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Monitoring Groundwater for Pesticides at Selected Mixing/Loading Sites in Arkansas

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Groundwater monitoring studies have been conducted in recent years to survey contamination due to pesticides, yet few have addressed wells where pesticides are mixed, loaded, or rinsed. Beginning in 1990, a monitoring study conducted over a 2-year period included five collections at each of 16 mixer/loader locations to assess any pesticide and nitrate contamination. At sites in 11 counties, samples for pesticide analysis were extracted with solid-phase extraction (SPE) disks. Samples were screened using gas chromatography-electron capture detection (ECD) and high-performance liquid chromatography−UV detection (LCUV) for 17 pesticides commonly used in Arkansas. Detections were confirmed by gas chromatography−mass spectroscopy (MS) or co-chromatography. Fourteen samples revealed atrazine (1 detection), cyanazine (4), parathion-methyl (2), metolachlor (2), norflurazon (1), pendimethalin (1), propanil (2), or trifluralin (1) at eight locations during the 2-year study. Two detections of parathion-methyl and one detection of trifluralin were above the Lifetime Health Advisory Level (LHAL) of 2 μg L^{-1}. Data suggested a high correlation between pesticide used and pesticide detected at sites sampled. Three wells contained NO_3-N concentrations of 10 mg L^{-1} or higher, but these did not correlate with pesticide concentrations. The pesticide's proximity to the wells during mixing, rinsing, or loading was considered to be a greater influence on temporary contamination of groundwater than chemical or site-specific characteristics.

Introduction

Point source contamination of groundwater has been a topic of escalating importance during the last several years. The detection of aldicarb in Suffolk County, NY, may have been the single most important incident that heightened public awareness in the United States regarding potential groundwater problems (*1*). Since the documentation of that event, continued emphasis has been placed on groundwater monitoring studies to assess pesticide levels due to both point and non-point source contamination (*2*−*4*).

It has been estimated that, in 1990, 92% of the nearly 300 million ha used for agricultural production in the United States received herbicide applications and 31% of the acreage received insecticide treatments (*5*). Before application, pesticides are often loaded into spray tanks, mixed, and ultimately rinsed near potentially vulnerable well locations. The pesticides are brought into the proximity of the well, thereby increasing the potential for point source contamination of groundwater from inappropriate disposal of excess spray solution and rinsates, accidental spills, or back-siphoning. Additionally, high pesticide concentrations such as those potentially found at pesticide mixing and loading facilities may increase the relative mobility of some pesticides due to weaker adsorption and slower degradation (*6*).

Cohen et al. (*7*) distinguished the pesticides most likely to contaminate groundwater relative to the following pesticide-specific characteristics: a water solubility > 30 μg mL^{-1}; K_{oc} < 300−500; negatively charged at ambient pH; hydrolysis half-life > 25 wk; soil half-life > 2−3 wk; photolysis half-life of > 1 wk and Henry's law constant < 0.01 atm m^3 mol^{-1}. They also characterized site-specific field conditions conducive to groundwater contamination: precipitation and irrigation recharge > 25 cm yr^{-1}; an unconfined aquifer that underlies permeable soils; soil pH adequate for pesticide stability and high nitrate levels present as an indicator of agricultural recharge (*7*).

Monitoring studies have been the most widely used method for assessing groundwater contamination from pesticides. Pesticides detected during monitoring of groundwater in Pennsylvania (*8*), Nebraska (*9*, *10*), Iowa (*11*), and Arkansas (*12*) have included atrazine, cyanazine, simazine, alachlor, and metolachlor. The pesticide detections from these studies corroborated observations of Cohen et al. (*7*), where two or more of the pesticide characteristics showed values in the ranges of the most probable contaminants. Other results of monitoring studies conducted in Arkansas indicated no detection of pesticides (*13*). The lack of pesticide detections was attributed to the low permeability of clay and silt deposits of the confining unit overlying the aquifer (*13*).

Compiled information on the occurrence of pesticides in groundwater tested across the United States indicates 17 pesticides have been detected across 17 states at levels exceeding the lifetime health advisory level (LHAL) (*2*). The National Pesticide Survey (NPS) report in 1990 stated that 1.2% of community water system (CWS) wells and 2.4% of rural domestic wells contained pesticides (*3*). None of the detections of CWS wells were above either the maximum contaminant level (MCL) or LHAL, but in rural domestic wells, alachlor, atrazine, dibromochloropropane (DBCP), ethylene dibromide (EDB), and γ-HCH (lindane) were detected above these limits (*3*).

Although several monitoring studies have been done to assess groundwater quality on a regional scale, few researchers have assessed groundwater quality where contamination may originate from a spill or inappropriate disposal around the site of loading or mixing. In one such study in Wisconsin, soil or water at 18 of 20 mixing sites contained quantifiable levels of pesticides that were often above the LHAL (*14*). Of the 19 pesticides detected, atrazine, cyanazine, alachlor, and metolachlor were four of the most frequently detected. Of the 37 concentrations detected from these pesticides, 18 were above their respective LHAL. The greatest concentrations of these compounds occurred at acute spill areas, burn piles, discarded pesticide container storage areas, and mixing/loading areas (*14*). In a similar study done in Illinois, the herbicides alachlor, metolachlor, metribuzin, cyanazine, atrazine, trifluralin, butylate, and pendimethalin were detected most frequently at mixer/loader facilities (*15*). The detections in Illinois were attributed to past and current practices at these facilities including back-siphonage, sloppy mixing and loading procedures, lack of rinsate collection, and improper waste disposal. The results of these studies suggest that wells at or near mixing/loading sites are especially vulnerable. No information has been available on the quality

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TABLE 1. Background Information on Specific Groundwater Sampling Sites in Mixer/Loader Study

site no.	general soil series and texture[a]	drainage description	approx well depth (m)	approx depth to groundwater (m)	drastic index[c] (m)
1	Crowley silt loam	poor	34	27	130
2	Dundee silt loam	poor	24	8	170
3 and 4	Hebert silt loam	poor	31	9	170
5	Alligator silty clay loam	poor	53	12	170
6	Savannah fine sandy loam	moderately well	46	18	180
7	Jackport silty clay/Crowley silt loam	poor	31	8	150
8	Bosket fine sandy loam	poor	15	5	170
9	Calloway/Calhoun silt loam	poor	50	NA[b]	170
10	Sharkey silty clay	poor	15	3	170
11	Sharkey silty clay loam	poor	52	NA	130
12	Crowley/Calloway silt loam	poor	31	6	130
13	Crowley/Calloway silt loam	poor	31	21	130
14 and 15	Henry/Loring silt loam	poor/well	37	12	170
16	Dubbs/Dundee fine sandy loam	well/poor	31	23	170

[a] Information taken from county soil survey maps at locations in the general vicinity of the sampled wells. [b] NA, not available. [c] Drastic Index, estimated groundwater variability from state scale Drastic map based on depth to groundwater, recharge, aquifer media, soil media, topography, impact of vadose zone, and hydraulic conductivity. The maximum value is 248. The higher the number, the more vulnerable the groundwater to pesticide contamination. Values calculated are based on 250-m^2 resolution.

of groundwater at similar sites in Arkansas. The objective of this study was to assess the temporal groundwater quality regarding potential pesticide contamination at selected pesticide mixing/loading sites including commercial ground and aerial applicator facilities as well as mixing/loading areas at farm facilities.

Experimental Section

General Information. Several commercially licensed pesticide applicators and producers were contacted by mail. County agents aided in contacting farmers who were interested in cooperating in the study. An introductory letter was sent giving background information on the planned experiment. An accompanying questionnaire included questions concerning characteristics of the well site such as soil texture, depth of well, and pesticides mixed near the well site. Approximately 80 commercial applicators received the letter/questionnaire. Sites were selected based on available funds, geographic distribution, and questionnaire responses. Through contacts from the county agents and questionnaire responses, a sampling scheme was conceived that ultimately included 16 sampling sites located in 11 counties of eastern Arkansas. The sites sampled represented counties throughout the eastern part of the state as well as varying agronomic situations, pesticide applications, and facility management schemes. The study included sites chosen at four aerial applicators and one commercial ground applicator. The other sampling sites were at on-farm mixing/loading locations as part of a farm production operation. Specific characteristics of each well site are provided in Table 1.

Sample Collection. Samples were collected five times over a 2-year period. In 1990, collections were made during June 13−20 and October 4−20, and in 1991, samples were collected May 10−23, July 20−26, and November 5−11. These sampling intervals were chosen to include different types of pesticide applications that occur during the year. Preplant incorporated (ppi) and preemergence (pre) pesticides typically are applied in the spring. In the summer, fewer ppi or pre pesticides are applied, but postemergence (post) pesticide use increases. The fall sampling represented a period when infrequent pesticide applications would be expected.

At each location, samples were collected by flushing the well for 1 min and then collecting the sample in a 1-L amber glass jar. Four jars of water were collected at each location. Two samples were fortified immediately in the field with 4.5 mL of a methanol solution to 0.9 L of water to correct for any pesticide degradation or dissipation that occurred between the time a sample was collected to the time of sample analysis. The methanol solution contained all pesticide analytes at a concentration of 4 μg mL^{-1}, except imazaquin, which was 10 μg mL^{-1}. The level of fortification was 20 μg L^{-1} of each pesticide except for imazaquin. Due to poor method sensitivity, imazaquin was fortified at 50 μg L^{-1}. Once the samples were collected, the jars were capped with Teflon lids and placed on ice until they could be transported to the laboratory for more permanent cold storage at 4 °C prior to extraction. Samples for inorganic analysis were also collected in 500-mL Nalgene bottles and stored on ice until they reached the laboratory where they were transferred to a freezer and stored at approximately −20 °C. Nitrate analyses were done by the University of Arkansas Soil Test Laboratory by cadmium reduction.

Pesticide Extraction. All solvent used in pesticide extraction was high-performance liquid chromatography grade (Fisher Scientific Company, Fairlawn, NJ). A 250-mL subsample of water from the 1-L jars was measured by graduated cylinder and placed in a 250-mL Erlenmeyer flask. Two milliliters of methanol was added to the water sample to keep the solid-phase extraction (SPE) disk conditioned during filtration. An extraction disk was placed on a sintered-glass filter funnel apparatus attached to a vacuum source. The solid-phase extraction disks used were 47-mm diameter Empore disks for environmental analysis (3M Industrial and Electronic Sector, New Products Department, St. Paul, MN, distributed by Varian Sample Preparation Products, Harbor City, CA). A total of 10 mL of a 1:1 methylene chloride/ethyl acetate solvent was added to the filter funnel as a cleaning solvent and was drawn through the disk at a rate of approximately 10 mL s^{-1}. Air was then drawn through for 1 min. A 10-mL sample of methanol was then added. As the solvent was drawn through, the vacuum was removed when a film of methanol covered the disk. This technique prevented drying and subsequent slow filtration through the disk. Deionized water (10 mL) was added to the thin film of methanol and drawn through until a thin film of deionized water covered the disk; the vacuum was again removed. The entire 250-mL subsample was then added to the filter funnel and drawn through at approximately 25−30 mL min^{-1}, and the filtrate was discarded.

After the sample had been drawn through, the vacuum was left on for 5 min to allow the disk to dry. The pesticides were eluted from the disks with two 5-mL portions of ethyl acetate and collected in 20-mL borosilicate glass vials placed in the base of the vacuum manifold. During each addition of ethyl acetate, the vacuum was applied and removed quickly to allow some ethyl acetate to penetrate the entire disk thickness for 2 min. Vacuum was then reapplied, and the

TABLE 2. Characteristics of Pesticides Analyzed in Mixing/Loading Study[a]

pesticide	chemical name	water solubility (mg L^{-1})	soil half-life (d)	soil sorption(K_{oc})
alachlor	2-chloro-*N*-(2,6-diethylphenyl)-*N*-methoxymethyl)acetamide	240	15	170
atrazine	6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine	33	60	100
azinphos-methyl	*S*-(3,4-dihydro-4-oxobenzo[d]-1,2,3]-triazin-3−ylmethyl) *O*,*O*-dimethyl phosphorodithioate	29	10	1000
benomyl	methyl 1-(butylcarbamoyl)benzimidazol-2−ylcarbamate	2	240	1900
captan	1,2,3,6-tetrahydro-*N*-(trichloromethylthio)phthalimide	5	3	200
cyanazine	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile	170	14	190
fluometuron	*N*,*N*-dimethyl-*N'*-[(3-trifluoromethyl)phenyl]urea	110	85	100
imazaquin	2-[4,5-dihydro-4-methyl-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-3-quinolinecarboxylic acid	600	60	20
parathion-methyl	*O*,*O*-dimethyl *O*-4-nitrophenyl phosphorothioate	24	14	5000
metolachlor	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-2-methoxy-1-methylethyl)acetamide	530	90	200
metribuzin	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4−triazin-5(4*H*)-one	1220	40	60
norflurazon	4-chloro-5-(methylamino)-2-(3−(trifluoromethyl)phenyl)-3(2*H*)-pyridazinone	28	90	600
pendimethalin	*N*-(1-ethylpropyl)-3,4-dimethyl-2,6−dinitrobenzenamine	0	90	5000
profenofos	*O*-4-bromo-2-chlorophenyl *O*-ethyl *S*-propyl phosphorothioate	28	8	2000
propanil	*N*-(3,4-dichlorophenyl)propanamide	200	1	149
simazine	6-chloro-*N*,*N'*-diethyl-1,3,5-triazine-2,4-diamine	6	60	130
trifluralin	2,6-dinitro-*N*,*N*-dipropyl-4−(trifluoromethyl)benzenamine	0	60	8000

[a] Data extracted from Wauchope et al. (*21*). These data represent values taken at 20−25 °C.

remainder of the ethyl acetate was eluted into the glass vials. Anhydrous sodium sulfate (4 mL) was added to the vial to remove any excess water. The ethyl acetate was decanted into a calibrated test tube. The glass vials were rinsed three times with ethyl acetate and each time decanted into the calibrated test tube. The final volume was brought to 5 mL of ethyl acetate by a stream of dry nitrogen as the vials were immersed in a 30−35 °C water bath. A 1.5-mL aliquot of the ethyl acetate was placed into a sample vial for gas chromatography (GC) analysis. The remaining 3.5 mL was brought to dryness by the dry nitrogen and then redissolved with the liquid chromatography (LC) mobile phase to a 3.5-mL final volume. A 1.5-mL aliquot was collected for LC analysis.

Freshly fortified samples and appropriate blanks were included and extracted with each batch to ensure sample integrity. Fortified samples consisted of 250 mL of water with 1 mL of 5 μg mL^{-1} methanol/pesticide solution such that the final concentration in water of each pesticide was 20 μg L^{-1} except imazaquin (50 μg L^{-1}).

Analytical Methodology. Water samples were screened for the 17 pesticides listed along with some of their physical characteristics in Table 2. Analytical standards (>98% purity) from various manufacturers were used to prepare fortification and standard solutions. These pesticides were chosen as target analytes based on experiences of extension and research personnel regarding frequency of use in the state. Included in the analyte list were pesticides detected in previous monitoring surveys.

All analytes were co-identified and quantified by gas chromatography (GC) and/or high-performance liquid chromatography (LC). Compounds determined by GC were analyzed by a Shimadzu GC-14A equipped with an electron capture detector (ECD). The 2-μL injected sample was split to two columns, each 0.53 mm × 15 m, containing SPB-5 and SPB-608 stationary phases, respectively. The temperature program was 180 °C for 2 min, increased at 1 °C min^{-1} to 190 °C for 0 min, increased at 2 °C min^{-1} to 220 °C for 7 min. Injector and detector temperatures were 250 and 300 °C, respectively. The flow rate through the column was 4 mL min^{-1}.

The LC analyses were performed by injecting the sample via a 50-μL loop while pumping mobile phase through a 4.6 mm × 12.5 cm Whatman C_{18} Partisphere column. The mobile phase consisted of 40% methanol, 45% deionized water, and 15% pH 7 buffer mixture and was pumped at a flow rate of 2 mL min^{-1}. The pH 7.4 buffer was made by mixing 244 mL of 0.067 M Na_2HPO_4 plus 156 mL of 0.067 M KH_2PO_4. Pesticides were detected with an Isco 2250 UV variable wavelength detector set at 225 or 254 nm with sensitivity set at 0.05 absorbance units full scale (aufs).

The GC−ECD and LCUV provided primary screening techniques. If a pesticide was detected by either of these techniques, confirmation was attempted with gas chromatography−mass spectroscopy (MS). Most of the pesticides were confirmed by injecting the sample into a Varian 3400 gas chromatograph equipped with Saturn II mass spectrometer. A 1-μL injection in ethyl acetate was made with a septum programmable injector (SPI) in which the temperature could be altered to allow better resolution for the selected pesticides. The temperature program set for the SPI injector was 70 °C initially for 0.25 min, increased to 260 °C at 180 °C min^{-1}, and then held for 2 min before cooling back to 70 °C. The column used was a 0.25 mm × 30 m capillary DB-5 with a temperature program of 70 °C for 0.25 min to 300 °C at a rate of 10 °C min^{-1} and then held for 4 min for a 28-min run time. The transfer line temperature was set at 260 °C. The analytes were ionized by electron impact. Pesticide detections were confirmed by matching the retention time and library mass spectrum of a pesticide standard to those of the unconfirmed analyte. Not all of the pesticides were confirmed with MS. Benomyl, fluometuron, and imazaquin were confirmed by co-chromatography with LCUV detection set at 254-nm wavelength absorbance.

Results and Discussion

Analytical Methodology. The mean percentage recovery and standard error for each pesticide analyzed in the extraction method are listed in Table 3 along with the lower limit of quantitation (LLQ) and method(s) of detection. Mean recoveries ranged from 82 to 98% for the pesticide analytes. The LLQ for the pesticides analyzed ranged from 0.1 to 1 μg L^{-1} in water.

Pesticide Detections. Of the 1360 total possible detections from the 80 samples collected, 14 total detections of 8 different pesticides were confirmed by MS over the 2-year survey period (Table 4). Concentrations corrected for degradation and percentage recovery ranged from 0.3 to 27.9 μg L^{-1}. Three of the 14 detections were above the LHAL. Alachlor, azinphos-methyl, benomyl, captan, fluometuron, imazaquin, and profenofos were mixed or loaded in the vicinity of the well site according to questionnaire responses but were not detected in the study. Atrazine and trifluralin were the most commonly mixed pesticides in the study, yet they were only detected once each. Cyanazine was detected at four of the

TABLE 3. Analyte Mean Percentage Recovery, Standard Error, Method of Detection, and Lower Limit of Quantitation (LLQ) As Determined by Laboratory Quality Control Samples Fortified at 20 μg L^{-1} in Mixer/Loader Groundwater Survey

pesticide	mean recovery[a] (%)	standard error[a] (%)	method of detection	LLQ[b] (μg L^{-1})
alachlor	87.1	3.7	ECD,[c] MS[d]	0.1
atrazine	82.4	6.4	LCUV,[e] MS	0.1
azinphos-methyl	97.8	5.4	LCUV, MS	0.3
benomyl	85.1	5.2	LCUV	0.4
captan	82.1	6.7	ECD, MS	0.2
cyanazine	91.6	2.8	ECD, LCUV, MS	0.1
fluometuron	92.8	6.7	LCUV	0.4
imazaquin	87.8	5.1	LCUV	1.0
parathion-methyl	89.9	2.3	ECD, MS	0.2
metolachlor	92.0	3.9	ECD, MS	0.1
metribuzin	90.4	3.2	ECD, LCUV, MS	0.1
norflurazon	87.5	2.7	ECD, LCUV, MS	0.3
pendimethalin	96.4	3.8	ECD, MS	0.1
profenofos	91.0	2.5	ECD, MS	0.2
propanil	85.1	3.5	ECD, LCUV, MS	0.2
simazine	83.6	5.0	LCUV, MS	0.1
trifluralin	88.7	3.6	ECD, MS	0.1

[a] Mean recovery and standard error were calculated from values obtained from quality control samples. [b] LLQ, lower limit of quantitation is defined as the level at which a pesticide was detected and quantified with co-chromatography and then confirmed with either gas chromatography−mass spectroscopy or co-chromatography assuming a 3:1 signal to noise ratio. [c] ECD, gas chromatography−electron capture detection. [d] MS, gas chromatography−mass spectroscopy. [e] LCUV, high-performance liquid chromatography−UV detection.

five sites that had mixed or loaded the pesticide in the vicinity of the wells, but never exceeded the LHAL (Tables 4 and 5). The positive detections in this study represented two aerial applicators at sites 1 and 7. The rest of the detections were a result of samples collected at on-farm mixing/loading facilities.

No pesticides were detected at any of the well sites from samples collected during the first sampling period in the summer of 1990 (Table 5). No pesticides were detected at any of the sampling periods at sites 6, 8, 9, 11, 13, 15, or 16. Both metolachlor and atrazine were detected in the fall of 1990 at site 5. Metolachlor was the only pesticide of the 14 detections that was not known to have been applied or mixed near the well site according to information from the cooperator's responses to the questionnaire. This result indicated a high correlation between the pesticide mixed or applied in the area to the pesticides detected. Also, these data imply that the metolachlor detection at site 5 could have been a result of long-term soil contamination as detailed by some researchers (*16*) or by non-point source contamination as others have determined (*2, 11, 12, 14*). The contamination more likely originated elsewhere and spread throughout the aquifer or through downward leaching from field applications to the shallow water table (12 m) at the site (Tables 1 and 5). Metolachlor detections in other surveys have been well documented to support this conclusion (*2, 11, 12, 14*). The concentrations of atrazine and metolachlor detected during this sample collection were below the LHAL.

There were two cyanazine detections and one pendimethalin detection from the third sampling period at sites 2 and 4. There were six pesticide detections at sites 1, 3, and 10 from the fourth sampling period in 1991, which was the highest frequency of detections during the study. Pesticides detected during this sampling were cyanazine, parathion-methyl, norflurazon, pendimethalin, and propanil. No pesticides were detected at sites 1, 2, 3, 4, or 10 prior to the third sampling period.

Parathion-methyl, propanil, and metolachlor were detected at sites 1, 7, and 12, respectively. The parathion-methyl detection at site 1 was the only recurring detection of a pesticide at a given site in the survey. Both detections, however, were above the LHAL of 2 μg L^{-1}. Therefore, further monitoring of the site for residual parathion-methyl would be appropriate before suggesting ameliorative action since there were no prior detections (Table 5).

Although multiple pesticide detections occurred at sites 1, 3, 4, and 5 during the 2-year period, site 1 was the only site that showed repeat detections, suggesting that chronic contamination did not occur at other sites (Table 5). Further monitoring would be needed at sites 7 and 12 where propanil and metolachlor, respectively, were detected at the final sample collection.

One of the two detections of propanil was greater than 27 μg L^{-1}. Only two other detections of propanil have been reported in groundwater. Both were reported in Missouri at concentrations less than 0.1 μg L^{-1} (*4*). Other surveys of Arkansas irrigation wells resulted in no detections of propanil (*12*). However, other studies have shown a lag phase of approximately 24 wk before a rapid degradation of propanil occurred when samples from three different groundwater

TABLE 4. Site Use, Total Detections, and Pesticide Concentrations Confirmed by Gas Chromatography−Mass Spectroscopy from Water Samples Collected at 16 Mixer/Loader Sampling Sites at Five Sample Collection Dates[a]

pesticide analyzed	sites using the pesticide (no.)	total detections (no.)	concentration range (μg L^{-1})	LHAL[b] (μg L^{-1})	detections above LHAL
alachlor	6	ND[c]	NA[d]	2[f]	NA
atrazine	10	1	0.6[e]	3	0
azinphos-methyl	5	ND	NA	NA	NA
benomyl	6	ND	NA	NA	NA
captan	2	ND	NA	NA	NA
cyanazine	5	4	0.5−1.8	10[g]	0
fluometuron	4	ND	NA	NA	NA
imazaquin	8	ND	NA	NA	NA
parathion-methyl	7	2	2.3−2.7	2	2
metolachlor	7	2	2.3−4.5	100	0
norflurazon	6	1	2.4[e]	NA	NA
pendimethalin	8	1	0.3[e]	NA	NA
profenofos	1	ND	NA	NA	NA
propanil	5	2	1.6−27.9	NA	NA
simazine	0	0	NA	4	NA
trifluralin	10	1	2.4[e]	2	1
total		14			3

[a] Sample collection dates were June 13−20, 1990; October 4−20, 1990; May 10−23, 1991; July 20−26, 1991; and November 5−11, 1991. [b] LHAL, lifetime health advisory level. [c] ND, not detected. [d] NA, data not available. [e] Concentration range not applicable since pesticide was detected only once or not detected. [f] Value represents the maximum contaminant level rather than the LHAL for alachlor. This value is an enforceable level set by the Environmental Protection Agency for drinking water standards. [g] During the study the LHAL was lowered from 10 to 1 μg L^{-1}. Since 10 μg L^{-1} was the level for the duration of the study, it was the LHAL reported.

TABLE 5. Concentrations of Pesticides Detected and Confirmed during Sampling Periods 2–5[a] from 1990 and 1991 at 16 Mixer/Loader Sampling Sites[b]

	concentration (μg L^{-1})											
	site 1				site 2				site 3			
pesticide	2[c]	3[d]	4[e]	5[f]	2	3	4	5	2	3	4	5
cyanazine			1.3			0.5					1.8	
parathion-methyl			2.7	2.3								
norflurazon											2.4	
propanil											1.6	

	concentration (μg L^{-1})											
	site 4				site 5				site 7			
pesticide	2	3	4	5	2	3	4	5	2	3	4	5
atrazine					0.6							
cyanazine		0.6										
metolachlor					4.5[g]							
pendimethalin		0.3										
propanil												27.9

	concentration (μg L^{-1})							
	site 10				site 12			
pesticide	2	3	4	5	2	3	4	5
metolachlor								2.3
trifluralin			2.4					

[a] No pesticides were detected from samples collected during the first sampling period of June 13–20, 1990; therefore, columns for data from period 1 have been omitted. Also, no pesticides were detected at sites 6, 8, 9, 11, 13, 14, 15, and 16 during the 2-year survey and have also been omitted from the table. [b] Sites where pesticides were detected included two aerial applicators at sites 1 and 7. The other sites represented on-farm facilities. [c] Second sampling period was collected October 4–20, 1990. [d] Third sampling period was collected May 10–23, 1991. [e] Fourth sampling period was collected July 20–26, 1991. [f] Fifth sampling period was collected November 5–11, 1991. [g] Detection was not consistent with records of pesticide mixing or application at this site.

TABLE 6. Descriptive Statistics from Results of pH and Nitrate–N Analyses of Groundwater Samples Collected at Five Sample Collection Dates[a] in Mixer/Loader Survey

	pH			nitrate–N (mg L^{-1})		
site no.	mean	min	max	mean	min	max
1	7.4	6.8	8.0	0.4	0.0	1.6
2	7.6	7.2	8.2	0.1	0.0	0.4
3	8.5	8.3	8.8	0.2	0.0	0.4
4	8.5	8.3	8.8	0.2	0.0	0.4
5	7.5	6.6	8.0	0.1	0.0	0.3
6	7.8	7.3	8.1	0.2	0.0	0.4
7	7.7	7.0	8.5	0.1	0.0	0.3
8	6.4	5.7	6.8	5.7	3.0	10.0[b]
9	7.1	6.7	7.4	0.2	0.0	0.4
10	7.3	7.0	7.7	0.6	0.0	2.1
11	7.3	6.8	8.0	0.2	0.0	0.4
12	7.7	7.2	8.1	0.1	0.0	0.3
13	7.6	7.3	8.3	0.1	0.0	0.4
14	7.6	7.1	8.2	8.2	3.4	13.0[b]
15	7.5	7.2	7.7	5.8	0.0	10.5[b]
16	7.3	6.6	7.7	0.1	0.0	0.4

[a] Sample collection dates were June 13–20, 1990; October 4–20, 1990; May 10–23, 1991; July 20–26, 1991; and November 5–11, 1991. [b] Concentration of nitrate–N was equal to or exceeded the lifetime health advisory level (LHAL) of 10 mg L^{-1} for drinking water.

sources were fortified at 5 and 1 μg L^{-1} (*17*). Over 12 wk had passed since the previous sample collection had been made at site 7 where no propanil was detected. Assuming a spill or back-siphoning occurred directly after the fourth collection, the quantity of propanil that had not adsorbed to the soil and had reached the groundwater may have been in a degradative lag phase as the aquifer microflora adapted to the concentrated propanil (*17*). Also, the average water pH of 7.7 at this site (Table 6) over the 2-year study would not be conducive to propanil degradation since propanil has demonstrated resistance to hydrolysis at pH 7 and pH 9 (*18*).

Although the concentration of propanil detected was several times higher than that of the next highest concentration detected in the study, it is difficult to assess significance concerning toxicity because no health advisories have been associated with propanil to date. However, 3,3′,4,4′-tetrachloroazobenzene (TCAB) and 3,3′,4,4′-tetrachloroazoxybenzene (TCAOB), known contaminants and degradation products of propanil, are more toxic, more persistent, and potentially more mobile than propanil (*18*).

Results in this survey share some agreement with other pesticide survey results and some differences. The detections of atrazine, cyanazine, and metolachlor that represented 50%, or 7 of 14, of the total confirmations in this survey are consistent with earlier studies at Wisconsin pesticide mixing/loading facilities (*14*). However, the detections in Arkansas were lower in frequency and at concentrations below the LHAL. According to critical values reported by Cohen et al. (*7*), atrazine, cyanazine, and metolachlor would be the most likely compounds to be detected based solely on chemical characteristics.

Two consecutive parathion-methyl detections and one trifluralin detection exceeded the LHAL during the 2-year survey. In other surveys, these pesticides have been detected infrequently and typically at concentrations below the LHAL (*2, 4*). Trifluralin has been observed in the national pesticide surveys but at concentrations ≤ 1 μg L^{-1}. However, of the 56 wells tested at Illinois mixing facilities, trifluralin was detected in 27% of the samples at a maximum concentration of 10 μg L^{-1} (*14*). Norflurazon has not been detected in any of the groundwater studies conducted in the United States in recent years (*2–4*). However, results of leaching studies conducted in Lousiana have shown that leaching could be an important dissipation mechanism for this compound (*19*).

Inconsistencies with the national data may be explained by site-specific differences of the sampling sites in the surveys, specifically the proximity of the well to concentrated pesticides. Although the soils of the specific sampling sites typically did not exhibit characteristics of well-drained soils, some pesticide detections still occurred. According to chemical characteristics and field characteristics conducive for groundwater contamination, some of these detections seem unlikely to occur (*7*). Therefore, the dominating influence on temporary contamination of the groundwater at the specified sites may be that these water sources have a higher frequency of exposure to pesticide concentrates, thereby increasing the probability of point source contamination via spills or back-siphoning. Similar conclusions have been reached in regard to atrazine occurrence in the Mahantango Creek watershed where corn production intensity was the dominant factor controlling atrazine concentrations regardless of the soil, geologic, and well-site characteristics (*8*). Also, according to the NPS Phase II Report (*20*), pesticide detections did not correlate to either pesticide properties or Drastic Indices as determined in this study. Therefore, these findings support the conclusion that point source contamination is the major factor influencing well contamination at these sites.

Nitrate Analysis. Some researchers have discussed the increasing probability of pesticide detections as nitrate–NO_3 levels increase (*7, 8*). Maximum concentrations were much greater than the LHAL of 10 mg L^{-1} for NO_3-N at sites 8, 14, and 15, but there was no corresponding pesticide concentration. Sites 14 and 15 demonstrated high levels of NO_3-N

during the sampled intervals probably due to a liquid nitrogen bulk tank within 12−15 m of the mixing well. A ponded depression formed during wet weather in front of the well, which was toward the bottom of a gradual slope from the nitrogen tank. Moving the nitrogen tank to an alternate location further from the mixing well at site 14 might alleviate concentration of nitrate and leaching to the well and subsequent contamination of the nearby well at site 15, which was approximately 30 m away. Nitrate concentration at site 8 reached 10 mg L^{-1} once over the 2-year survey but did not remain at this level. There were no obvious causes for the higher nitrate level that could be determined at that site.

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