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Watershed Vulnerability to Losses of Agricultural Chemicals: Interactions of Chemistry, Hydrology, and Land-Use

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The objective of this study was to conduct a multibasin reconnaissance survey to determine the relative importance of chemical properties, land-use, and hydrology to agricultural chemical contamination of streams in northern Missouri. In 1994 and 1995, samples were collected from 140 sites on 95 different streams and rivers throughout northern Missouri. Samples were collected under preplant and postplant conditions and analyzed for common herbicides and dissolved nutrients. Atrazine, the most frequently detected herbicide was detected in all postplant samples and 99% and 90% of the preplant samples in 1994 and 1995, respectively. The study area has significant variations in soils, hydrology, and land-use (row-cropping intensity). The hydrology is largely determined by the soils, as reflected by soil hydrologic groups. Nitrate and herbicide concentrations showed opposite trends across the study region. Streams draining watersheds with runoff-prone soils had the highest herbicide concentrations, while streams draining watersheds with more groundwater recharge had low herbicide concentrations but the highest NO_3–N concentrations. Current data are sufficient to develop a conceptual framework for assessing watershed vulnerability based on three key factors. The primary factor is the chemistry of the compound, which determines the potential hydrologic transport pathways for that chemical to be lost from the soil. Nitrate can potentially be leached or lost in runoff. Moderately sorbed compounds, such as atrazine, are more likely to be lost in runoff or degraded within the soil than leached. The hydrology of a region is the secondary factor, as it determines the relative importance of the leaching and runoff transport pathways. The third factor then is the land-use, which includes the percentage of a watershed that is cropped, the locations within the watershed that are cropped, and the chemicals applied. Management practices to improve water quality must be designed in accordance with the dominant problems and transport pathways of a watershed.

Introduction

Increased monitoring of streams and public water supplies in recent years has heightened public concern about water quality degradation due to agricultural chemicals. Many reports have dealt with the presence of commonly used herbicides, although public perception of pesticides is probably strongly impacted by reports of environmental problems associated with older organochlorine pesticides.

The United States Geological Survey (USGS) has conducted regional surveys of herbicide contamination of ground and surface water in the midwestern United States. Concentrations found in streams [1] and surface water reservoirs [2] were significantly higher than those found in groundwater [3]. Streams were found to have their highest herbicide concentrations during the spring, shortly after the chemicals were applied [4–7]. A significant portion of groundwater recharge takes place in the fall and winter, after the herbicides have been through multiple degradation half-lives [8]. Occurrence and transport of herbicides in surface water have been measured at scales from edge of field (e.g. ref 9) to the whole Mississippi River Basin [5, 10, 11]. Larson et al. [12] provide an extensive review of pesticides in surface water.

Increasing emphasis is currently being placed on assessing and managing the problem of nonpoint source contamination on a watershed basis. Assessment requires monitoring data and an understanding of the factors controlling agrichemical fate within the watershed. Numerous attempts have been made to predict vulnerability on the basis of soil and chemical properties (e.g. refs 13 and 14). Other attempts have been made to determine the factors most responsible for herbicide loss by correlating factors such as pesticide chemical properties, land-use, applied mass, and soil properties with monitoring data. The mass flux of pesticides in the Mississippi River was only marginally correlated with the pesticide's chemical and environmental properties [11]. In a Swedish watershed, pesticide chemical properties were less important to losses in streams than was the applied mass [15]. Numerous other studies have also reached the conclusion that either the applied mass or the row cropping intensity was the most important factor determining herbicide concentrations or mass flux in streams (e.g. refs 16–18). In a multiscale, multibasin study of the Lake Erie Basin, herbicide concentrations were higher in smaller tributaries and in runoff prone basins than in the basin with higher infiltration soils [19, 20]. However, the row cropping intensity was less in the basin with greater infiltration than in the runoff prone basins, so the importance of differences in infiltration could not be evaluated. Goodwater Creek, a small watershed in north-central Missouri, had peak atrazine concentrations exceeding 100 μg L^{-1} despite having only about 20% of the watershed annually treated with atrazine [7]. This suggests that land-use may not be the dominant factor controlling herbicide contamination of streams.

Previous studies have not been able to determine the relative importance of chemistry, land-use, soils, and hydrology to the loss of agricultural chemicals because they either did not encompass an area with enough variation in these factors or covered such a large area that the variability in climate and sample collection timing masked the impact of these factors. The objective of this study was to conduct a multibasin reconnaissance survey of northern Missouri

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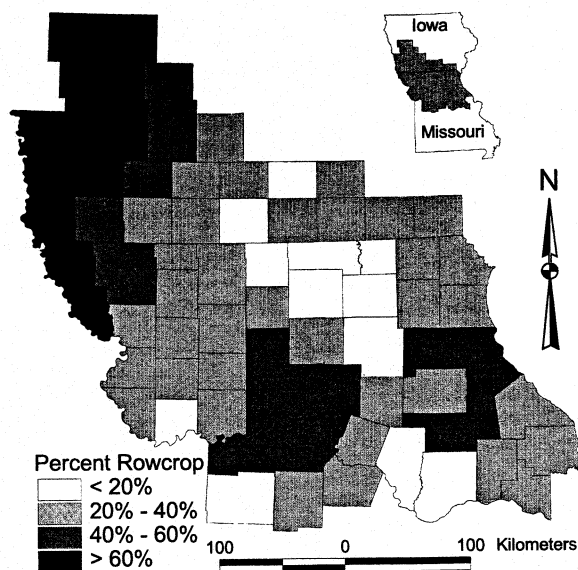‡ USDA-Agricultural Research Service.

FIGURE 1. Location of study area and percent of county area in rowcrops, 1994.

FIGURE 2. Percent of area in Hydrologic Soil Groups C and D and boundaries of Major Land Resource Areas (MLRA) within study area. MLRAs (boundaries in white) are as follows: 107, Iowa and Missouri Deep Loess Hills; 108, Illinois and Iowa Deep Loess and Drift; 109, Iowa and Missouri Heavy Till Plain; 113, Central Claypan Areas; and 115, Central Mississippi Valley Wooded Slopes.

streams, encompassing watersheds with significant differences in soils and row-cropping intensity, to determine the relative importance of land-use and hydrology to agricultural chemical contamination of streams in northern Missouri.

Materials and Methods

Study Area. The study area was in northern Missouri and southern Iowa. Land-use in the study area is dominantly agricultural, but the division between row-crops versus hay and pasture is not uniform (Figure 1). Row-cropping intensity is highest in southwestern Iowa and northwestern Missouri and lowest in north-central Missouri. Soybeans and corn account for about 90% of the cropped acreage. Sorghum, which is treated with many of the same herbicides as corn (21), is a significant crop in some counties of Missouri. For the sake of brevity, corn and sorghum will be referred to as corn in the remainder of the paper.

Baseflow of the streams in the study area is provided by groundwater flowing through alluvial deposits, pre-Illinoian glacial till, and Illinoian and Wisconsin loess. Groundwater in the bedrock aquifers bypasses these streams and discharges at the Missouri and Mississippi Rivers (22). Loess deposits are thickest near the Missouri and Mississippi Rivers. Nonalluvial soils were formed in the loess and underlying glacial till. Tile drainage is not a common practice in the region.

Soils show variations across the study area especially in the properties which contribute to the hydrology of the region. These soil properties have been summarized in an interpretive parameter called the Hydrologic Group (23). Hydrologic Group A soils have the lowest runoff potential and Hydrologic Group D soils have the highest runoff potential. The percent Hydrologic Group C and D soils shows the variation in soil hydrology across the study area (Figure 2). Major Land Resource Areas (MLRA (24)) within the study area were defined primarily on differences in soils (Figure 2).

Stream Sampling. Samples were collected from about 140 sites representing 95 streams and 41 river basins (Figure 3). Most of the sample sites were in Missouri, but many of the river basins have drainage areas which include portions of southern Iowa. Drainage areas ranged from 100 to 20 400 km². The location of pesticide dealerships was considered in choosing sample sites, to minimize the impact of potential point sources. Samples were collected at preplant (March–April) and postplant (June–July) of 1994 and 1995. Each
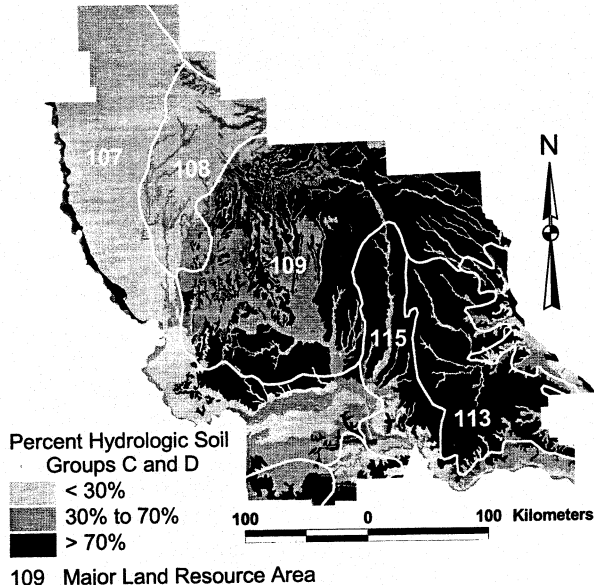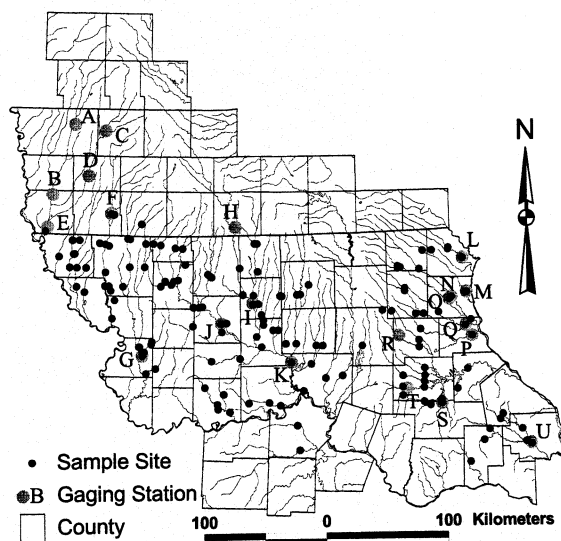

FIGURE 3. Location of stream sample sites and selected USGS gaging stations in study area.

sample set was collected within a 2 week period so that all samples within a set were as comparable as possible. Baseflow conditions predominated for both preplant sets and the 1994 postplant set. Runoff conditions existed for most of the 1995 postplant samples. Corn planting was complete prior to collection of the 1994 postplant samples and at least 50% complete for the 1995 postplant samples. Acquiring all samples within a 2 week period required collection of grab samples. In smaller streams a single sample was collected in the main flow path. In larger streams, a more representative sample was collected by taking samples at two to three locations in a transect across the stream. The samples were transported in iced coolers (about 2–4 °C) and filtered through 0.45 μm nylon filters within 1–3 days of collection. For the larger streams, all samples were mixed just before filtration to provide a single composite sample. Filtered samples were stored refrigerated. Sample sets were reviewed

to make certain that they were representative of the collection period. For example, previous studies of northern Missouri and midwestern streams (4, 7) demonstrated that the presence of alachlor and significant levels of metolachlor did not occur under preplant conditions. Several of the April 1994 samples contained significant levels of alachlor or metolachlor (>1 μg L^{-1}) or were collected after planting was known to have occurred and were therefore not included in the analysis of preplant samples.

Chemical Analyses. Samples were analyzed for the following commonly used herbicides: alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], atrazine [6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine], cyanazine [2-((4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl)-amino)-2-methylpropanenitrile], metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], and metribuzin [4-amino-6-(1,1-dimethylethyl)-3-methylthio-1,2,4-triazin-5(4H)-one]. The sample bottles, sample collection procedure, chemicals, reagents, and processing procedure for herbicide residue determination were described earlier (6, 7, 25). In brief, following cleanup with C$_{18}$-solid-phase extraction columns, sample quantitation was by gas chromatography and N−P detection or by high

performance liquid chromatography and UV detection for cyanazine. The limits of detection (LOD) are in Table 1. A quality control program was instituted with field and lab blanks, field duplicates, and field and lab spikes (6, 7).

Dissolved NO$_3^-$ analyses were usually conducted within 5 days of filtration. If samples could not be analyzed for NO$_3^-$ within 5 days, they were frozen, and analysis was done within 30 days of filtration. Nitrate was measured colorimetrically by reduction to NO$_2^-$ using a Cd column and a continuous flow autoanalyzer (Lachat Instruments, Milwaukee, WI) [Mention of trade names or specific products is made only to provide information to the reader and does not constitute an endorsement by the University of Missouri or the USDA-Agricultural Research Service.] with a detection limit of 0.1 mg/L N. This method combines NO$_3^-$ and NO$_2^-$. For the remainder of this paper NO$_3^-$ + NO$_2^-$ results will be referred to as NO$_3^-$.

Results and Discussion

Herbicides and Nitrate. The herbicide analyses from the four sampling periods (Table 2) demonstrate that herbicide contamination of study area streams was common during both the preplant and postplant time periods. Under preplant conditions in both 1994 and 1995, atrazine and cyanazine were frequently detected, while alachlor, metolachlor, and metribuzin were not detected in 1994 and infrequently detected in 1995. Part of the higher prevalence of atrazine and cyanazine is due to their lower LODs (Table 1). The only preplant exceedance of water quality standards (26) was in 1994 when 4% of the samples had cyanazine concentrations exceeding the 1 μg L^{-1} Health Advisory Level. The lower postplant prevalence of alachlor and metolachlor in 1995 than in 1994 may reflect the differences in masses applied (Table 1).

There were dramatic differences between the preplant and the postplant samples (Table 2). The large increases in concentrations and prevalence of all the herbicides indicate that the primary source of the herbicides in the streams was that year's field applications. The fact that herbicide concentrations were higher during 1994 postplant baseflow than preplant baseflow in 1994 and 1995 indicates a short-term concentration increase in near-stream groundwater. It is highly unlikely that herbicide leaching to groundwater in stream flood plains would cause rapid changes in concen-

TABLE 2. Statistical Summary of Herbicide Analyses[a]

| period	year	analyte	detections (%)	concentration (μg L^{-1})				percentage $\geq$ MCL or HAL (%)
				max.	min.	mean	median	
preplant	1994	alachlor	0	nd	nd	nd	nd	0
		atrazine	99	1.39	nd	0.50	0.40	0
		cyanazine	85	2.26	nd	0.41	0.37	4
		metolachlor	0	nd	nd	nd	nd	0
		metribuzin	0	nd	nd	nd	nd	0
	1995	alachlor	1	0.34	nd	nd	nd	0
		atrazine	90	1.54	nd	0.20	0.16	0
		cyanazine	57	0.81	nd	0.10	0.07	0
		metolachlor	3	0.80	nd	nd	nd	0
		metribuzin	2	0.53	nd	nd	nd	0
postplant	1994	alachlor	15	3.87	nd	nd	nd	1
		atrazine	100	32.1	0.54	5.09	3.50	57
		cyanazine	97	21.9	nd	2.45	1.83	72
		metolachlor	78	12.6	nd	1.31	0.80	0
		metribuzin	6	1.04	nd	nd	nd	0
	1995	alachlor	6	8.02	nd	nd	nd	1
		atrazine	100	136.	0.04	5.84	2.39	42
		cyanazine	99	21.4	nd	2.55	0.86	47
		metolachlor	59	30.9	nd	2.20	0.69	0
		metribuzin	25	4.57	nd	0.19	nd	0

[a] Not detected, nd.
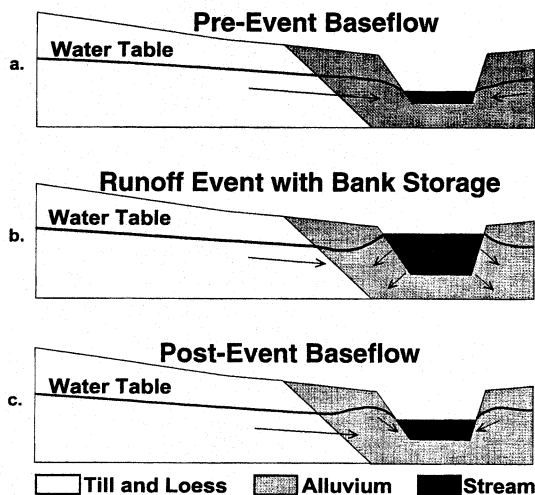
FIGURE 4. Schematic diagrams showing (a) movement of groundwater from loess and till through alluvium and discharging at the stream as pre-event baseflow; (b) movement of streamwater from stream into alluvium (bank storage); and (c) movement of bank storage groundwater back to stream as part of postevent baseflow.

FIGURE 5. Atrazine plus cyanazine concentrations, June 1994.

trations of herbicides in groundwater discharging to the streams. This rapid concentration change is most likely due to surface water–groundwater interactions. A gradient reversal can occur during runoff events, causing streamwater to be pushed through the stream bed and banks and become groundwater; a process called bank storage (Figure 4). This bank storage groundwater will then return to the stream as part of the postevent baseflow. Squillace et al. (27) discussed the potential importance of this process to herbicide transport.

Atrazine and metolachlor were applied in nearly equal masses within the study area, while the other target herbicide masses were ranked cyanazine > alachlor > metribuzin (Table 1 (21, 28–31)). Differences in prevalence of the herbicides was a function of the mass applied, degradation rates, and LODs. Sorption is not likely to be the cause of prevalence differences, as the range of K_d (Table 1) reported for each herbicide is similar (32). The lower prevalence and concentrations of alachlor and metribuzin are consistent with their lower usage. The lower median and maximum concentrations of metolachlor compared to those of atrazine and cyanazine do not match the usage data. A more complete understanding of transport can be gained by analyzing stable metabolites. Atrazine metabolites constitute a significant portion of the total atrazine transport (25). Stable metabolites may be an even more important part of the total metolachlor transport (33).

The highest and lowest atrazine and cyanazine concentrations were in streams with 100–400 km^2 drainage area. Concentration variability decreased with increasing drainage area, while the median concentration as a function of drainage area was nearly invariant. Apparently the larger basins or watersheds integrated the variability of the smaller subwatersheds. This implies that despite probable variations in travel time and concentration dynamics, the sample downstream of a junction was similar to the volumetric average of the upstream sites. The data also suggest that no significant herbicide degradation was occurring within the streams.

Regional Differences in Contamination. Atrazine and cyanazine have similar ranges of reported K_d (Table 1) and, within the study area, were used individually or in combination to control broadleaf weeds in corn. Because of these similarities and to provide a more comprehensive analysis of vulnerability to contamination by triazine herbicides, the
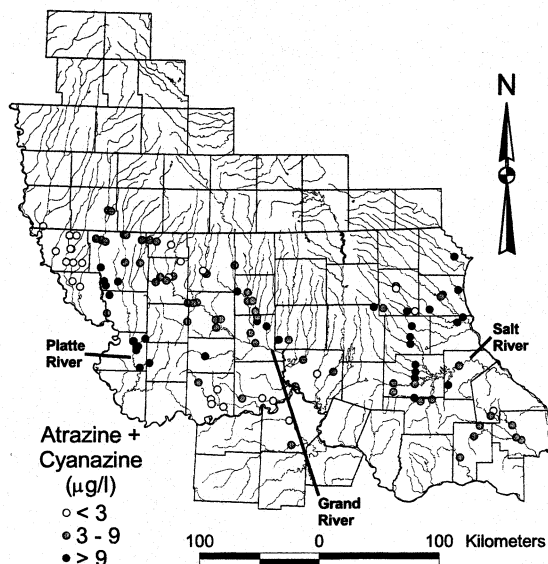
atrazine and cyanazine concentrations were summed for each sample to provide a single value which could be compared across the study area. The geographic distribution of the postplant 1994 atrazine plus cyanazine (Figure 5) shows that there are distinct areas with below average and above average concentrations. The highest concentrations are found in the eastern part of the study area within the Salt River Basin and the Mississippi River tributaries north of the Salt River. Additional areas of high concentration were in some tributaries of the Platte and Grand Rivers. Low concentrations were found in southwestern Iowa and northwestern Missouri, an area known as the Deep Loess Hills. The postplant 1995 atrazine plus cyanazine showed a similar geographic distribution, despite being collected under runoff conditions as opposed to the 1994 baseflow samples.

A visual comparison of the geographic distribution of county-level row-cropping data (Figure 1) with Figure 5 clearly shows that herbicide contamination of streams is not strictly a function of the cropping intensity within the watershed. The Deep Loess Hills, which had the greatest cropping intensity had the lowest atrazine plus cyanazine. The highest atrazine plus cyanazine concentrations were found in areas with one-third to one-half the corn cropping intensity of the Deep Loess Hills. The area cropped to corn in 1995 was less than that of 1994, but the regional distribution of cropping intensity was very similar.

Sample sites with low atrazine and cyanazine concentrations (Figure 5) were found in areas with less than 30% Hydrologic Group C and D soils (Figure 2). Sample sites were aggregated by MLRAs, which serve as an imperfect but useful surrogate for soils. Sample sites were only included in the MLRA aggregated datasets if they were sampled in the preplant 1995 and the two postplant data sets. Sample sites which were downstream of other sample sites were excluded to avoid double representation of watersheds. MLRAs 108 and 115 were not included in these analyses, because they had too few sampling sites for the statistical analyses.

Box plots of atrazine plus cyanazine by MLRA for 1994 and 1995 (Figure 6) show distinct differences between MLRAs. MLRA 107 is low both years, with the highest atrazine plus cyanazine concentrations being in small streams which have soils more typical of MLRAs 108 and 109. MLRA 109 and MLRA 113 are high both years. The MLRA 107 datasets were statistically different from either the MLRA 109 or 113 sets, which were statistically similar ($p > 0.05$) as determined with the Wilcoxon rank sum test.
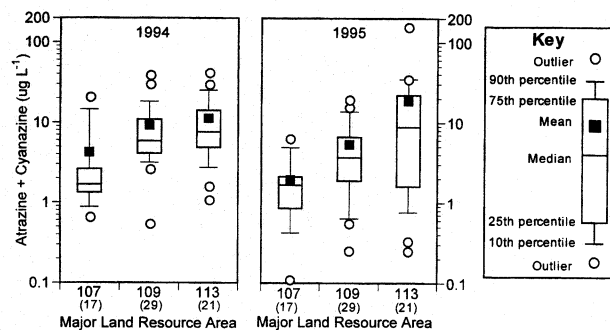
FIGURE 6. Boxplots of postplant atrazine plus cyanazine concentrations by MLRA for 1994 and 1995.
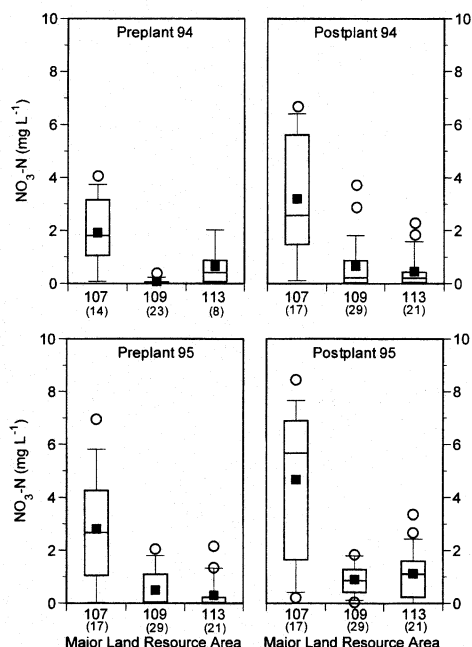

FIGURE 7. Boxplots of preplant and postplant NO_3−N concentrations by MLRA for 1994 and 1995.

Box plots of NO_3−N by MLRA (Figure 7) are distinctly different from the box plots of atrazine plus cyanazine (Figure 6). The preplant 1994 data are different than the other four data-sets. The reasons for this are unclear, although the tremendous volume of water which flushed through these systems during the flooding of 1993 may be part of the answer. The highest median NO_3−N concentration for each MLRA was in the postplant 1995 sample set, which was collected under runoff conditions. No attempt was made to determine the sources (i.e.: crop fertilizer, animal waste, human waste, atmospheric input, soil mineralization, etc.) of N in the streams. In addition it should be recognized that NO_3−N measured in the stream may not be from that year's input of nutrients, whether the sample is collected under runoff or baseflow conditions. Although the N source cannot be determined with this data-set, it is apparent that the highest NO_3−N values are in MLRA 107, which is the most intense corn growing region. This is true at preplant and postplant and under both baseflow and runoff conditions. The great spread in MLRA 107 NO_3−N concentrations is a reflection of distinct subregions. The high values are found in the true Deep Loess Hills, while the low values are found in streams which primarily drain the Missouri River flood plain. Previous studies showed that domestic well NO_3−N concentrations were higher in northwest Missouri than in the Missouri River flood plain (34, 35).

The Impact of Chemistry on Potential Loss Pathways. If land-use or applied mass alone was the dominant factor
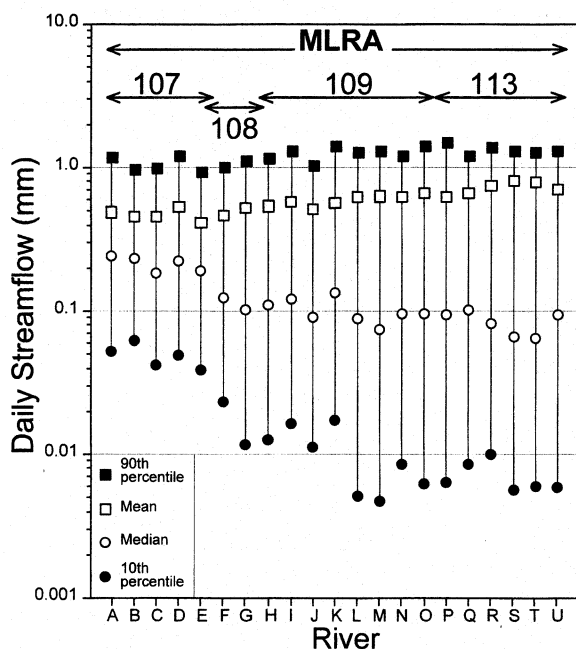

FIGURE 8. Daily streamflow values for USGS gaging stations (locations: Figure 3)

in watershed vulnerability, then the Deep Loess Hills should have the highest concentrations of NO_3−N and atrazine plus cyanazine. The fact that the geographic distributions of NO_3−N and atrazine plus cyanazine are different indicates that the chemistry of the compounds is a crucial factor in determining the potential hydrologic loss pathways. Compounds such as NO_3^- and some herbicide metabolites, which are weakly sorbed and slowly degraded (33), can potentially be leached or lost in runoff, depending on the hydrology. Moderately sorbed compounds, such as atrazine, are more likely to be lost in runoff than leached, especially when taking into account the timing of groundwater recharge with respect to the timing of chemical application and the degradation rate (8).

Hydrology. The question then becomes whether the contamination differences between the MLRAs (Figures 6 and 7) and potential loss pathways fit with the actual hydrology of the MLRAs. The regions with a high percentage of Hydrologic Groups C and D soils (Figure 2) correspond to the sample sites with higher atrazine plus cyanazine (Figure 5). MLRA 107, which had low atrazine plus cyanazine but high NO_3−N, is dominated by Hydrologic Group B soils.

The Hydrologic Groups represent arbitrary categories of runoff potential. The differences in runoff potential are verified by long-term records from the U.S. Geological Survey (USGS) gaging stations, which demonstrate that the actual hydrology of the study area streams varies significantly. The USGS publishes annual compilations of the average daily streamflow for all active, continuous-record gaging stations (e.g. ref 36). Included in these data are the calculated values for the mean and median average daily streamflow and the flow which is exceeded 10% (90th percentile of flow) and 90% (10th percentile of flow) of the days. These data were normalized by drainage area and plotted (Figure 8) for most of the active gaging stations in the study area (locations shown in Figure 3). Data were not included from stations where flow is strongly regulated by dams, influenced by public water supply withdrawals near the station, where the 10th percentile of flow was reported as 0.00 ft³/s, or where data have been collected for less than 25 years.

The greatest hydrologic contrast is between MLRAs 107 and 113 (Figure 8). The MLRA 107 gaging stations are in the true Deep Loess Hills portion of this MLRA. Hydrologically,
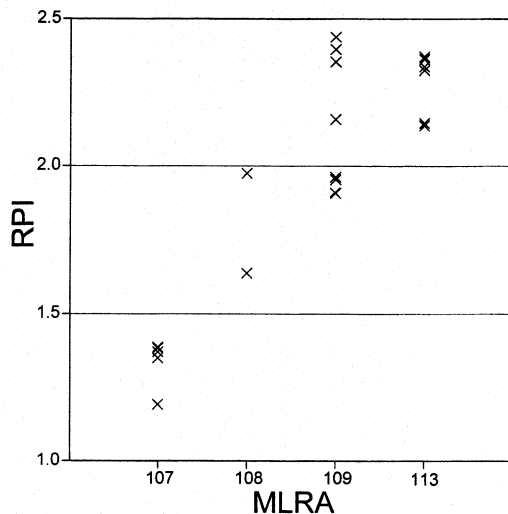
FIGURE 9. Runoff Propensity Index versus Major Land Resource Areas for USGS gaging stations.

MLRA 108 and 109 are transitions between MLRAs 107 and 113, except for the MLRA 109 streams of northeastern Missouri (Rivers M—P) which respond much like MLRA 113 streams. The higher median and 10th percentile of flow in MLRA 107 indicates stronger baseflow (greater groundwater discharge) despite receiving about 10% less annual precipitation. The greater spread between 90th and 10th percentiles in MLRA 113 is indicative of runoff dominated streams. To have a single number to compare the hydrology of these streams, we define a Runoff Propensity Index (RPI):

$$RPI = \log_{10}(\text{90th percentile}/\text{10th percentile}) \quad (1)$$

A plot of RPI vs MLRA (Figure 9), shows significant variations between the MLRAs. These differences are not a function of drainage area. As before, the northeast Missouri MLRA 109 streams (Rivers M—P) plot similarly to the MLRA 113 streams, while the other streams in MLRAs 108 and 109 are hydrologic transitions between MLRAs 107 and 113. The geographic transition of RPI values between MLRAs 107 and 113 fits with the spatial distribution of Hydrologic Group C and D soils (Figure 2). Arbitrarily calling RPIs high if greater than 2 and low if less than 1.5, we find that high RPIs are in areas with greater than 70% Hydrologic Group C and D soils and low RPIs are in areas with less than 30% Hydrologic Group C and D soils. Thus RPI, which is a direct measure of hydrology, is consistent with the indirect measure, the Hydrologic Soil Groups. This indicates that the differences in the hydrologic properties of the soils are the probable cause of the observed differences in stream hydrology.

For discussion purposes, we will focus on distinctions between MLRAs 107 and 113. Two major hydrologic differences exist between MLRAs 107 and 113. MLRA 107 has greater slopes and better drained soils than MLRA 113 (24). The claypan of MLRA 113 soils is a naturally occurring argillic horizon, with an abundance of smectitic clays, which impedes percolation. A greater proportion of the annual precipitation should percolate to groundwater in MLRA 107 than in MLRA 113. The greater topographic slopes in the Deep Loess Hills should impart a greater hydraulic gradient for groundwater flow. The greater percolation and hydraulic gradient are consistent with the stronger baseflow observed in MLRA 107 streams.

The mechanisms of streamflow generation cause much debate within the hydrologic community. For discussion purposes, we will define surface runoff as water which has interacted with the surface soil during the rainfall event. During a runoff event, the two major components of

streamwater will be baseflow and surface runoff. The ratio of baseflow to runoff water during an event will be greater in low RPI (MLRA 107) streams than in high RPI (MLRA 113) streams. High RPI streams are more likely to exhibit the groundwater—surface water interactions depicted in Figure 4.

Effects of Hydrology on Contaminant Transport. Leaching and groundwater transport of NO_3^- should be greater than that of the herbicides and should be the greatest in low RPI systems. The preplant samples, which were collected under baseflow conditions demonstrate the greater leachability of NO_3^- than the herbicides. Preplant herbicide concentrations were low in all regions of the study area. Nitrate-N was highest in low RPI areas, which have better infiltration. Within the study area, these low RPI areas have the greatest cropping intensity, which presumably indicates higher N fertilizer input.

Nitrate and herbicides should be transported in surface runoff. The postplant runoff samples (1995) had the highest mean and maximum herbicide concentrations (Table 2). In the high RPI areas, postplant NO_3—N concentrations were higher under runoff than under baseflow conditions. In low RPI systems, herbicides were higher under postplant runoff conditions (1995) than under baseflow (1994). During a runoff event, the streamwater is a mix of surface runoff and baseflow. The ratio of runoff to baseflow is higher in high RPI streams, and since herbicides are preferentially transported by surface runoff, herbicide concentrations are higher in these streams. The MLRA 107 streams with low RPIs are less prone to runoff than the high RPI streams of MLRA 113. However, if the ratio of runoff water to baseflow is high enough during an event, the herbicide concentrations can be elevated (37).

The preplant (baseflow) and 1995 postplant (runoff) datasets fit the potential hydrologic loss pathways with high NO_3—N in low RPI systems and high herbicides during runoff in high RPI systems. The relationship between contaminant chemistry and hydrology in the postplant baseflow sample set (1994) is less straightforward but also more illuminating about the complexities of the hydrologic and chemical processes controlling contaminant transport. During runoff events, bank storage is more likely to occur in high RPI than in low RPI streams. During postevent baseflow, the bank storage water returning to the stream will represent a significant portion of the streamwater in high RPI streams. During the postplant period, stream concentrations of herbicides and NO_3—N will be elevated during a runoff event. As some of this water moves into the alluvium (bank storage), it will also transport dissolved chemicals into the alluvium. The magnitude of transport will depend on the hydraulic gradient between the stream and the alluvial groundwater, the duration of the reversed gradient, the permeability of the alluvium, and the chemical processes affecting transport including sorption and chemical reactions. The discharge of this bank storage water as postevent baseflow causes the observed pattern of high baseflow herbicide concentrations in high RPI areas. These elevated herbicide concentrations are therefore a function of elevated runoff concentrations, not of a greater degree of leaching and transport through groundwater. Nitrate is more mobile than the herbicides and should be easily transported in and out of the alluvium. However, NO_3—N is not as elevated in postplant baseflow of high RPI streams as are the herbicides. This indicates a loss of NO_3^-, possibly due to denitrification or uptake by riparian and instream vegetation.

RPI is a long-term parameter that does not account for the timing and intensity of individual rainfall events or chemical use. Rather, RPI is a measure of the dominant hydrologic pathways and thus of the type of contaminants to which a watershed is vulnerable to off-site transport.

Interactions of Chemistry, Hydrology, Land-Use, and Climate. Clearly there is not a direct relationship between row-cropping intensity and agricultural chemical contamination of study area streams. The fact that the geographic distributions of NO_3-N and herbicides in study area streams were different, demonstrates that the vulnerability of a watershed to losses of agricultural chemicals is not a simple function of land-use or hydrology. Watersheds with high RPIs, > 70% Hydrologic Group C and D soils, and moderate row-cropping intensity had the greatest herbicide contamination. Conversely, watersheds with low RPIs, < 30% Group C and D soils, and high row-cropping intensity had the greatest levels of NO_3-N but relatively low levels of herbicide contamination. Using our regional dataset, we propose a conceptual framework for assessing the vulnerability of a watershed, based on four categories: (1) contaminant chemistry, (2) watershed hydrology, (3) land-use, and (4) climate.

The chemistry of the contaminant determines the potential hydrologic transport pathways for that chemical to be lost from the soil. Contaminants with $K_d < 1$ can potentially be leached or lost in runoff. Moderately sorbed compounds, such as herbicides with $1 < K_d < 10$, are more likely to be transported in runoff than leached. Transport by sorption to eroding sediment is the most likely transport pathway for highly sorbed contaminants ($K_d > 10$).

The hydrology of a region is the secondary factor, as it determines the relative importance of the transport pathways. Of prime importance, is the proportion of precipitation which percolates to groundwater versus that which becomes surface runoff. Calculating the RPI of streams with long-term gaging data provides a relatively easy method of assessing the balance between runoff and baseflow and the consequent transport pathways. Intermediate RPI streams may have soils subject to both percolation and runoff or have a mixture of high RPI and low or moderate RPI tributaries. Within the study area, the hydrology of the soils determines the hydrologic response of the watershed. In other areas, the subsurface geology or the presence of tile drains may control or strongly influence the hydrology.

The third factor is the land-use. As an independent correlate, land-use is a poor predictor of stream contamination. However, for areas where the potential loss pathways for a contaminant match actual flow paths, the vulnerability of watersheds to losses of agricultural chemicals will be dependent on the row-cropping intensity. The location of row-cropping within a watershed may also be important, as vulnerability will be higher if crop production is on those soils within the watershed that are most vulnerable to losses of the particular contaminant.

The fourth factor is the climate. In reality, the climate is already represented in the RPI, because the streamflow represents the hydrologic response of the watershed to the climate. A drawback to the RPI is that all seasons are represented equally. The percolation versus runoff balance is most critical during the 2 months following application for atrazine and compounds with similar half-lives. In this study area, the frequency, intensity, and duration of rainfall events following chemical application is a critical factor in determining the extent of contaminant transport. In a small watershed, 80–90% of the annual atrazine transport may occur during a few postapplication runoff events (7). For an individual rainfall event, there may be enough precipitation to shift the proportions of water which percolate or runoff. Under runoff conditions all studied MLRAs can have elevated herbicides, depending on the ratio of baseflow to surface runoff water in stream.

Within the study area, differences in soils and land-use have led to different water quality problems. Monitoring programs can be made more efficient by tailoring them to watershed hydrology. Management practices must be tailored to the water quality problems which do exist and to fit the hydrology of the watershed, rather than assuming that generic best management practices can be applied or be effective throughout the region.

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