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Comparative Study of Transport Processes of Nitrogen, Phosphorus, and Herbicides to Streams in Five Agricultural Basins, USA

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Agricultural chemical transport to surface water and the linkage to other hydrological compartments, principally ground water, was investigated at five watersheds in semiarid to humid climatic settings. Chemical transport was affected by storm water runoff, soil drainage, irrigation, and how streams were linked to shallow ground water systems. Irrigation practices and timing of chemical use greatly affected nutrient and pesticide transport in the semiarid basins. Irrigation with imported water tended to increase ground water and chemical transport, whereas the use of locally pumped irrigation water may eliminate connections between streams and ground water, resulting in lower annual loads. Drainage pathways in humid environments are important because the loads may be transported in tile drains, or through varying combinations of ground water discharge, and overland flow. In most cases, overland flow contributed the greatest loads, but a significant portion of the annual load of nitrate and some pesticide degradates can be transported under base-flow conditions. The highest basin yields for nitrate were measured in a semiarid irrigated system that used imported water and in a stream dominated by tile drainage in a humid environment. Pesticide loads, as a percent of actual use (LAPU), showed the effects of climate and geohydrologic conditions. The LAPU values in the semiarid study basin in Washington were generally low because most of the load was transported in ground water discharge to the stream. When herbicides are applied during the rainy season in a semiarid setting, such as simazine in the California basin, LAPU values are similar to those in the Midwest basins.

Agricultural activities can contribute residues of applied chemicals to rivers and streams. Nutrient enrichment of streams from agricultural activities is one of the most fundamental problems affecting the management of river basins on a worldwide basis (Salvia-Castellvi et al., 2005). Nitrogen enrichment is partially attributable to the increase in use over the last half century. Estimates of nitrogen use in the Mississippi Basin suggest a 600% increase since the 1950s (Donner et al., 2002). This increase in use and other factors resulted in a tripling of nitrate export from the Mississippi Basin to the Gulf of Mexico over that time period (Goolsby et al., 2000). Nutrient enrichment of aquifer systems can also affect drinking water supplies and can be a major source of nitrate to the base flow of streams (Spalding and Exner, 1993). Pesticides entering surface water systems are a concern for ecological and human health (Solomon et al., 1996; Giddings et al., 2000).

Although it is commonly assumed that rainfall- or irrigation-induced runoff from fields in proximity to streams is the primary transport route of agricultural chemicals to streams, effective management requires insight into how these chemicals move through the various hydrological compartments of the watersheds during annual cycles and what types of transformation processes are important. Understanding the detailed hydrological mechanisms of chemical movement may best be accomplished in small basins. By choosing representative basins, effective management decisions based on the results of these studies might be achieved by gaining knowledge of the role of precipitation or irrigation, the unsaturated zone, and ground water transport with respect to stream loads. Although significant amounts of nitrate might be transported through the unsaturated zone and remain unaltered in ground water, denitrification along flow paths might affect the nitrate load when the water discharges into a stream.

To better understand the fate and transport of agricultural chemicals in the hydrological cycle, a study was conducted at a diverse group of five small- to intermediate-sized watersheds in representative agricultural settings of the USA. Capel et al. (2008) described the design of the overall study. The study design was to complete a mass balance of water and agricultural chemicals from rain and irrigation, losses of

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Abbreviations: DEA, deethylatrazine; ESA, ethane-sulfonic acid; LAPU, load as a percent of use; OXA, oxanilic acid.

Table 1. Basin characteristics, discharge, and agricultural practices in the basins studied. Data are for Water Year 2004, 1 Oct. 2003 through 30 Sept. 2004.

	State				
Basin characteristic	**California**	**Washington**	**Nebraska**	**Indiana**	**Maryland**
Site	Mustang Creek	DR2 Drain	Maple Creek	Leary Weber	Morgan Creek
Area, km^2	17.5	5.5	950	7.5	31
Discharge, m^3	193,370†	4,414,500†	62,814,460†	3,095,120†	15,622,720†
Stream flow	ephemeral	continuous	continuous	ephemeral	continuous
Precipitation, mm	272	187	708	1109	1000
Tile drains	no	no	no	yes	no
Irrigated land, %	>95	>95	30	0	10
Crops	almonds, vineyards, row crops (corn, grain and other)	row crops, vineyards, orchards, dairies	corn and soybeans	corn and soybeans	corn and soybeans
Soils	sands, silts, clays, hardpans	well drained sands to clays	aeolian sand, silt, and loess	poorly drained glacial till	file silt loams

† USGS (2006).

water from evapotranspiration, subsequent movement of water and chemicals to recharge shallow ground water, and all processes, including chemical transformations, contributing to stream flow, and loading of agricultural chemicals to those streams. These basins were chosen in major agricultural settings across a range of climatic, land-use, and irrigated settings. The western basins (California and Washington) used irrigation. Sites were chosen such that imported water was the source of irrigation water in one and locally pumped ground water in the other. A Nebraska basin was typical of corn–soybean rotation in the mid-west, and an Indiana basin allowed for a comparison of processes in a tile-drainage system. A Maryland basin was chosen because of the major role of ground water discharge in regard to stream flow and chemical transport. Stream hydrology and connections to other environmental compartments, especially ground water and the relationships between discharge and chemical loads in the streams, were the major considerations for this portion of the overall study. The specific goals were to measure the total annual stream discharge and to collect a sufficient number of water samples to characterize the annual mass load of nutrients and selected herbicides and to use the data collected from other portions of the overall study to interpret transport processes to the streams.

This paper describes loads of nutrients and organonitrogen herbicides in five streams; the hydrologic linkages of the streams to other environmental compartments (especially ground water); the dominant transport processes affecting transport; and the relative importance of ground water, overland flow, or tile drainage. These streams are then compared to determine similarities and differences based on crop types, chemical usage, hydrology, climate, and types of irrigation methods with respect to transport processes.

Descriptions of Study Areas

Five watersheds—one each in California, Washington, Nebraska, Indiana, and Maryland—were chosen for study. A map showing the locations of these basins, sampling sites, and a more detailed description of each basin appears in a separate article (Capel et al., 2008). These watersheds encompass a variety of cropping patterns and irrigation requirements, which are described here briefly. Basin characteristics such as area, annual discharge during the period of study, crops, and soil types are given in Table 1. The use of nitrogen, phosphorus, and selected herbicides is given in Table 2.

The Mustang Creek watershed is typical of California Central Valley agriculture, with orchards, vineyards, row crops, and animal operations. Mustang Creek is ephemeral, with virtually all flow occurring after winter rains. Irrigation return flows are minor within the lower Merced River basin, of which Mustang Creek is nested (Domagalski and Munday, 2003), and overland runoff from storms occurs mainly in the winter. The crops grown within the Mustang Creek basin are entirely dependent on irrigation because little to no rain falls during the growing season. The source of irrigation water is locally pumped ground water. Intensive ground water use in this region has resulted in a long-term decline in water levels. The depth to water below land surface increased by 24 m from 1975 to 2001. There is virtually no connection of the stream with the underlying ground water system because the present-day depth to water is about 53 m below land surface, although some leakage from the streambed does infiltrate into the unsaturated zone.

Table 2. Nitrogen, phosphorus, and pesticide use. Pesticide use statistics for California are from the California Department of Pesticide Regulation (2004). Pesticide use statistics for other basins are from Capel et al. (2008).

Basin	Total N	Total P	Atrazine	Metolachlor	Simazine
			kg		
Mustang Creek, California	209,078†	9650‡	NA§	NA	174
DR2, Washington	62,237¶	29,452¶	47	115	26
Maple Creek, Nebraska	4,666,160#	1,536,650#	36,425	37,108	NA
Leary Weber Ditch, Indiana	47,627	8300††	243††	36	NA
Morgan Creek, Maryland	226,300‡‡	145,000 ‡‡	3463	1997	2162

† Use statistics obtained from local growers or University of California estimates.

‡ Use estimated from land-use (crop map) data compiled by California Department of Water Resources (1997, 1999, 2003).

§ NA: Data not available, or pesticide not reported, or use was very low.

¶ Estimates based on crop types.

USDA (2003).

†† Indiana Agricultural Statistics Service (2004).

‡‡ University of Maryland Cooperative Extension and the USDA (2002).

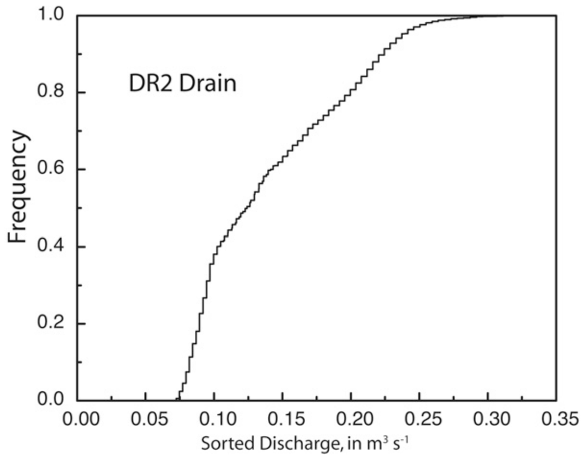

Fig. 1. Cumulative frequency plot of discharge for the DR2 Drain, Washington. Period of record, 1 Oct. 2003 through 30 Sept. 2004.

The DR2 Drain is located within the Yakima River Basin of Eastern Washington. This agricultural region is also dependent on irrigation water. Because of a long history of irrigation with surface water imported via canal from upland reservoirs, ground water discharge provides base flow to the drain on a year-round basis. Soils are generally well drained, sandy to clayey in texture, with depths ranging from shallow to deep. Irrigated agriculture—mainly orchards, row crops, and vineyards—greatly influences the hydrology. There was no evidence of a stream network before agricultural development, and substantial rises in the water table were noticed as early as the 1900s (K.L. Payne, U.S. Geological Survey, written communication, 2006); because of this and locally poor drainage, the U.S. Bureau of Reclamation designed drainage systems. Under the current irrigation system, a shallow ground water flow system is responsible for perennial flow in the DR2 Drain.

The major crops grown in the Maple Creek watershed (a tributary to Elkhorn River) of eastern Nebraska are corn and soybeans, and most water requirements are met by rainfall. Where available, irrigation water supplements water requirements. Maple Creek flow is perennial. Ground water influx constitutes most of the stream flow during the late growing season and through the winter. Rainfall-induced runoff, primarily during spring to summer, contributes flow, sometimes at high discharge levels.

The Leary Weber Ditch, a small ephemeral drainage, is within an agricultural land use planted in corn and soybeans, nested within the Sugar Creek watershed of Indiana. Soils were derived from glacial tills, and because of poor drainage, tile drains were installed. Edge-of-field ditches collect the tile-drain discharge, which is then directed to other local drains and to the Ditch. Direct rainfall contributes little flow to Leary Weber Ditch, and there is no ground water inflow. Overland flow and tile-drain discharge contribute almost all of the water to Leary Weber Ditch. During storms both of these sources contribute to the flow of the ditch, and between storms the tile drains flow until all of the available water in the soils above the elevation of the drains is removed (Baker et al., 2006).

The Morgan Creek watershed in eastern Maryland is nested within the Chester Branch, a tributary to Chesapeake Bay. Climate in the Morgan Creek watershed is humid and subtropical. Precipitation is relatively evenly distributed throughout the year but may be more intense during warmer months because of thunderstorms. Natural precipitation is generally sufficient to support agriculture, and crops (mainly corn and soybeans) are irrigated only where soils are well drained. Slightly more than half (59%) of the flow of Morgan Creek is contributed by ground water; the remainder is derived from overland runoff during and after precipitation (Böhlke and Denver, 1995; Hancock and Brayton, 2006). Ground water discharges directly through the streambed in the upper part of the watershed but likely reaches the stream primarily via floodplain seeps farther downstream, where the floodplain is wider and streambed sediments are less permeable (Hancock and Brayton, 2006).

Annual rainfall amounts among the five basins are highly variable (Table 1), and the within-year distribution differs among the basins. Most of the precipitation in the California basin occurs in the winter, whereas spring to fall thunderstorms contribute most of the precipitation in Nebraska, Indiana, and Maryland. The lowest measured precipitation was recorded for the DR2 basin.

A cumulative flow frequency plot for the DR2 Drain (Fig. 1) is relatively uniform through the range of flow because of the managed application of irrigation water and very little rainfall. Stream flow at the other two basins that have continuous discharge (Maple Creek and Morgan Creek) has the typical pattern of base flow with infrequent spikes in discharge as a result of storm water runoff. As a result of the combination of base flow and infrequent runoff events, a cumulative flow frequency curve for Morgan Creek is highly skewed (Fig. 2). The discharge at Leary Weber discharge is mainly the result of tile drainage with a small component from overland flow. Cumulative flow frequency for Mustang Creek, Maple Creek, and Leary Weber Ditch are skewed similarly to that of Morgan Creek.

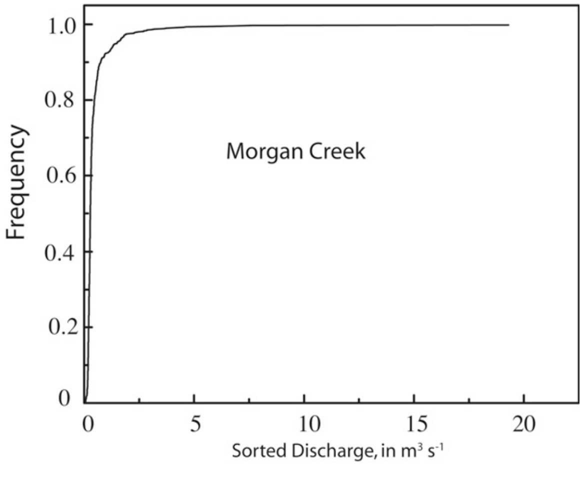

Fig. 2. Cumulative frequency plot of discharge for Morgan Creek, Maryland. Period of record, 1 Oct. 2003 through 30 Sept. 2004.

Materials and Methods

Stream discharge was measured using standard USGS techniques (Buchanan and Somers, 1969; Kennedy, 1984). Continuous discharge was recorded at all sites. Water samples were collected manually, using methods that ensured the samples were width- and depth-integrated (Wilde et al., 1999), or by an automatic sampler, when storm-induced conditions made manual collection of samples impractical or unsafe. The samples were collected at times coinciding with storm-induced runoff during the rainy season and at fixed intervals at other times, usually every other week. Water samples were collected in Teflon or glass bottles using Teflon tubing. Part of each water sample was filtered through a 0.45-μm polysulfone membrane. Water samples were analyzed for nutrients (ammonia, nitrite, nitrate, total nitrogen, ortho-phosphorus, and total phosphorus, expressed in this paper in mg L^{-1} as N or P), major ions, and alkalinity. Total nitrogen and total phosphorus samples measure the amount of each constituent present in a whole water sample, including the suspended sediment. All samples were collected in a manner designed to collect a representative sample of dissolved and suspended constituents (Wilde et al., 1999). Ground water samples were analyzed for the same set of constituents, except for total nitrogen and total phosphorus. Selected ground water samples were analyzed for N_2 and argon to estimate the amount of nitrogen present as a result of denitrification (Heaton and Vogel, 1981; Vogel et al., 1981; Puckett et al. 2002). Some samples also were analyzed for nitrogen and oxygen isotopes in nitrate to determine the origin of nitrate or to test for denitrification processes. Further information on analytical methods and quality control is provided by Capel et al. (2008).

Water samples for pesticide analysis from stream water and rain were processed by filtering through glass-fiber 0.7-μm filters. Pesticide analysis was by gas chromatography/mass spectrometry according to the method of Zaugg et al. (1995) with detection limits generally between 0.005 to 0.01 μg L^{-1}. Analyzed pesticides that are discussed in this paper include atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine); deethylatrazine (DEA), a degradate of atrazine; (2-amino-4-chloro-6-(isopropylamino)-s-triazine); simazine (6-chloro-N2, N4-diethyl-1,3,5-triazine-2,4-diamine); metolachlor (2-chloro-N-(2-ethyl-6- methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide); metolachlor ethane-sulfonic acid, a metolachlor degradate (2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid); and metolachlor oxanilic acid, another metolachlor degradate, (2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid).

The mass loads of agricultural chemicals were calculated by more than one method. One approach was the application of the software program LOADEST2, which uses a rating-curve method (Cohn et al., 1989; Crawford, 1991) and regresses seasonal stream discharge against measured constituent concentrations. Seasonal differences in concentrations of agricultural chemicals in the streams can be accounted for by separation of the discharge–concentration relation on a seasonal or monthly basis. LOADEST2 optimizes the estimation of daily chemical loading by building models that use yearly, seasonal, or user-defined periods. In all cases, summary statistics are calculated, and the model with the most favorable statistical summary is chosen. LOADEST2 output also includes daily simulated concentrations. In all cases, these simulated concentrations were compared with the measured values to determine how well the model conformed to actual measurements. The LOADEST2 software program does not calculate a load if the correlation between stream flow and concentration is poor. The LOADEST2 input requires a minimum of 25 observations (water quality samples) over a period of 2 yr. Continuous records of stream flow are used. The software requires convergence on a single solution to a modeled set of data; otherwise, an error message is reported. This was never observed with the data sets used in this study. An examination of the variance among simulations showed that associated errors in loads were generally less than 25%. LOADEST2 was used to calculate loads for the Nebraska (Maple Creek), Indiana (Leary Weber), and Maryland (Morgan Creek) streams. Because of the ephemeral nature of Mustang Creek (CA), the use of LOADEST2 was not practical because the associated errors would have been unacceptably high. For Mustang Creek, the mass of water was calculated from storm hydrographs. Concentrations in water samples collected at various stages of the hydrograph were used to estimate the storm-driven loads. An "annual load" of water and chemical constituents for Mustang Creek was calculated by summing the individual loads from each storm. The LOADEST2 method was not considered appropriate for estimating loads for the DR2 Drain because of within-season variation of the ground water input to the stream. Thus, an interpolation method was used to calculate all loads for DR2 Drain.

Linkages of stream chemistry to other environmental compartments, especially shallow ground water, were evaluated with various techniques as determined by the hydrologic settings. One technique that was used, mixing analysis (sometimes referred to as end-member mixing analysis), exploits unique chemical signatures, such as specific conductance, a chemical, or an isotope, from individual sources of water, such as rain, ground water, tile drains, or overland flow, to determine the relative contributions of water from these sources to the stream. By determining how to mix the proportions of water with different concentrations of these end-members, an estimate of the relative contribution from each end-member can be obtained. Examples of the application of mixing analysis method can be seen in Christophersen and Hooper (1992) and in Burns et al. (2001). Samples of local ground water, overland flow, and rain were analyzed as part of this overall study and were used to evaluate mixing of different water sources at appropriate sites. Mixing analysis was primarily used to interpret the water inputs to the DR2 Drain and to a lesser extent the Leary Weber Ditch. Inputs of chemicals from rain were also directly estimated by using the chemical analyses of samples from the rain collectors and the volumes of rainfall from the rain gauges. Rain inputs to the basins were more fully investigated by Vogel et al. (2008). Flow separation was used to determine the relative loads transported through base flow and overland runoff at sites where the end-member mixing analysis was not appropriate because of the lack of unique chemical signatures in the possible sources of water. Plots referred to as cumulative frequency, based on flow separation, were constructed to analyze loads associated with specific discharges. These were produced using the output from the LOADEST2 simulations or the loads calculated from the interpolation method. Similar types of plots were used in Royer et al. (2006) to discuss nitrate and phosphorus loading in streams of Illinois. In either case, measured discharge and associated loads from LOADEST2 or other methods of load calculation were sorted from lowest to highest, and the subsequent plots were then generated.

Table 3. Basin loads of nutrients and pesticides and basin yields (in parentheses) for Water Year 2004 (1 Oct. 2003 through 30 Sept. 2004).†

	Stream				
Constituent	DR2 Drain	Mustang Creek	Maple Creek	Leary Weber Ditch	Morgan Creek
Ammonia	140 (0.3)	16.5 (0.01)	67,100 (0.7)	NA‡	7320 (2.2)
Nitrite	140 (0.3)	4.8 (0.003)	8300 (0.1)	330 (0.5)	750 (0.2)
Nitrate	17,100 (32)	172 (0.1)	311,000 (3.3)	11,300 (16)	39,000 (12)
Total N	20,000 (37)	648 (0.4)	623,000 (6.6)	13,700 (19)	56,000 (17)
Total P	1330 (2.1)	286 (0.2)	509,000 (5.4)	520 (0.7)	4200 (1.3)
Ortho-P	610 (1)	138 (0.08)	20,000 (0.2)	130 (0.2)	1100 (0.3)
Atrazine	0.2 (0.3)	NA	1323 (13.9)	8.0 (11)	8.0 (2.4)
DEA§	0.005 (0.09)	NA	15 (0.16)	0.7 (1.0)	1.6 (0.5)
Metolachlor	NA	0.001 (0.0006)	103 (1.08)	0.6 (0.8)	8.3 (2.5)
Metolachlor ESA¶	NA	NA	7.3 (0.08)	0.7 (1.0)	36 (10.9)
Metolachlor OXA#	NA	NA	NA	0.6 (0.8)	7.6 (2.3)
Simazine	0.08 (0.2)	2.7 (1.5)	NA	0.04 (0.06)	3.6 (1.1)

† Basin loads are in kg; basin yields are in kg ha^{-1} for nutrients and g ha^{-1} for pesticides.

‡ NA, not applicable. Load not calculated because of insufficient data.

§ DEA, deethylatrazine.

¶ ESA, ethane-sulfonic acid.

OXA, oxanilic acid.

Results and Discussion

Transport Processes and Cumulative Loads

DR2 Drain, Washington

The annual loads for the DR2 Drain (Table 3) show that the nitrate and total nitrogen load exceeded that of the other nutrients. Most of the water in the DR2 Drain is ground water discharge that originated as imported irrigation water. The DR2 drain discharge increases during the irrigation season, and subsequent changes in water chemistry occur during the irrigation season. For example, the specific conductance of the drain water averaged about 0.6 to 0.7 dS m^{-1} before irrigation but decreased to about 0.4 dS m^{-1} during the irrigation season when the imported water with lower conductance entered the system. The canal water used for irrigation has a specific conductance near 0.1 dS m^{-1} with very little or no nitrate. Therefore, irrigation water dilutes the specific conductance of DR2 and provides no additional nitrate. In turn, nitrate concentrations in the DR2 Drain also decreased during the irrigation season, presumably because of dilution by the irrigation water, suggesting that the seasonal change in water chemistry might be attributed to the relative difference in the amounts of base flow and introduced canal water. Another possible explanation for the decrease in nitrate is an increase in denitrification or in-stream nutrient uptake because of warmer temperatures. A mass balance and mixing analysis approach was used to approximate the relative percentages of base flow and canal water in the DR2 Drain and to determine if other sources of water might account for the seasonal change in water chemistry. As a first approximation, the approach was to assume that the water in the drain was a combination of base flow and canal water, using the following equations:

$$Q_{\text{DR2 summer total}} = Q_{\text{DR2 ``base flow''}} + Q_{\text{Agricultural}} \qquad [1]$$

$$[QC]_{\text{DR2 summer total}} = [QC]_{\text{DR2 ``base flow''}} + [QC]_{\text{Agricultural}} \qquad [2]$$

and

$$C_{\text{Agricultural}} = ([QC]_{\text{DR2 summer total}} - [QC]_{\text{DR2 ``base flow''}}) / (Q_{\text{DR2 summer total}} - Q_{\text{DR2 ``base flow''}}) \qquad [3]$$

where Q is discharge, and C is concentration.

On the right hand side of the equations, DR2 "base flow" discharge and concentration are the only unknowns. The constituent concentrations in the introduced canal water can be solved by assuming values for the base-flow discharge and concentration. A simplifying assumption to solve for the unknowns was that the ratios of upward hydraulic gradients (dh/dl) of water discharging into the DR2 Drain, which were measured along two transects of the stream bed during summer and winter, could provide the proportion of irrigation-season to non–irrigation-season water. Each of the transects had continuous water level recorders so that hydraulic gradients could be evaluated.

Using this approach,

$$(dh/dl_{\text{summer}})/(dh/dl_{\text{winter}}) = \text{ratio of hydraulic gradients} \qquad [4]$$

The average upward hydraulic gradient during the irrigation season was 0.241, and that for the non-irrigation season was 0.299. Therefore, the ratio of the gradients was 0.806.

Using that ratio,

$$Q_{\text{DR2 summer ``base flow''}} = 0.806\, Q_{\text{DR2 winter ``base flow''}} \qquad [5]$$

and

$$C_{\text{DR2 summer ``base flow''}} = C_{\text{DR2 winter ``base flow''}} \qquad [6]$$

Nitrate concentrations in samples collected from shallow piezometers beneath the streambed indicate that nitrate concentrations were virtually identical in spring and fall (Puckett et al., 2008).

Using this analysis method, the summer base flow was 0.076 m^3 s^{-1}. The total summer flow was the sum of this base flow plus the amount from introduced canal water, from irrigation, of 0.11 m^3 s^{-1} for a total summer flow of 0.19 m^3 s^{-1}.

Although this analysis assumes that base flow and introduced canal water were the only sources of water to DR2, an analysis of a "conservative" constituent or property, such as specific conductance, indicated that another source of water was present in the drain. It was assumed that overland flow would be the most likely additional source. Using the values for specific conductance in base flow, introduced canal water, and overland flow, the measured values are best accounted for by a mixture of 41% base flow, 40% introduced canal water, and 19% overland flow.

A similar combination of water sources can account for the measured nitrate concentrations, although the water in DR2 Drain is slightly enriched in nitrate because the introduced canal water transports "new" nitrate through the unsaturated zone. The median concentrations of nitrate in base flow (about 4.9 mg L^{-1}) are less than the median concentration in nearby ground water (6.2 mg L^{-1}) ($p = 0.022$). There are some indicators that denitrification occurs under the streambed, including lower concentrations relative to the adjacent ground water and stream water, low dissolved oxygen, and elevated concentrations of iron or manganese. Enriched $\delta^{15}N$ values (8.52–12.18‰) and excess N_2 gas (500 μm L^{-1}) were observed. Puckett et al. (2008) provides further information on denitrification processes at this site. Therefore, the nitrogen load in DR2 can be accounted for as a continual input to the drain of ground water base flow containing nitrate with a median concentration of 5 to 6 mg L^{-1} in the non-irrigation season, which is diluted by excess irrigation water to 2 to 4 mg L^{-1} during the irrigation season.

The cumulative load of nutrients, in percent, for the DR2 Drain is shown in Fig. 3. This and subsequent plots show the amount transported across the range of flow during the time of this study. The shape of the cumulative load for each of the nutrient species present in DR2 is similar to the cumulative discharge plot because changes in ground water discharge plus a small amount of overland flow controls the loading of these chemicals to the drain.

In general, the lowest loadings of pesticides for this study were those of the DR2 Drain. Pesticide annual loads and basin yields are shown in Table 3. The percent cumulative loads of atrazine, DEA, and nitrate in the DR2 Drain are shown in Fig. 4. The cumulative loads for atrazine and DEA (Fig. 4) differ from nitrate and are shifted to the right of the plot for nitrate, suggesting a greater amount of overland flow responsible for the pesticide and degradate transport.

Mustang Creek, California

Mustang Creek flows only in response to rainfall of sufficient intensity to generate runoff. Annual loads for nutrients and selected pesticides were calculated as the sum of the loads from the individual storms (Table 3). The land-use of the Mustang Creek watershed is very different from the other study areas because of the presence of almond orchards. Almond orchard management includes application of nitrogenous fertilizer in the spring through summer irrigation season and the use of insecticides during winter dormancy to protect the trees from over-wintering insects. Very little runoff of irrigation water occurred, and no streamflow was recorded at the gauging station after the rainy season. Because there was no rainfall during the spring through fall growing season, the stream loads of nitrate throughout that portion of the year were zero.

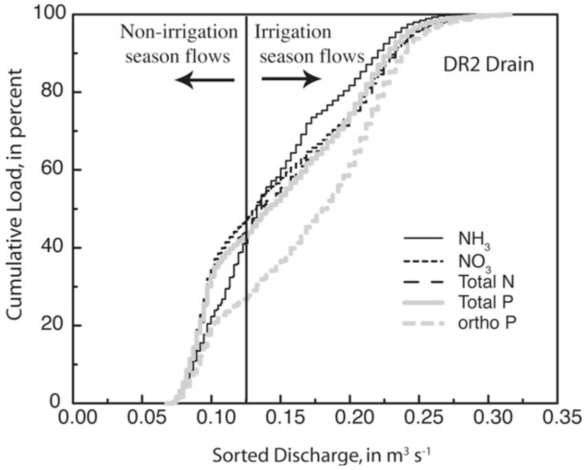

Fig. 3. Cumulative load of nutrients, in percent, for the DR2 Drain, Washington. Period of record, 1 Oct. 2003 through 30 Sept. 2004.

The nitrate load at Mustang Creek (Table 3) was only about 27% of the total nitrogen load, in contrast to DR2 where the nitrate load was 85% of the total nitrogen. Because of the lack of a connection of Mustang Creek with ground water, much of the applied nitrate does not enter Mustang Creek. Most of the total nitrogen load measured during the storms was probably organic soil nitrogen associated with suspended sediment.

Simazine is one of several herbicides that are co-applied with the insecticides in the winter. Simazine has been frequently detected in streams of the California Central Valley during the winter (Domagalski et al., 1997; Kratzer, 1998). The use of simazine on orchards was invoked in previous studies to explain the occurrence of this herbicide and the co-occurrence of simazine with organophosphorus insecticides such as diazinon and chlorpyrifos during the winter rainy period. Simazine was frequently detected in rainwater (data collected as part of this study during all rainfall events contributing to flow in Mustang Creek), but the highest concentration was only 0.17 μg L^{-1}. In 2004, the minimum concentra-

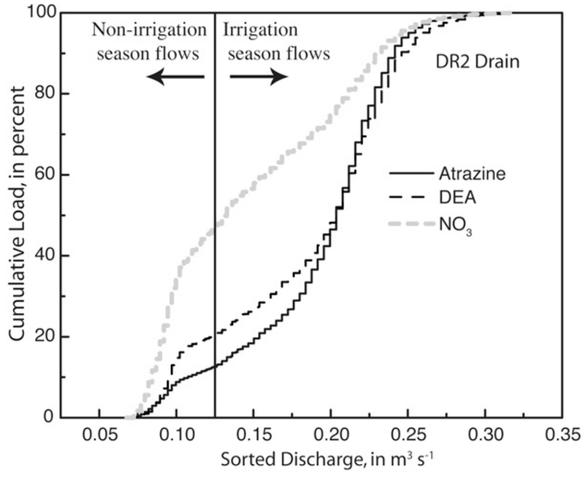

Fig. 4. Cumulative load, in percent, of atrazine, deethylatrazine (DEA), and nitrate in the DR2 Drain. Cumulative load was calculated for the period of 1 Oct. 2003 through 30 Sept. 2004.

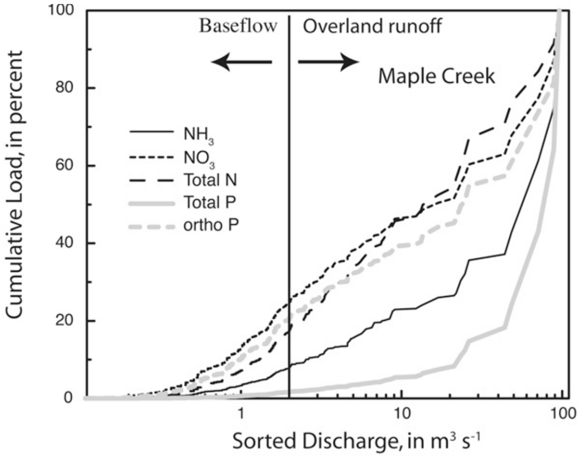

Fig. 5. Cumulative load of nutrients, in percent, for Maple Creek, Nebraska. Period of record, 1 Oct. 2002 through 30 Sept. 2004.

tion of simazine in Mustang Creek was 0.08 μg L^{-1}, the maximum was 65.5 μg L^{-1}, and the median was 21.7 μg L^{-1}. Although some simazine was scavenged from rain, overland flow from orchards and other crops is a more likely transport process for simazine.

Maple Creek, Nebraska

A percent cumulative load plot of nutrients for the Maple Creek basin is shown in Fig. 5. Total nitrogen has the greatest load of nutrient compounds; total phosphorus loads are slightly less. About 50% of the total phosphorus load of Maple Creek is transported at discharges above 75 $m^3 s^{-1}$, whereas about 50% of the total nitrogen is transported at discharges below 20 $m^3 s^{-1}$. Cumulative loads at flows of less than 2 $m^3 s^{-1}$ are the result of primarily ground water discharge (base flow) (Fig. 5). Most of the nutrient load is transported at higher flows (approximately 60% of the nitrate and total nitrogen at flows >5 $m^3 s^{-1}$). Transport of total phosphorus is distinctly different from that of the other nutrients at Maple Creek, with most transported under higher flow conditions (above approximately 60 $m^3 s^{-1}$). Because flows less than 2 $m^3 s^{-1}$ in Maple Creek consist primarily of ground water discharge (and therefore do not include a substantial component of overland flow), these data indicate that ground water is contributing to the high concentration of nitrate, total nitrogen, and (to a lesser extent) orthophosphorus at low flows. Indicators of redox conditions under the Maple Creek streambed indicate the potential for denitrification with low dissolved oxygen and the presence of dissolved iron. Values of $\delta^{15}N$ (7.33–13‰) show an enrichment in the heavy isotope and concentrations of excess N_2 gas in the water under the stream bed ranged up to 164 μmol L^{-1} (Puckett et al., 2008). However, ground water nitrate levels in the basin can reach concentrations as high as 38 mg L^{-1}, and nitrate concentrations above the US maximum contaminant level drinking water standard of 10 mg L^{-1} as N (USEPA, 2006) were detected in samples from a substantial number of wells (in the Maple Creek basin). Puckett et al. (2008) suggested that the transport time of water and nitrate (median residence time of 0.02 d m^{-1}) are faster than the biogeochemical processes that result in denitrification. Therefore, although nitrate reduction does occur in the streambed, the faster movement of water relative to denitrification limits the reduction of load from ground water discharge.

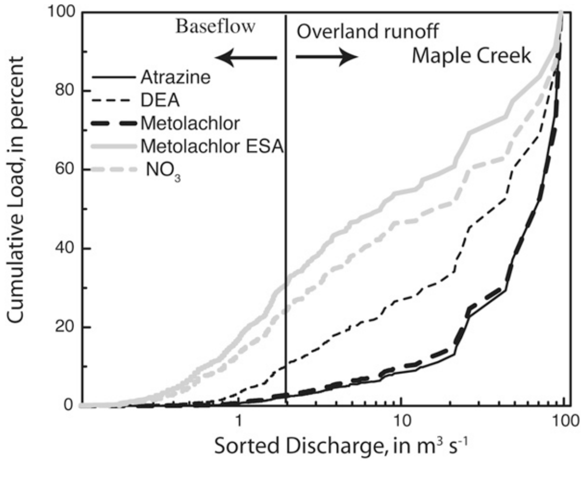

Fig. 6. Cumulative load of atrazine, deethylatrazine (DEA), metolachlor, metolachlor ethane-sulfonic acid (ESA), and nitrate, in percent, for Maple Creek. The period of calculation was 1 Oct. 2002 through 30 Sept. 2004.

Herbicide loads for Maple Creek are shown in Table 3, and a plot of the percent cumulative load for atrazine, DEA, metolachlor, and metolachlor ethane-sulfonic acid (ESA) is shown in Fig. 6. The percent cumulative load plot for atrazine and DEA shows some differences in transport of these two constituents in the low-flow range (<10 $m^3 s^{-1}$). A break in slope above 10 $m^3 s^{-1}$ (Fig. 6) can be attributable to a shift from ground water (base-flow–derived) dominated transport to overland-flow transport at the higher discharges. The plot of percent cumulative load (Fig. 6) shows that the line for DEA is shifted to the left relative to the line for atrazine, indicating the greater role of ground water transport for this degradate and that more of the atrazine is moved into the stream via overland runoff. Less than 1% of the cumulative load of atrazine is accounted for by flows less than 1 $m^3 s^{-1}$. This transport pattern is different from that seen in the cumulative frequency plot for nitrate (Fig. 6). Up to about 40% of the nitrate load was contributed by ground water, with the remainder contributed by overland flow, as suggested by the cumulative flow plot (Fig. 6). The cumulative load of DEA is intermediate between that of nitrate and atrazine and about 20% of the DEA load of Maple Creek is contributed by ground water.

Atrazine concentration and the fraction of the degradation product, DEA, to the total amount of atrazine in Maple Creek change over the course of the year. Concentrations of atrazine are low during the late fall to early spring period and then increase briefly during late May through June. The increase in May can be attributed to new applications of atrazine and its transport to Maple Creek by overland flow. The increases in concentration lower the fraction of DEA with respect to total atrazine (i.e., the sum of the atrazine and DEA molarity). The overland-flow transport of the newly applied atrazine results in a decrease of the fraction of the DEA measured in Maple Creek because most of the degradation product is transported in the ground water. The fraction of DEA increases during the remainder of the summer months to levels of the previous fall as overland flow becomes less important and ground water transport becomes more important for loading to the creek.

The transport processes and loads of metolachlor and its most important degradation product in this basin, metolachlor ESA, are similar to those for atrazine and DEA. About 40% of the load of metolachlor ESA in the Maple Creek basin is transported through ground water at the low end of the discharge (Fig. 6). In contrast, more than 80% of metolachlor is transported at discharges greater than 10 $m^3 s^{-1}$, indicating that most of its mass is transported by overland flow processes at the higher river flows.

Leary Weber Ditch and Sugar Creek, Indiana

The discharge of Leary Weber Ditch is mainly the result of tile-drain discharge with an additional component of overland flow (Stone and Wilson, 2006; Baker et al., 2006). Nutrient discharges from these tile drains are high in nitrate, and the total annual load of nutrients in the Leary Weber Ditch (Table 3) consists mostly of total nitrogen, mainly in the form of nitrate. Cumulative loads of Leary Weber Ditch (not shown) resemble those shown for DR2 Drain with the exception that the Ditch is ephemeral and therefore a plot would have its origin at zero discharge. Because the Leary Weber discharge is controlled mainly by tile-drain discharge, the cumulative load represents nutrient loading across a range of tile-drain discharge, except at the highest discharge, where overland flow becomes important. About 90% of the load is accounted for by tile drain discharge, with the remainder being a result of overland flow. There is no connection of the ditch with the local ground water system, so base flow does not contribute any of the load. Because most of the flow of Leary Weber Ditch is discharge from the tile drains, it is not surprising that only nitrate and total nitrogen are of importance with respect to the total amount of nutrients transported. Only a small amount of total phosphorus moves through the soil and is discharged through the drains to the ditch.

Annual loads of pesticides for the Leary Weber Ditch are shown in Table 3. The highest annual loads were for atrazine, with a relatively small amount for DEA. In contrast to the load of DEA, loads of metolachlor ESA exceeded the loads of the parent herbicide at Leary Weber.

Tile drainage in the Leary Weber Ditch basin effectively lowers the natural water table so that ground water does not flow directly into the ditch. An analysis of the major ion chemistry for water in tile drains and overland flow to Leary Weber water indicates that the water in the tile drains and in Leary Weber Ditch are similar, whereas the water coming from overland flow has less magnesium and lower concentrations of certain anions, such as sulfate, compared with Leary Weber water. Although the major element chemistry of water in the tile drains and in Leary Weber Ditch are similar, as would be expected from field observations that flow in the ditch is related to tile-drain discharge, there are differences in the chemistry of pesticides and degradation products in samples from the two sources. The highest peak concentrations of atrazine (9.8 $\mu g L^{-1}$ in 2004 and 9.3 $\mu g L^{-1}$ in 2003) were measured in Leary Weber Ditch relative to a tile drain (0.26 $\mu g L^{-1}$ in 2004 and 1.05 $\mu g L^{-1}$ in 2003) each year of the study. Atrazine concentrations were higher in 2004 (median concentrations 0.5 $\mu g L^{-1}$ in 2003 and 0.7 $\mu g L^{-1}$ in 2004), probably because a greater percentage of the land was planted in corn, as opposed to soybeans, during 2004. Some of the higher concentrations of atrazine in Leary Weber Ditch (peak concentration, 10 $\mu g L^{-1}$) relative to concentrations in the tile drain (peak concentration, 0.3 $\mu g L^{-1}$) in 2004 might also be attributed to the contributions from overland flow to the ditch. The fraction of total atrazine that was DEA was lower in Leary Weber Ditch than in the tile drainage, and many of the ditch samples contained more of the parent compound than DEA. This can probably be attributed to new applications of atrazine reaching Leary Weber Ditch through overland flow and a greater percentage of total atrazine, from the previous year's applications, in the form of DEA in the tile drainage. In contrast, for metolachlor, the concentrations of the degradation products in Leary Weber Ditch were higher than those of the parent compounds, indicating that the tile drains might be the major source of those degradates and that more of the parent pesticides degraded relative to the situation for atrazine. Transport of the parent herbicide to the tile drain is less favored because of greater sorption to the sediments relative to the degradation products. As a result, the discharge from the tile drains has a greater percentage of the degradation product. The values for K_{oc} (soil organic carbon partition coefficient) in soil for metolachlor, metolachlor oxanilic acid (OXA), and metolachlor ESA are 200 (Capel et al., 2008), 29.8, and 30.6 L kg^{-1} (Krutz et al., 2004), respectively. Fractions of metolachlor ESA in the tile-drain effluent range from 0.3 to 1.0, and those for the Leary Weary Ditch range from 0.2 to 0.7. The slightly lower values of the fraction of metolachlor ESA in the ditch are the result of transport of the parent herbicide during high-flow events through overland flow directly to Leary Weber Ditch after the most recent application.

Morgan Creek, Maryland

Nutrient loads for Morgan creek are shown in Table 3, and cumulative load plots, in percent, for the Morgan Creek basin are shown in Fig. 7. The total nitrogen load makes up the greatest part of the load of all of the nutrient species in Morgan Creek; the nitrate load is about 70% of the total N. The ammonia load is elevated in Morgan Creek relative to that in some of the other streams studied, possibly because of the presence of dairies in the watershed and the use of manure as a fertilizer and possibly because of sediment processes (Duff et al., 2008). A substantial amount of the nutrient load for the period of this study was transported at flows of less than 0.4 $m^3 s^{-1}$ (the 75th percentile of mean daily discharge), indicating that ground water base flow is an important contributor of nutrients to Morgan Creek. About half of the estimated load of nitrate in Morgan Creek during the study period occurred when mean daily discharge was less than 0.4 $m^3 s^{-1}$, and 70% of the load occurred at discharges below 1 $m^3 s^{-1}$. The median concentration of nitrate in ground water sampled in the Morgan Creek watershed is 10.3 mg L^{-1} (data collected as part of this study), with a maximum measured concentration of 18.5 mg L^{-1} and a minimum concentration of 1.6 mg L^{-1}. Indicators of redox conditions show that the ground water was generally oxic but did span a range of conditions including iron reduction (Puckett et al., 2008). Values of δ^{15} N of 3.07 to 5.98‰ in ground water near the stream were similar to fertilizer applications. Concentrations of

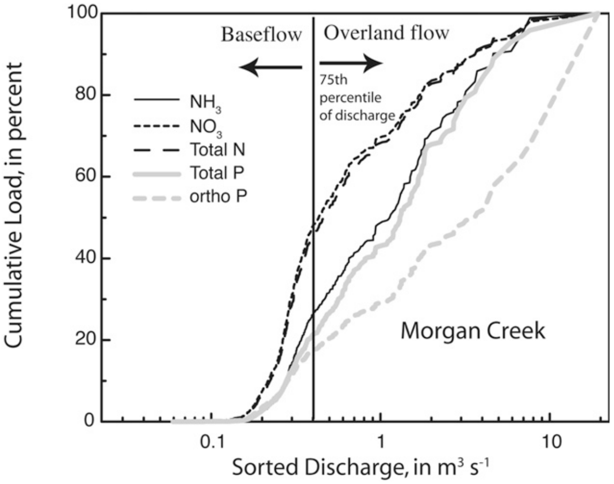

Fig. 7. Cumulative load of nutrients, in percent, for Morgan Creek, Maryland. Period of record, 1 Oct. 2002 through 30 Sept. 2004.

excess N_2 gas of 0 to 250 μmol L^{-1} in the nearby ground water also indicated that denitrification was negligible (Puckett et al., 2008). Therefore, year-round base flow is of greatest importance for most of the nitrate load , with the remainder contributed by infrequent runoff events.

Loads and yields of pesticide compounds in the Morgan Creek basin are shown in Table 3. Pesticide compounds are transported to Morgan Creek through overland flow and ground water discharge. The relative importance of these processes at Morgan Creek is related to the solubility and persistence of individual compounds, the timing of precipitation relative to applications periods, and geohydrologic conditions within the Morgan Creek basin. Some pesticide compounds (such as atrazine and metolachlor) move primarily with overland flow after precipitation (particularly in the spring and summer), but these compounds also move into Morgan Creek in ground water discharge from the unconfined surficial aquifer throughout the year. Percent cumulative load plots for atrazine, DEA, metolachlor, metolachlor ESA, metolachlor OXA, and nitrate are shown in Fig. 8. There is considerable overlap for the lines for atrazine and DEA, indicating that the transport processes for the two compounds are the same. About 21% of the load of these two compounds occurred at discharges below 0.4 m^3 s^{-1}, and about 45% of the load occurred at discharges below 1 m^3 s^{-1}.

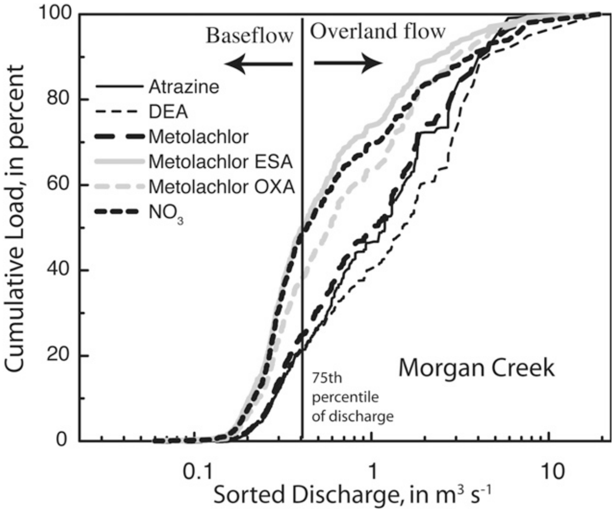

Fig. 8. Cumulative load, in percent, for atrazine, deethylatrazine (DEA), metolachlor, metolachlor ethane-sulfonic acid (ESA), metolachlor oxanilic acid (OXA), and nitrate for Morgan Creek. The period of calculation was from 1 Oct. 2002 through 20 Sept. 2004.

Concentrations of soluble compounds such as metolachlor ESA are relatively high in unconfined ground water of the Morgan Creek basin but may be diluted in Morgan Creek during high flow. Metolachlor ESA was detected in 93% of the wells sampled in the basin during this study (minimum concentration: 0.9 μg L^{-1}; maximum concentration; 16 μg L^{-1}; median concentration: 5.3 μg L^{-1}). In contrast, metolachlor was detected in only 55% of the wells sampled (maximum concentration: 0.1 μg L^{-1}; median concentration: 0.002 μg L^{-1}). The percent cumulative load of the various metolachlor species in the Morgan Creek basin is shown in Fig. 8. At the 75th percentile of daily discharge (0.4 m^3 s^{-1}), 50% of the metolachlor ESA load is accounted for, but only 25% of the load of metolachlor is accounted for. The line for metolachlor ESA is similar to that for nitrate, indicating a similar transport process. The shift in the position of the line for metolachlor ESA to the left of the lines for metolachlor and metolachlor OXA indicates that a greater percentage of this compound is transported to Morgan Creek through ground water discharge than metolachlor or metolachlor OXA. This can probably be attributed to degradation processes of metolachlor that occur in the soil, resulting in an enrichment of the degradate compounds in the unsaturated zone. Overland flow after precipitation carries most of the load of some pesticide compounds to Morgan Creek. More than 60% of the estimated load of atrazine and metolachlor in the stream during the study period occurred during days when the mean daily flow exceeded 0.4 m^3 s^{-1}, the 75th percentile of mean daily discharge. The fraction of the degradate DEA to the total atrazine dissolved in water shows that mainly the degraded form of atrazine is present, except after the spring application of new atrazine, which occurs in April. The fraction of DEA in ground water in this basin is high and exceeds 0.9, indicating that most of the atrazine present is DEA. Rainfall runoff transports the newly applied atrazine to Morgan Creek, and during those times, the fraction of DEA is lower. Concentrations of atrazine during the late fall to the subsequent spring are probably the result of the discharge of ground water into Morgan Creek. The nitrate and total nitrogen percent cumulative load plot (see Fig. 7) indicate that a discharge of 0.4 m^3 s^{-1} represents an approximate threshold at which overland flow may become more important in the watershed because the slope of the lines change. Although atrazine, simazine, DEA, and metolachlor are detectable throughout the year and during a variety of flow conditions in Morgan Creek, concentrations generally increase (commonly by an order of magnitude or more) during high flow periods.

Discussion

Comparison of Basin Yields and Transport Processes of Nutrients and Pesticides

Basin yields of nutrients for the watersheds are presented in

Table 3. The yields are substantially different among the basins, but the yields of total nitrogen were always greater than those of total phosphorus. The DR2 Drain had the highest yield of nitrate and total nitrogen, followed by Leary Weber Ditch. The yields for Morgan Creek were slightly less than those for Leary Weber Ditch. The nitrogen yield for Maple Creek was lower than those for the other basins that were planted in corn and soybeans, but the total phosphorus yield was higher. The Maple Creek basin had the highest yield of total phosphorus, probably because of erosive transport of fine-grained soils (Fredrick et al., 2006). The lowest yields of nitrate and total nitrogen were those for Mustang Creek. The DR2 Drain had the highest yield of orthophosphorus. Although orthophosphorus was not particularly elevated in ground water samples collected in the DR2 Drain basin during this study (0.05 mg L^{-1} in ground water and 0.097 mg L^{-1} in the stream during the non-irrigation season), the year-round flow of the DR2 Drain with ground water discharge containing phosphorus at this concentration can account for one third of the phosphorus load in the drain. Input of ground water containing higher concentrations of P—ranging from 0.006 to 0.193 mg L^{-1} throughout the year—than the median and some returns of irrigation overland flow runoff may account for the remainder of the phosphorus load in the DR2 Drain.

The loads of nitrogen and phosphorus transported relative to the amounts applied (LAPU) are shown in Table 4. Nutrients are applied to fields several times throughout the spring and summer in the Mustang Creek basin. The relatively low yields of nitrate from this basin can be explained by the ephemeral nature of Mustang Creek and the lack of a connection to a ground water flow system. The period when flow occurs is several months after nitrogen or phosphorus fertilizers are applied. The export of phosphorus, relative to the amount applied, from DR2, Mustang Creek, Leary Weber, and Morgan Creek basins is similar, but that for Maple Creek is considerably higher (Table 4). The export of phosphorus, relative to the amount applied, may be higher from the Maple Creek basin than from the other basins (Tables 3 and 4) because of the large amount of overland flow that supplies water to the creek and the presence of easily erodible soils.

Transport processes affecting basin yields of nutrients at these locations are the result of the relative amounts of base flow and associated concentrations in the ground water, the relative amounts of overland runoff, drainage characteristics, soil characteristics, source of irrigation water, and climatic factors. Denitrification was shown to occur at the DR2 Drain, Maple Creek, and Morgan Creek basins (Puckett et al., 2008, Green et al, 2008), but the process did not eliminate nitrate and ground water discharge was a significant source of nitrate to those three streams. Although the climate of the DR2 Drain and Leary Weber Ditch basins are vastly different, nitrate yields were very high in each location. Because of the use of imported water and poor drainage at DR2 Drain, a rise in the water table resulted in shallow flow paths contributing nitrate-rich water to the drain throughout the year. The poor soil drainage of the Leary Weber Ditch basin coupled with high rainfall, no contribution from deeper ground water, and discharge of tile drain water high in nitrate resulted in high yields of total nitrogen mainly in the form of nitrate. Inputs of nitrate from baseflow at the basin scale greatly affected the annual load and yields at DR2, Maple Creek, and Morgan Creek.

Table 4. Basin load as a percent of use (LAPU).

Stream	LAPU values				
	N	P	Atrazine	Simazine	Metolachlor
	%				
DR2 Drain	32	5	0.3	0.3	NA†
Mustang Creek	0.3	3	NA	1.6	0.0006
Maple Creek	13	33	3.6	NA	0.3
Leary Weber	29	6	3.3	0.06	1.7
Morgan Creek	25	3	0.2	0.2	0.4

† NA, not applicable (insufficient data to calculate a value).

Pesticide yields and LAPU values from the basins are shown in Tables 3 and 4. Atrazine and metolachlor, as the parent compound or the degradate, had the greatest yields in the basins of high use (Nebraska and Indiana). The percentage of atrazine transported relative to the amount applied was highest for Maple Creek and lowest for Morgan Creek. Capel and Larson (2000) and Capel et al. (2001) compared atrazine LAPU and other pesticide LAPU values across a range of basin sizes. The atrazine study (Capel and Larson, 2000) showed that the LAPU does not vary across a range of watershed size but that individual basins have year-to-year variability because of meteorological conditions. In many of the basins, LAPU levels of 1 to 3% were observed. In the Sugar Creek (IN) basin, which contains the Leary Weber Ditch basin, LAPU values ranged from 0.82% to 14.3% during a 5-yr period, with 3 yr having values of 1.1, 2.2, and 2.3%. The Sugar Creek LAPU in this study was 1.6%. The high level of 14.3% in the Capel and Larson (2000) study was attributed to overland runoff from a large precipitation event. Maple Creek also was included in the Capel and Larson (2000) report, where the atrazine LAPU was 1.4%. Although the Leary Weber Ditch is nested within the Sugar Creek basin, the LAPU at the Leary Weber Ditch was twice that of Sugar Creek (3.3%) during this study. This may be attributable to tile drainage being the main source of atrazine in Leary Weber, with tile drains, ground water, and overland flow important for Sugar Creek. Morgan Creek and the DR2 Drain had similar LAPU levels for atrazine (Table 4) despite the different climates in those basins. The relatively low LAPU value for atrazine for Morgan Creek (0.2%) might be attributable to the sandy soils in this basin and thus to the greater role of ground water in the transport of agricultural chemicals, especially the degradate compounds.

In contrast to the midwestern basins, relatively small basin yields and LAPU levels of pesticides were measured in the watersheds of the western USA, in most cases. This might be attributable to the low rainfall amounts in the west, which limit the amount of overland flow and transport of pesticides to streams by that route. This was especially true for the DR2 Drain, where most of the transport was associated with ground water discharge. Although amounts of irrigation water applied in a semiarid basin may be similar to the amounts of precipitation in a humid basin, the effect on agricultural chemical transport is not the same. Runoff of irrigation water may be limited in regions of sandy soils with good drainage. Domagalski and Munday (2003) studied pesticide concentrations, loads, and yields in the lower

California Central Valley, where the Merced River and Mustang Creek are nested, during an irrigation season (April through September) and found LAPU values for insecticides ranging from 0.007 to 0.17%. Generally low LAPU values of other pesticides and herbicides were found in that study. However, in the current study, the annual LAPU for simazine at Mustang Creek was 1.4%, which is in the general range for herbicide LAPU values measured in the midwestern basins. Herbicides are used year-round in California, with extensive winter applications. Because these applications occur during the rainy season, annual LAPU values in California can be similar to those of the midwestern basins. The higher yields for the Nebraska basins are probably attributable to the greater role of overland flow for the transport of pesticides relative to the other basins in this study. Overland flow is of lesser importance to chemical transport in the Leary Weber Ditch, and ground water is of greater importance for pesticide transport in the Morgan Creek basin.

Conclusions

This comparative study of transport processes of nutrients and herbicides to streams illustrates climatic, hydrological, and agricultural management practices affecting the transport of chemicals. Different sources of irrigation water greatly affected transport in the semiarid settings. The long-term use of imported water in the DR2 basin of eastern Washington resulted in drainage problems that were solved by the construction of a drain network to move water from engineered small basins to larger collector streams. The imported water resulted in a rise of the regional water table and the subsequent year-round discharge of base flow to receiving streams. The shallow ground water flow paths eventually became rich in nitrate, which contribute to a year-round stream load. This drainage situation in a semiarid setting results in nitrogen basin yields that are similar to, or even greater than, those in a humid environment where tile drains were similarly installed to control drainage.

In contrast, agricultural land use within the semiarid Mustang Creek basin in California used locally pumped ground water because of the unavailability of imported water in that portion of California's Central Valley. Mining of local ground water decreased the water level such that streams are always losing and chemical transport only occurs in association with infrequent storms. Although Mustang Creek had low nutrient yields because of the lack of base flow, pesticide yields can be problematic from a management viewpoint because of applications during the winter rainy season. In that case, a semiarid setting can have pesticide yields similar to a more humid setting. Although the nitrate load and basin yield of Mustang Creek was relatively low, storage of nitrate in the unsaturated zone probably occurs and may become a significant source to ground water.

Varying amounts of pesticide inputs from base flow and overland flow from runoff were observed in the mid-western basins that had connectivity with ground water. Nitrogen input in the Morgan Creek basin (MD) was primarily from ground water discharge and implies that management of stream loads should be linked to nitrogen inputs to ground water. Pesticide loads in Maple Creek (NE) and Morgan Creek were primarily a function of storm water runoff after application; however, degradates of herbicides, such as metolachlor ESA, were transported in a similar manner to that of nitrate.

Phosphorus loads, as a percent of the amount applied, were similar for Mustang Creek, DR2 Drain, Leary Weber Ditch, and Morgan Creek but were much higher in the Maple Creek basin. That basin also had high basin yields of atrazine, which was primarily transported in overland flow. Therefore, management of phosphorus and herbicide runoff and subsequent transport to the creek should be directed toward reduction at the field level (reduction of soil erosion) or through the use of techniques that limit the entry of these chemicals to the stream, such as riparian buffer strips. Although ground water transport of phosphorus is not usually invoked as a potential source to streams, the basin yield of soluble phosphorus was high in the DR2 Basin even though runoff from storms did not generally occur. Transport mechanisms of phosphorus in these types of settings with shallow ground water flow paths should be considered for future research.

Maple Creek and Morgan Creek had substantial amounts of nitrate in the ground water system and base flow of high nitrate water to the stream but minimal to moderate amounts of denitrification limiting the nitrogen discharge to the creeks. Much of the Morgan Creek ground water was found to be oxic, and therefore the potential for denitrification was limited. Denitrification in the streambed zone of Maple Creek was found, but it was suggested that movement of ground water through this zone was fast relative to the rate of denitrification. This is in agreement with other studies of denitrification (e.g., Royer et al., 2004), which suggest that although the potential for denitrification exists for many streams, the focus of agricultural management on water drainage results in flow paths where denitrification is limited. Further research may test the effectiveness of the width or the type of vegetation within the riparian zone on the rate of denitrification.

Loads of pesticides as a percent of use values were, for the basins studied, similar to those of previously published studies for herbicides and insecticides. Some differences were attributable to local climatic or hydrologic conditions and did not exceed 3.6%. Although LAPU values in previously published research are similar, management of pesticide load reductions, especially to reduce toxicity of stream water from storm water runoff, is problematic because of the inability to determine which portions of the basin contributes to the small amount of load reaching the stream. Further work is needed on the relationships between proximity of specific fields to streams, application rates and timing, and soil characteristics to more effectively manage and lower the basin yields of soluble pesticides.

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