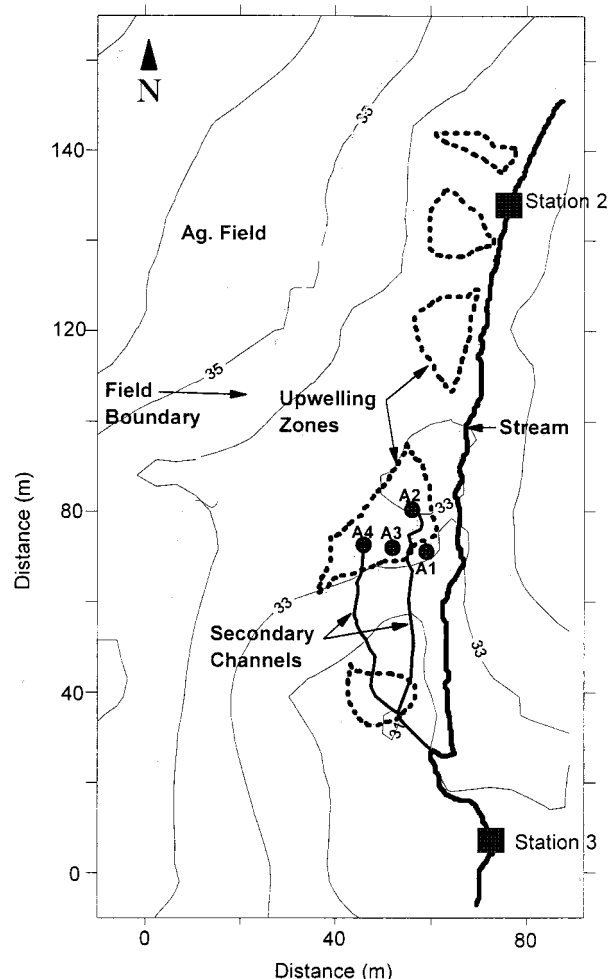


**Figure 1.** Three-dimensional view of watershed surface topography showing location of field edge, stream, sampling stations, and piezometers. The entire first-order stream length is  $\sim 1200$  m. Riparian zone lies between fields, alongside stream. Coordinates are in meters (origin at southwestern corner of catchment).

to describe the extent of groundwater contribution to stream flow (7); the higher the DAR, the greater the groundwater component. Most studies involving DARs have looked at high-order streams (7, 14), with DARs ranging from 0.1 to 1. Higher values ( $> 1$ ) may be more common in low-order streams, which are typically groundwater-dominated. However, one needs to be somewhat cautious of overinterpreting these DAR values, a point that will be expanded on below. The conditions under which pesticides and pesticide degradation products are most likely to be immobilized or decomposed remain unclear. Most research to date has focused on pesticide fate in well-drained soils, but information about pesticide behavior in anaerobic conditions is often contradictory. There are indications that atrazine and metolachlor can degrade in reducing environments, such as may be found in riparian wetland soils (15, 16), yet some researchers claim that atrazine should actually be stable under anaerobic conditions (17). Even less information is available on the specific behaviors of atrazine metabolites in wetland environments. Little work has been done to address the effect of hydrology (particularly preferential flow) on pesticide behavior in riparian systems and the overall impact of riparian wetlands on pesticide fate. The objective of this study was to assess the effect of a first-order riparian wetland on agricultural-influenced ground water and to determine the role of local hydrology in export from this ecosystem.

## MATERIALS AND METHODS

**Site Description.** The site is part of a larger study of field and riparian zone hydrology (including the fate of applied agrochemicals), called Optimizing Production Inputs for Economic and Environmental Enhancement (OPE<sup>3</sup>), conducted at the USDA–Beltsville Agricultural Research Center (BARC) in Beltsville, MD. The study site is contained within a first-order agricultural watershed in the mid-Atlantic coastal plain. The sub-watershed consists of a 20 ha agricultural field that drains into a riparian zone and a small, unincised, north-to-south flowing first-order stream. To the east of the riparian corridor lies a smaller upland field ( $\sim 8$  ha) and a low-lying wetland area. The riparian soils are mostly Typic Haplosaprists (Johnston silt-loam series),  $\sim 2$  m in depth, underlain by an oxic sand and gravel aquifer. The first-order stream length is  $\sim 1200$  m, at which point it joins a larger, higher order stream, marking the terminus of the study area (see **Figure 1**). The dominant tree species within the riparian zone is red maple (*Acer rubrum*), with an understory of skunk cabbage (*Symplocarpus foetidus*) in the spring and jewelweed (*Impatiens pallida*) in late summer. These obligate wetland species are shallow rooting because of nearly continuous surface saturation and



**Figure 2.** Close-up plan view of upper portion of riparian zone showing locations and approximate extents of upwelling zones and secondary channels. Stream channel, field boundaries, and sampling stations 2 and 3 are also shown. Upwelling zones (areas of permanent saturation) dominate the flood plain in this area. Nested piezometers (up to seven per nest) are depicted as single wells. Only the piezometer transect A1–A4 (discussed in the text) is depicted. Coordinates are in meters.

consequent anoxic conditions close to the surface. The stream channel is instrumented with five permanent stream sampling/monitoring stations, essentially breaking up the stream into four sections that can be analyzed independently. Each stream station consists of a constructed channel flume with a weir attached to the output end. Approximately 170 piezometers have been placed within the riparian zone, many of them nested (multiple piezometers sampling different depths at the same location) in transects (from field to stream) between the stream stations. Stream flow characteristics and groundwater behavior are highly variable in this system. The area that typically displays the highest concentrations of agrochemicals in surface water (both in the stream channel and in zones of groundwater emergence onto the flood plain) lies between stations 2 and 3 (see **Figure 2**). This area also receives the greatest quantities of water input per unit area, compared to the rest of the system. This part of the riparian zone is a groundwater-fed wetland with perennially saturated surface conditions. Much of the research for the past three years has focused on the riparian wetland area.

**Water Sampling and Analysis.** Streamwater samples were collected weekly for ion analysis, and monthly for pesticide analysis. Groundwater samples were gathered approximately every 4 months. Obtaining groundwater samples required pumping out at least one full well volume, waiting for full recovery, and then collecting the sample with a bailer. Only 20 mL is required for ion analysis, but pesticide samples require a minimum of 1 L in order to get adequate detection limits.

Samples from instantaneously recovering piezometers can be obtained at one time, because groundwater can be continuously pumped from these. Samples from slow-recovering wells were collected over a few days, because these wells yield very little water and take a long time to recover. Samples were collected with a minimum of atmospheric contamination. Plumb-bob-style "floats" were put into slow-recovering piezometers after pumping. As water level rises in the well, the float also rises, which helps prevent atmospheric O<sub>2</sub> from contaminating the samples. Samples were analyzed for nitrate-N, chloride, and sulfate using a Dionex (Sunnyvale, CA) ion chromatograph (IC), with detection ranges of 0.1–30 mg/L for NO<sub>3</sub><sup>-</sup>, 1–60 mg/L for Cl<sup>-</sup>, and 1–40 mg/L of SO<sub>4</sub><sup>2-</sup>. Groundwater sampling for dissolved gas analysis was also done periodically. This required the same basic collection procedure as sampling for ions, except the samples had to be sealed off from the atmosphere immediately upon bailing the well. This was done by overfilling a glass vial and carefully capping it such that no bubbles were introduced (18). Usually five to six vials had to be obtained from each piezometer so that a full range of gases could be analyzed. Samples were taken back to the laboratory and immediately refrigerated. Water temperature was also measured and recorded for each piezometer prior to pumping. Samples were analyzed for dissolved oxygen, dinitrogen, and argon using a gas chromatograph (GC) (19). The GC system used was a Tremetrics (Austin, TX) 540 fitted with an ultrasonic detector and a Tekmar (*Cincinnati, OH*) 7000 autosampler, according to the method in Mookherji et al. (18).

Stream flow (*Q*) was determined using previously established rating curves (water level/discharge relationships) and recorded water levels at each weir. Ground water emerging onto the flood plain was also sampled. In some places, groundwater discharge to the surface is so focused and rapid that the emerging water is channelized at the surface (from the discharge point) and flows aboveground to the stream channel. Discharge (*Q*) measurements were taken from these subchannels and the stream at the same time samples were collected. All *Q* values are averaged from a minimum of three measurements each. Contaminant fluxes (mass/time) in the stream, and from the groundwater upwelling channels, were obtained by multiplying *Q* (L/s) by concentration (mg, µg, or ng per L).

**Analysis of Herbicides and Herbicide Degradation Products.** The samples of water (stream or ground water), ~1 L each, were filtered through Whatman Puradisc GF/F glass fiber filters (25 mm diameter, 0.7 µm pore size) to remove particulates prior to solid-phase extraction using 200 mg of Isolute ENV+ cartridges (Jones Chromatography).

Just prior to use, each cartridge was conditioned sequentially with 6 mL volumes of dichloromethane, acetone, and deionized water. The samples were then passed through the cartridges by vacuum suction at 10 mL/min flow rates. The cartridges with their adsorbed samples were stored in the freezer until elution (typically within 1 month of collection). Prior to elution, the cartridges were thawed and dried by vacuum suction (~2 h), whereupon 6 mL of dichloromethane was passed through the column followed by a 9 mL mixture of acetonitrile and acetone (50:50 v/v). The eluents were combined and concentrated under N<sub>2</sub> gas until the mixed solvent was exchanged with acetonitrile (usually 1 mL in volume).

The samples were monitored for the presence of atrazine and metolachlor, which were the two herbicides sprayed on the adjacent experimental field. In addition to atrazine and metolachlor, the samples were also monitored for the presence of atrazine degradation products, 6-amino-2-chloro-4-(ethylamino)-s-triazine (CEAT, also called deisopropylatrazine) and 6-amino-2-chloro-4-(isopropylamino)-s-triazine (CIAT, also called deethylatrazine).

To monitor for possible losses of target compounds in the samples during their analysis, triphenyl phosphate (TPP) was added as a surrogate to each collected sample to yield a final concentration of 1 µg/L. The concentration of target compounds did not usually exceed 2 µg/L of collected samples.

GC was carried out in splitless mode on a DB-17 MS (J&W Scientific) column (length = 30 m; i.d. = 0.25 mm; film thickness = 0.25 µm) using the following temperature program: initial temperature, 130 °C, with the temperature program first increased at the rate of 5 °C/min to 240 °C, and then the rate was changed to 20 °C/min to a final temperature 280 °C and held for 5 min. The injection temperature

**Table 1.** Nitrate and Pesticide Fluxes at Different Points along the Stream Channel<sup>a</sup>

station	CIAT flux (ng/s)	CEAT flux (ng/s)	atrazine flux (ng/s)	DAR	nitrate-N flux (ng/s)	stream flow (L/s)
2	118	217	14	8.4	3.4	0.6
3	213	426	28	7.6	7.3	1.3
4	177	322	26	6.7	6.1	1.4
5	95	151	23	4.2	3.9	1.3

<sup>a</sup> Total CEAT (ng/s), CIAT (ng/s), atrazine (ng/s), and nitrate (mg/s) fluxes at stations 2–5 for May 15, 2000. Stream flow (L/s) and DAR values also given. Fluxes are often highest at station 3, although stream flow is not.

was 250 °C, and the detector interface temperature was maintained at 300 °C. Helium was used as a carrier gas at a constant flow of 1 mL/min.

All pesticide analyses were performed on a Hewlett-Packard model 5989A GC-MS operated in selection ion monitoring mode. The ions monitored in electron impact mode (EI) included *m/z* 200, 215, and 173 for atrazine; *m/z* 162 and 238 for metolachlor; *m/z* 173, 158, and 145 for CEAT; and *m/z* 172, 187, and 145 for CIAT. For quantification the most abundant ions were used: *m/z* 200 for atrazine, *m/z* 262 for metolachlor, *m/z* 173 for CEAT, and *m/z* 172 for CIAT.

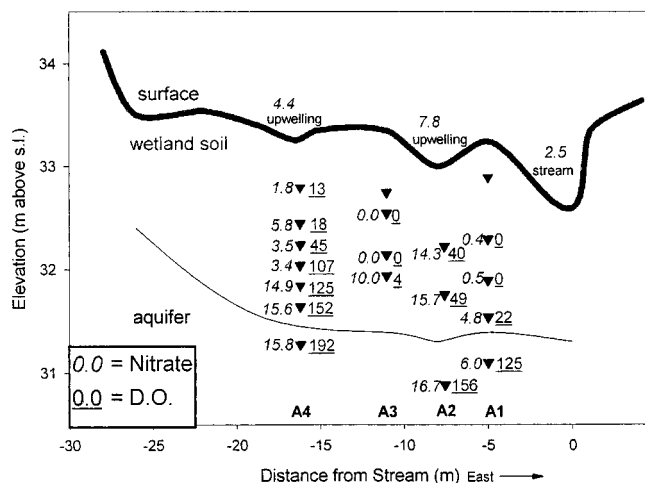
Anthracene-*d*<sub>10</sub> (Cambridge Isotope Laboratories) was used as an internal standard at a concentration equal to 1.34 ng/µL of sample. The concentration of target compounds was determined on the basis of five-point calibration curves obtained for standards ranging from 0.05 to 2.0 ng/µL. The surrogate recovery averaged 85–116%. Spike recoveries for the test analytes were as follows: CEAT, 80%; CIAT, 87%; atrazine, 97%. Minimum detection limits were 0.05 µg/L.

## RESULTS AND DISCUSSION

Flow added to the stream along different sections can be determined by comparing flows between stream stations. Analyzing the amount of stream flow added between stations and correcting for the approximate drainage area to each station allow areas that contribute disproportionately to total stream flow to be identified. If groundwater delivery patterns are the same over the entire catchment, the amount of stream flow generated per area should be roughly the same between each station. Notably, this is not the case. Flow added per unit of contributing drainage area was greatest between stations 2 and 3 ~60% of the time, over the three year study period. Much of this increased flow between stations 2 and 3 comes from discrete sources that are visible (and often measurable) at the site. These sources are upwelling zones (concentrated areas of groundwater discharge to the surface) and associated secondary channels. There are several runnels and subchannels on the flood plain that carry upwelling ground water to the stream. In addition, some streamside macropores also drain upwelling zones. Upwelling zones are not evenly distributed throughout the flood plain but are concentrated in the region between stations 2 and 3.

There are distinctive patterns in streamflow generation and nitrate and pesticide loading. The greatest contribution to total stream nitrate-N and pesticide fluxes comes from sections of the flood plain between stations 2 and 3. **Table 1** shows stream nitrate-N fluxes (mg/s) and atrazine parent and metabolite (CIAT and CEAT) fluxes (ng/s) at stations 2–5 for May 15, 2000. Nitrate-N fluxes decrease downstream, indicating in-stream N processing (hyporheic denitrification and/or assimilation by organic matter). Deethylatrazine (CIAT)/atrazine ratios (DAR) are also given. The high (>1) DARs are consistent with an overwhelming contribution of ground water to stream flow (7). Although total values change temporally, relative amounts are



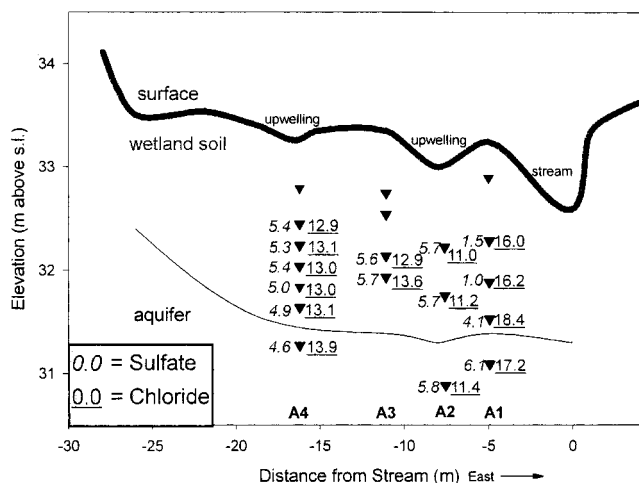


**Figure 3.** Side view subsurface map of A1–A4 transect showing nitrate-N concentrations and DO levels. Profile of A1–A4 transect of nested piezometers shows depths of screened intervals, surface topography, and aquifer surface. Inverted triangles depict locations of screened intervals. Piezometer designations (A1, A2, A3, A4) are listed beneath each nest. Nitrate-N concentrations (mg/L) in ground water obtained from each piezometer are listed in italics to the left; dissolved oxygen (DO) values (FM) are underlined to the right. Nitrate concentrations in emergent water taken from the surface at the two active upwelling zones of this transect are listed. Inactive areas exhibit nitrate and DO depletion rapidly up through the profile. Nitrate concentration in the adjacent stream channel is also shown. Slight indents at surface (approximately 17 and 8 m from the stream channel) represent the origin points of the secondary channels.

consistent for baseflow conditions throughout the three year study period. The DAR concept was originally proposed as a method to help distinguish ground water from surface runoff contributions to stream flow (7, 14). Barbash and Resek (20), however, commented that many authors have taken too much liberty with this DAR approach, especially in trying to apply it to systems where multiple processes may be active.

Much of the increase in stream N and pesticide fluxes between stations 2 and 3 comes from small areas of the riparian wetland. The origin points of many secondary channels consist of small zones of intensive groundwater upwelling to the surface. In some cases, single macropores are observed discharging large volumes of ground water. One particular upwelling zone/secondary channel system supplies 10–15% of total stream flow and 30–40% of total stream nitrate-N load. This section has been heavily instrumented. **Figure 2** shows a close-up plane view of this part of the site, with only one of the piezometer transects depicted. Groundwater upwelling zones, and the major secondary channels, are shown. The partial nested piezometer transect, which intercepts the origin points of the secondary channels, is labeled as A1, A2, A3, and A4. Two of these, A2 and A4, lie within the points of origin of each of two subchannels (see **Figure 2**). These are foci of intense groundwater exfiltration. A1 and A3 lie at points of little or no visible groundwater upwelling.

There is great variability in groundwater composition within the wetland soil above the sand aquifer. This is evident even on a small scale. Within the A1–A4 transect, nests at the active upwelling points (A2 and A4) exhibit different chemical signatures from those in the inactive zones (A1 and A3). **Figure 3** is a profile of this transect, showing the location of each piezometer nest and the depths of screened openings for each set. The A2 piezometer nest lies in the most active upwelling zone. This area not only exhibits the greatest rate of groundwater

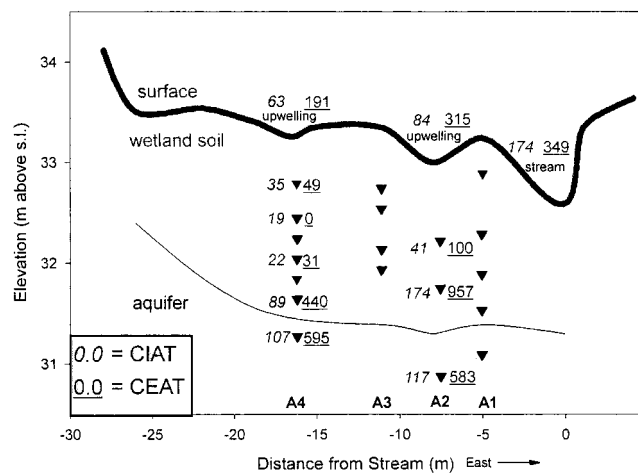


**Figure 4.** Side view subsurface map of A1–A4 transect showing sulfate and chloride concentrations. Profile of A1–A4 transect of nested piezometers shows depths of screened intervals, surface topography, and aquifer surface. Inverted triangles depict locations of screened intervals. Piezometer designations (A1, A2, A3, A4) are listed beneath each nest. Sulfate concentrations (mg/L) in ground water obtained from each piezometer are listed in italics to the left; chloride concentrations (mg/L) are underlined to the right. Values are fairly constant for all nests except A1. Sulfate concentrations decrease upward in the A1 nest, possibly due to sulfate reduction. Chloride concentrations are vertically steady within each nest, except at A1; groundwater sources may be slightly different at this nest location.

exfiltration in the entire system but also shows the highest surfacewater nitrate concentrations. Ground water in the soil directly beneath this nest has nitrate-N concentrations nearly as high as within the aquifer. The A4 nest lies in a somewhat less active exfiltration point. Nitrate-N concentrations become partially attenuated vertically but are still fairly high even in the upper soil. Nitrate-N disappears rapidly with decreasing depth in those areas that are inactive (A1 and A3). Dissolved oxygen (DO) levels indicate that ground water remains suboxic within the soil beneath the active zones, but oxygen is rapidly consumed in the inactive regions. Depletion of DO and nitrate-N in these nests (A1 and A4) occurs below the rooting zone and likely represents denitrification. This is further substantiated by dinitrogen and argon data (see Mookherji et al., 18). The histosol contains ample amounts of carbon (~25% throughout) to sustain microbial activity.

Sulfate and chloride can act as groundwater tracers and help determine the direction of groundwater movement. **Figure 4** shows the sulfate and chloride concentrations for the A1–A4 transect. Chloride concentrations are fairly consistent vertically at each nest, indicating that the ground water is probably from a common source and that vertical groundwater movement is likely. Hydraulic head data show higher total heads for deeper wells and lower total heads in the shallower piezometers, confirming that the probable direction of groundwater flow is vertically upward in these nests. Sulfate behaves in a similar fashion, except at the A1 nest, where the loss of S can be explained by the depletion of both DO and N, leading to sulfate reduction.

**Figure 5** shows concentrations for CIAT (ng/L) and CEAT (ng/L). Significant amounts of these atrazine metabolites emerge onto the surface with the exfiltrating ground water, and the patterns are similar to those of nitrate penetration through the soil. In the A4 nest, there is a substantial decrease in nitrate-N (**Figure 3**), CIAT, and CEAT (**Figure 5**) at the same depth

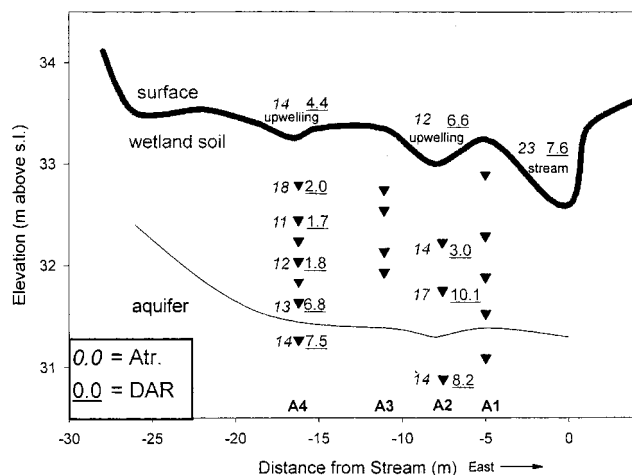


**Figure 5.** Side view subsurface map of A1–A4 transect showing atrazine degradate concentrations. Profile of A1–A4 transect of nested piezometers shows depths of screened intervals, surface topography, and aquifer surface. Inverted triangles depict locations of screened intervals. Piezometer designations (A1, A2, A3, A4) are listed beneath each nest. Deethylatrazine (CIAT) concentrations (ng/L) in ground water obtained from each piezometer are listed in italics to the left; deisopropylatrazine (CEAT) concentrations (ng/L) are underlined to the right. Significant amounts penetrate up through the soil profile at the A2 site; CEAT in the upwelling ground water is similar to stream water concentrations.

(~1.2 m below the surface). Concentrations of these constituents are actually higher in the emerging ground water than within the upper meter of soil. This is probably because much of the rapid groundwater discharge to the surface occurs preferentially through macropores, which are not sampled by the piezometers. At the A2 nest, there appears to be less attenuation of nitrate, CIAT, and CEAT in the soil profile. Note that CEAT concentrations in ground water exfiltrating from the A2 locus are nearly identical to adjacent streamwater values (**Figure 5**), and nitrate concentrations are significantly higher than the stream (**Figure 3**).

DAR values, represented in the soil profile in **Figure 6**, ranged from an average of 7.1 at the two deep well sites to 1.8 in the three shallower depths. Because the direction of flow was from the deeper sites upward to the shallow wells, it appears that a decrease in CIAT has taken place. This was not one of the mechanisms proposed in the original DAR concept. Although the DAR concept is typically used to distinguish groundwater sources from runoff water sources in stream water, processing of ground water through an anaerobic, high-organic matter (OM) wetland soil (and subsequent removal of CIAT) will alter the signal. Kruger et al. (15) reported that anaerobic processes were more active at removing atrazine and atrazine metabolites than were aerobic processes; Seybold et al. (16) also noted high atrazine degradation in anaerobic soil. High DAR values in oxic ground water, then, can diminish as ground water moves up through anoxic soil (**Figure 6**), as the degradate (CIAT) is consumed or adsorbed in that environment. Thus, it appears that microbial degradation of the CIAT (**Figure 5**) was enhanced because of the reduced  $O_2$  in the shallow soil layers (**Figure 3**). On a small scale then, it may be possible to trace a parcel of ground water as it moves up through a wetland soil profile and use decreasing DAR values as evidence of anoxic conditions and/or microbial degradate processing.

DAR values for nests A2 and A4 follow similar patterns, with DARs lowering with decreasing depth, as shown in **Figure 6**. Ratios for the upper levels of nest A4 are closer to 1, which



**Figure 6.** Side view subsurface map of A1–A4 transect showing atrazine concentrations and DAR values. Profile of A1–A4 transect of nested piezometers shows depths of screened intervals, surface topography, and aquifer surface. Inverted triangles depict locations of screened intervals. Piezometer designations (A1, A2, A3, A4) are listed beneath each nest. Atrazine concentrations (ng/L) in ground water obtained from each piezometer are listed in italics to the left; deethylatrazine/atrazine ratios (DAR) are underlined to the right of each piezometer. The very high (>1) DARs in the stream may reflect the overwhelming contribution of ground water to total stream flow.

probably reflects the influence of matrix flow on groundwater CIAT and atrazine. The high DAR values in the stream (**Table 1**; **Figure 6**) probably result from the sizable contribution of preferential groundwater flow to total stream discharge, especially at stations 2 and 3. DAR levels that are higher in the exfiltrating ground water but lower than aquifer values probably represent macropore flow and delivery from deeper in the soil profile, as was also observed in the  $NO_3^-$  signal (**Figure 3**). Thus, preferential flow, leading to rapid and focused groundwater discharge to the surface, can serve as a significant mechanism for delivery of several agricultural contaminants to surfacewater bodies.

Nitrate-N and pesticides found together in ground water indicate that areas susceptible to N contamination may also be susceptible to pesticide contamination (21). Hydrologic conditions, particularly preferential groundwater flow, can help explain this phenomenon. The presence of both nitrate and pesticides in aquifer water beneath the wetland appears to be co-indicative of agricultural influence. Within the soil zone (upper 2 m), changes in N and pesticide concentrations indicate the effect of local hydrology on contaminant movement.

Loss of CIAT and CEAT stream fluxes between stations 3 and 5 (**Table 1**), despite steady or increasing flows, indicates a net loss of atrazine metabolites in the stream. DAR values also decrease downstream. This requires a mechanism for removal of the degradates. One possibility is that there is some groundwater exchange within the lower part of the stream, with atrazine-bearing ground water being lost at some point and subsequently replaced by ground water from a different source. Alternately, there may be some form of in-stream atrazine metabolite reduction, either by further degradation or by sorption onto organic solids in the stream bed. Atrazine degradate and nitrate-N fluxes in the stream follow similar patterns, so relative susceptibilities to stream contamination appear to reflect groundwater behavior in different portions of the riparian system.

## CONCLUSION

The distribution of nitrogen and pesticides in this system is clearly heterogeneous. There are zones of emerging ground water on the riparian flood plain that display disproportionately high nitrate-N and atrazine metabolite concentrations. These same areas are also where a disproportionate amount of total stream flow is generated. Thus, zones of substantial N and atrazine groundwater delivery provide a disproportionate amount to total contaminant load carried by the stream. Rapid groundwater movement up through the soil profile can be traced by examining and comparing chemical constituents in ground water at different depths beneath the wetland. Highly active zones of groundwater upwelling show the highest concentrations in the emergent water. Less active upwelling zones (where exfiltration to the surface is much lower and intermittent) show somewhat lower average concentrations. Inactive regions do not appear to contribute much to surface water; however, groundwater concentrations of these chemicals tend to decrease rapidly with decreasing depths in these areas.

The rate at which ground water emerges onto the surface, and the extent to which that discharge is focused into a small area, largely accounts for observed differences in surface water nitrate-N and atrazine metabolite concentrations in different parts of the riparian zone. The upstream area, where the highest contaminant levels are usually found, is near the stream head and constitutes a true wetland (based on the nearly exclusive presence of obligate wetland species and permanently saturated surface conditions). Although this area should remove much of the subsurface agricultural pollution (8–10), most of the time it is the least effective portion of the riparian zone at contaminant mitigation. Other parts of the riparian system normally exhibit lower contaminant delivery potential. Spatial and temporal variations in contaminant delivery to the stream at this site appear to be more closely related to hydrologic conditions than to the criteria (such as riparian buffer width) most often used to estimate the pollution-mitigating capacity of a riparian system. Riparian zone regulations and initiatives should be based upon real knowledge of agrochemical movement in these environments. Much additional research is needed to determine the conditions under which riparian wetlands function as net sinks for pesticides and nutrients and as sites for loss of nitrate-N through denitrification.

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