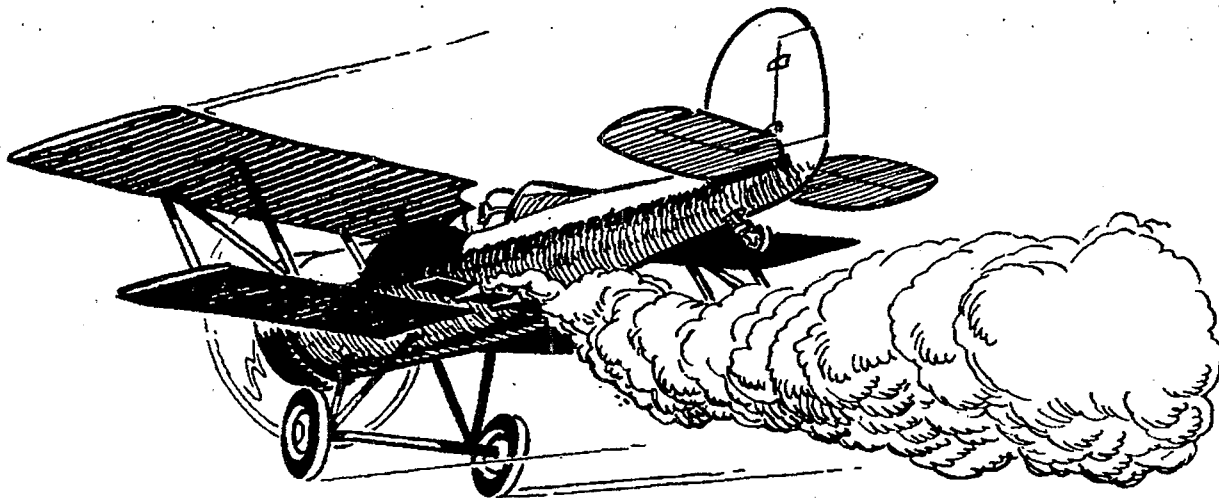


# PROGRAMS AND PROCEEDINGS OF SYMPOSIUM ON AGRICULTURAL NONPOINT SOURCES OF CONTAMINANTS: A FOCUS ON HERBICIDES

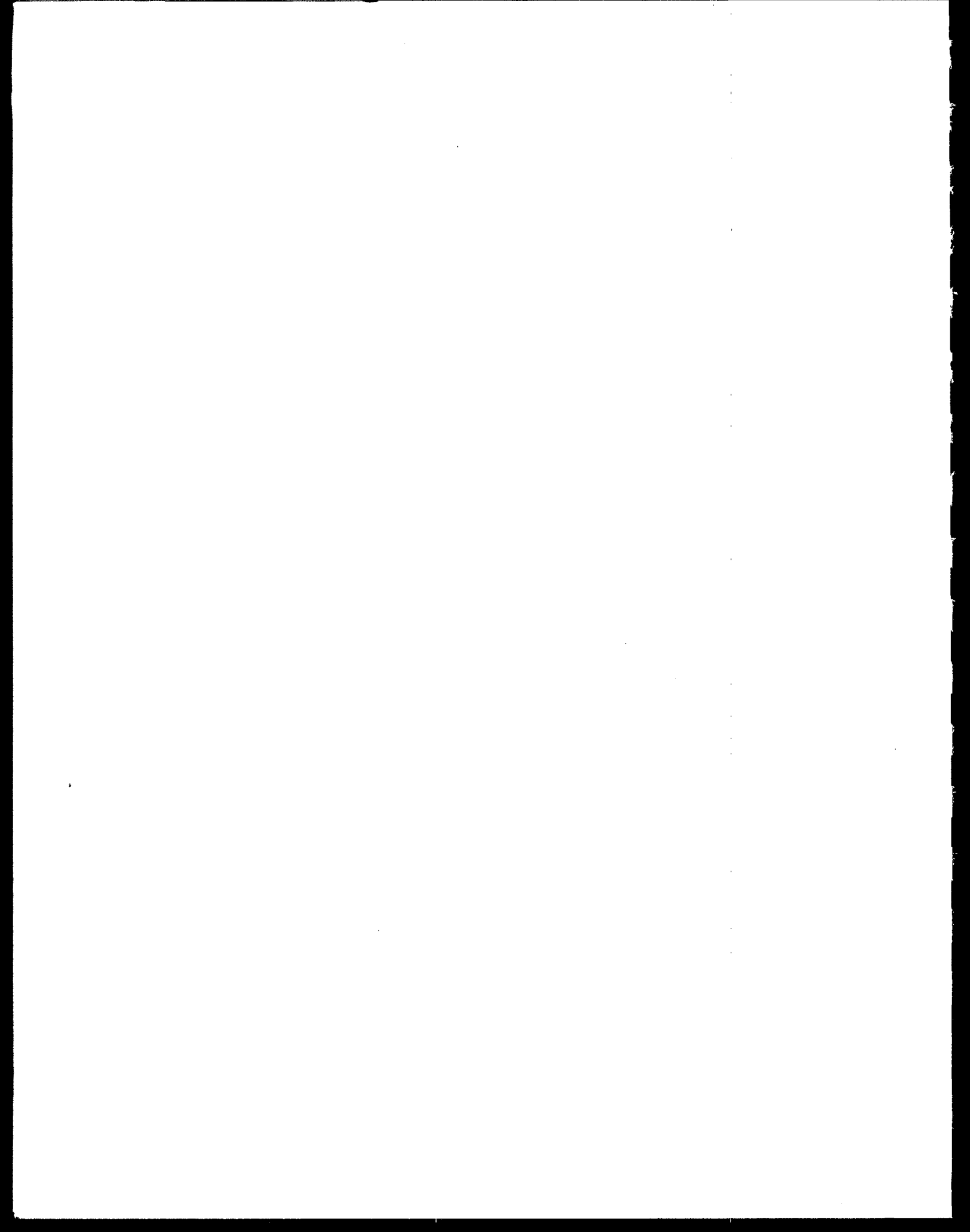
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September 28-29, 1993  
Lawrence, Kansas



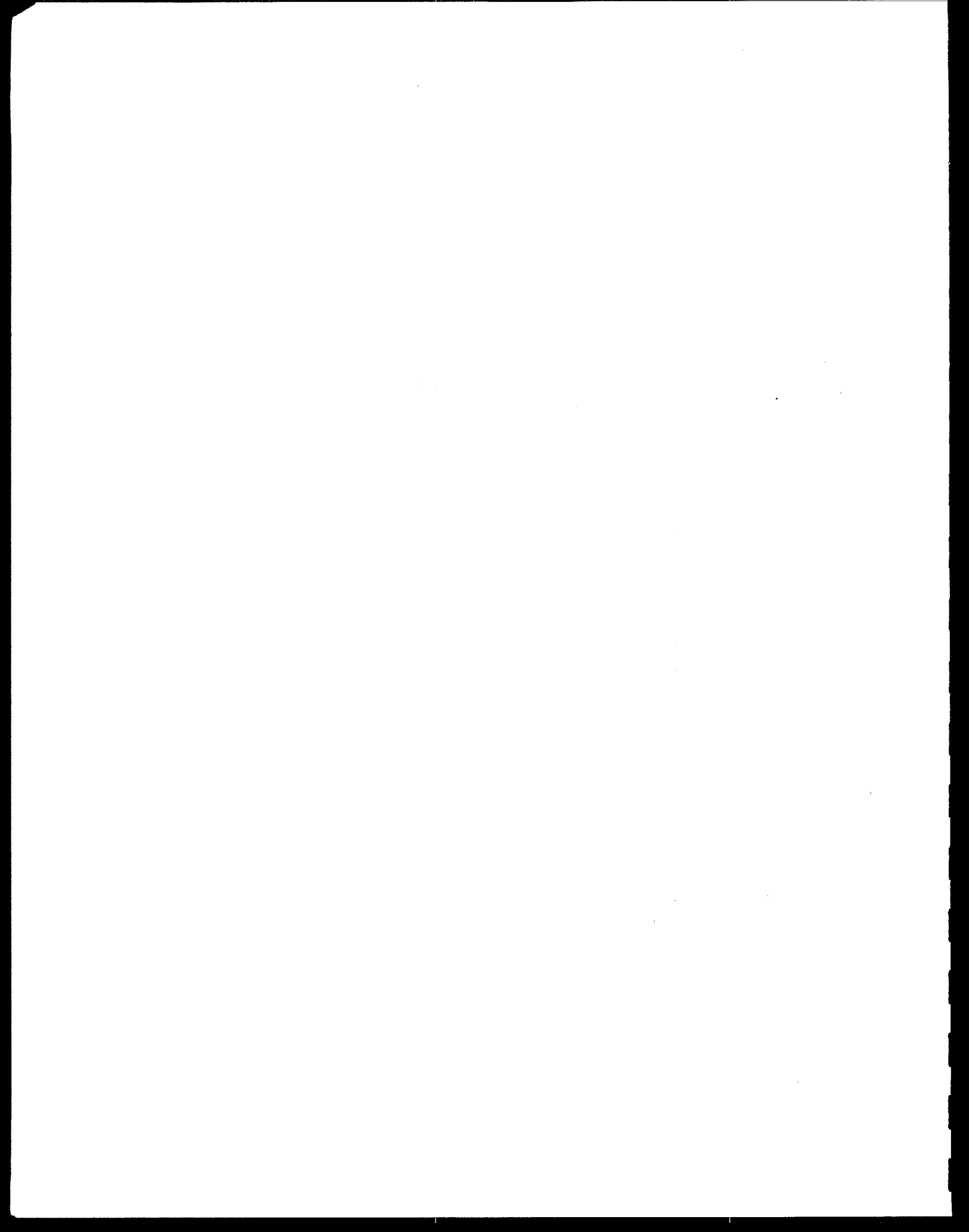
# PROGRAMS AND PROCEEDINGS OF SYMPOSIUM ON AGRICULTURAL NONPOINT SOURCES OF CONTAMINANTS: A FOCUS ON HERBICIDES

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September 28-29, 1993  
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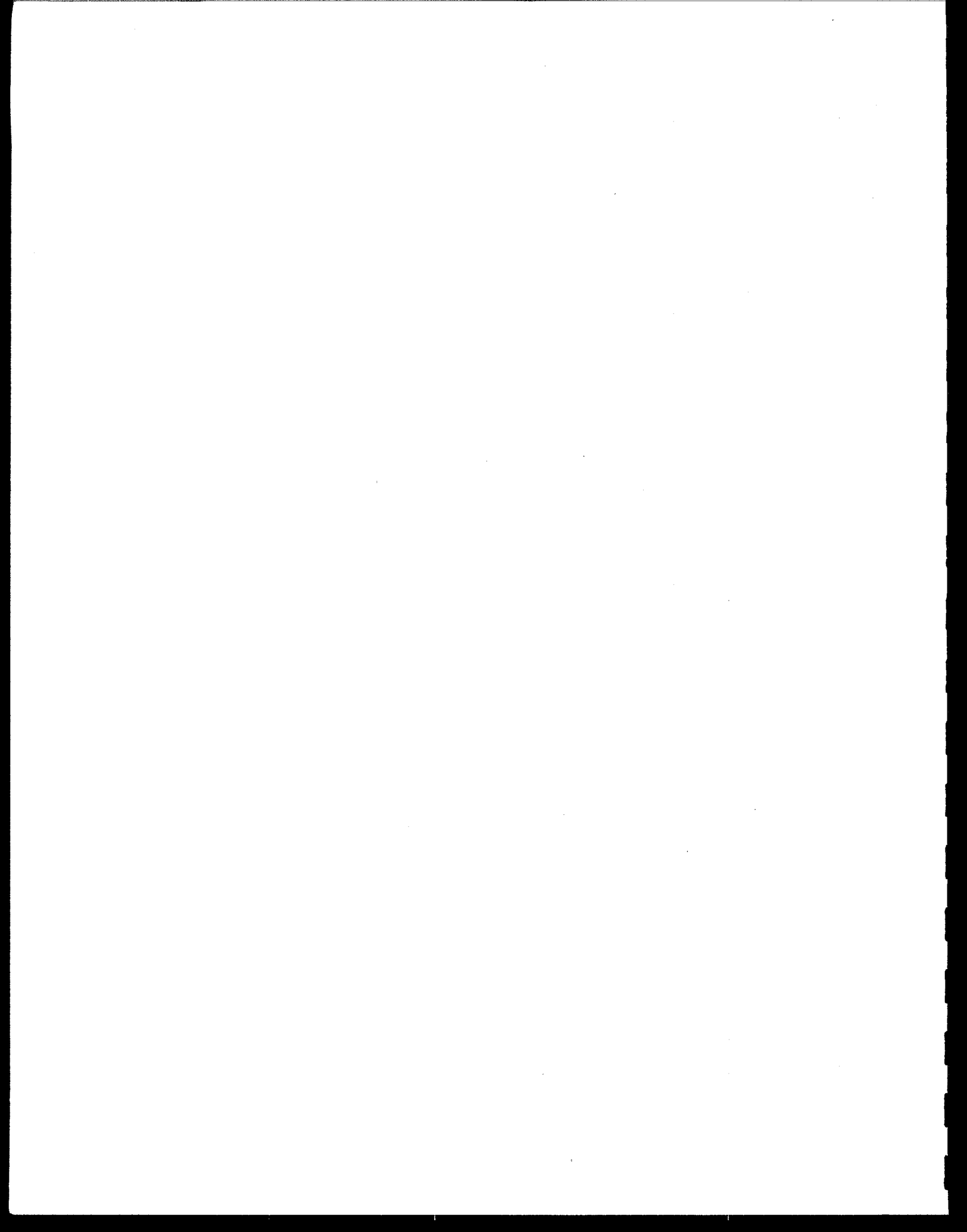
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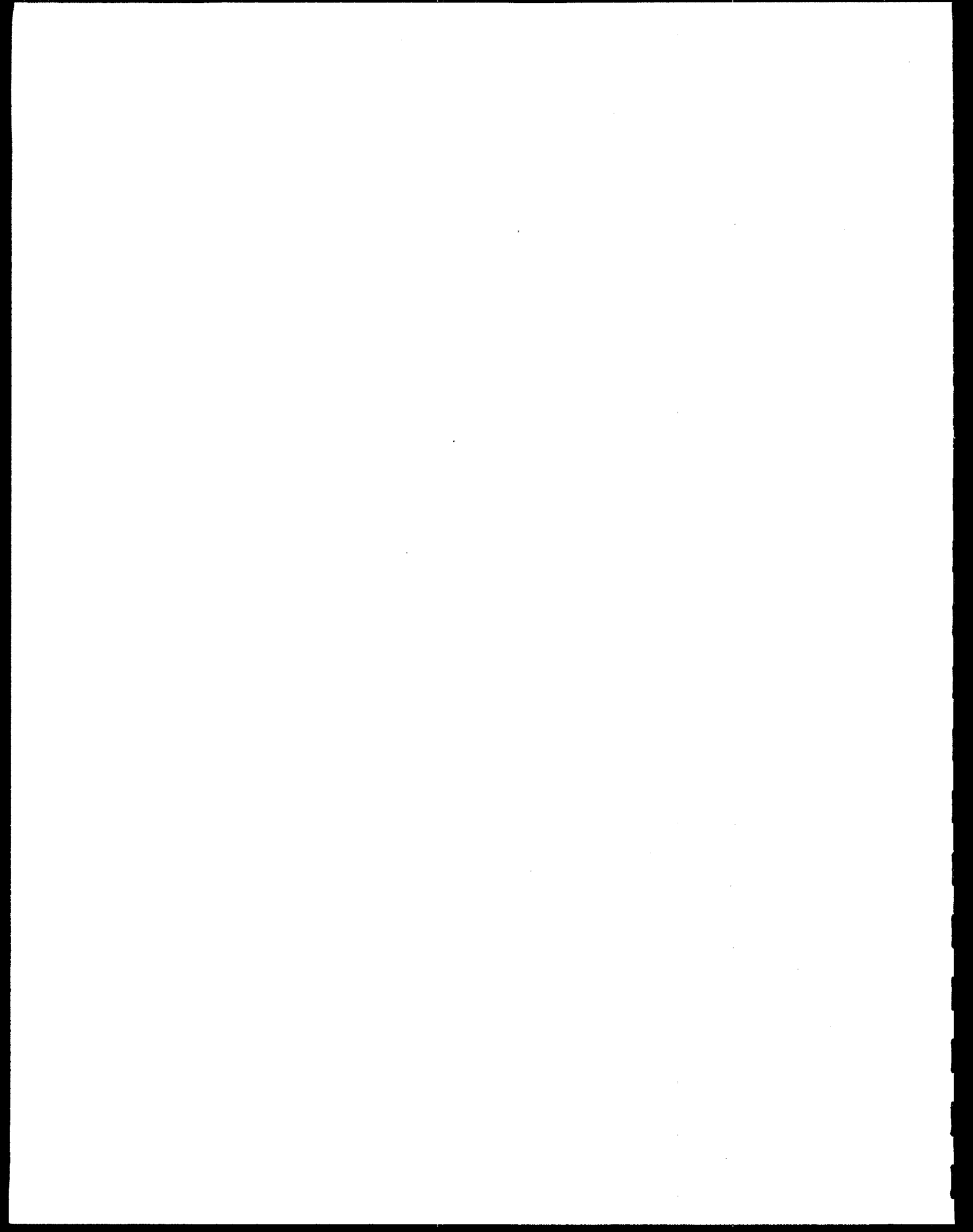
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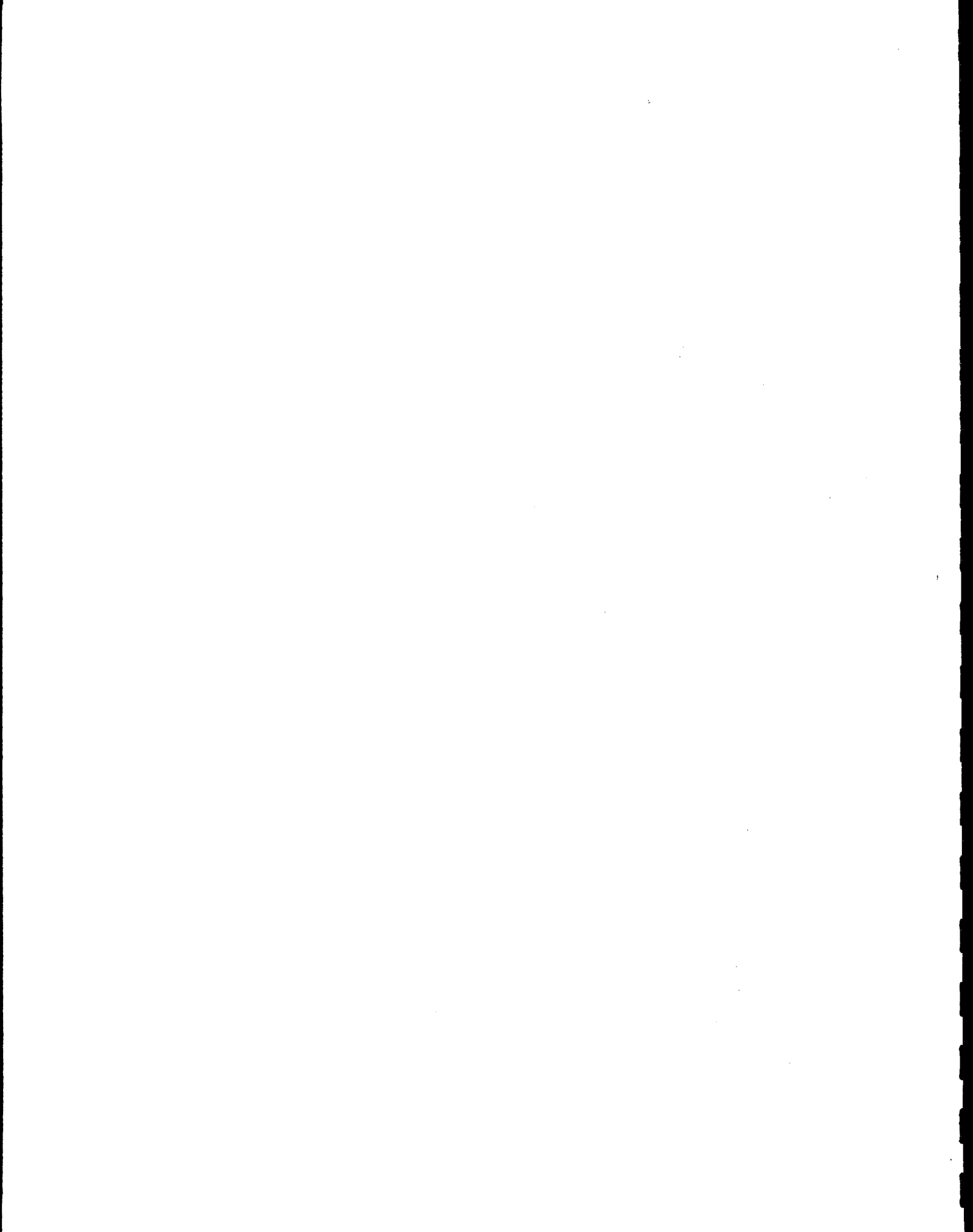
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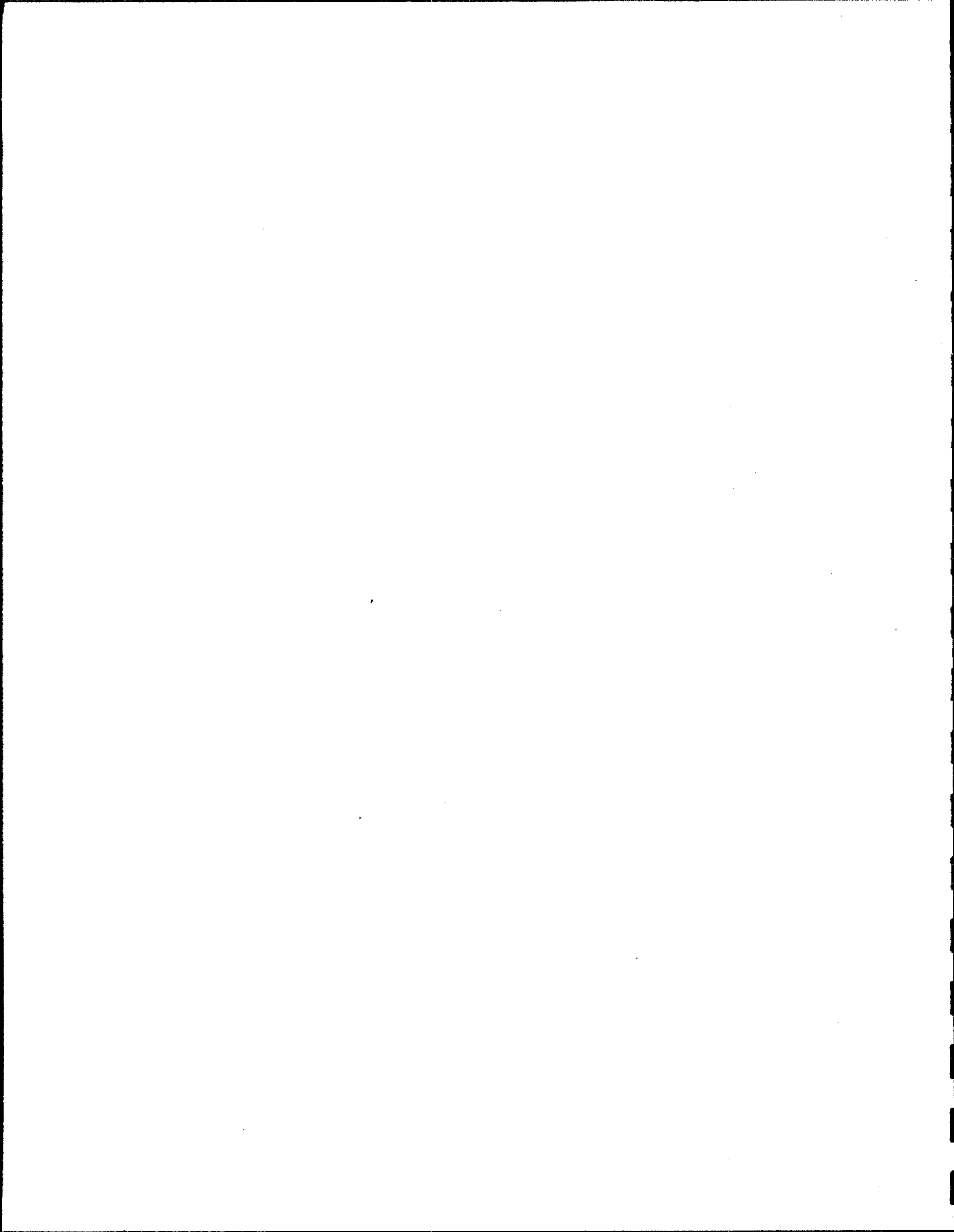
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# **AGENDA**

## **SYMPOSIUM ON AGRICULTURAL NONPOINT SOURCES OF CONTAMINANTS: A FOCUS ON HERBICIDES**

**Holiday Inn  
200 McDonald Drive  
Lawrence, Kansas**

**September 28-29, 1993**

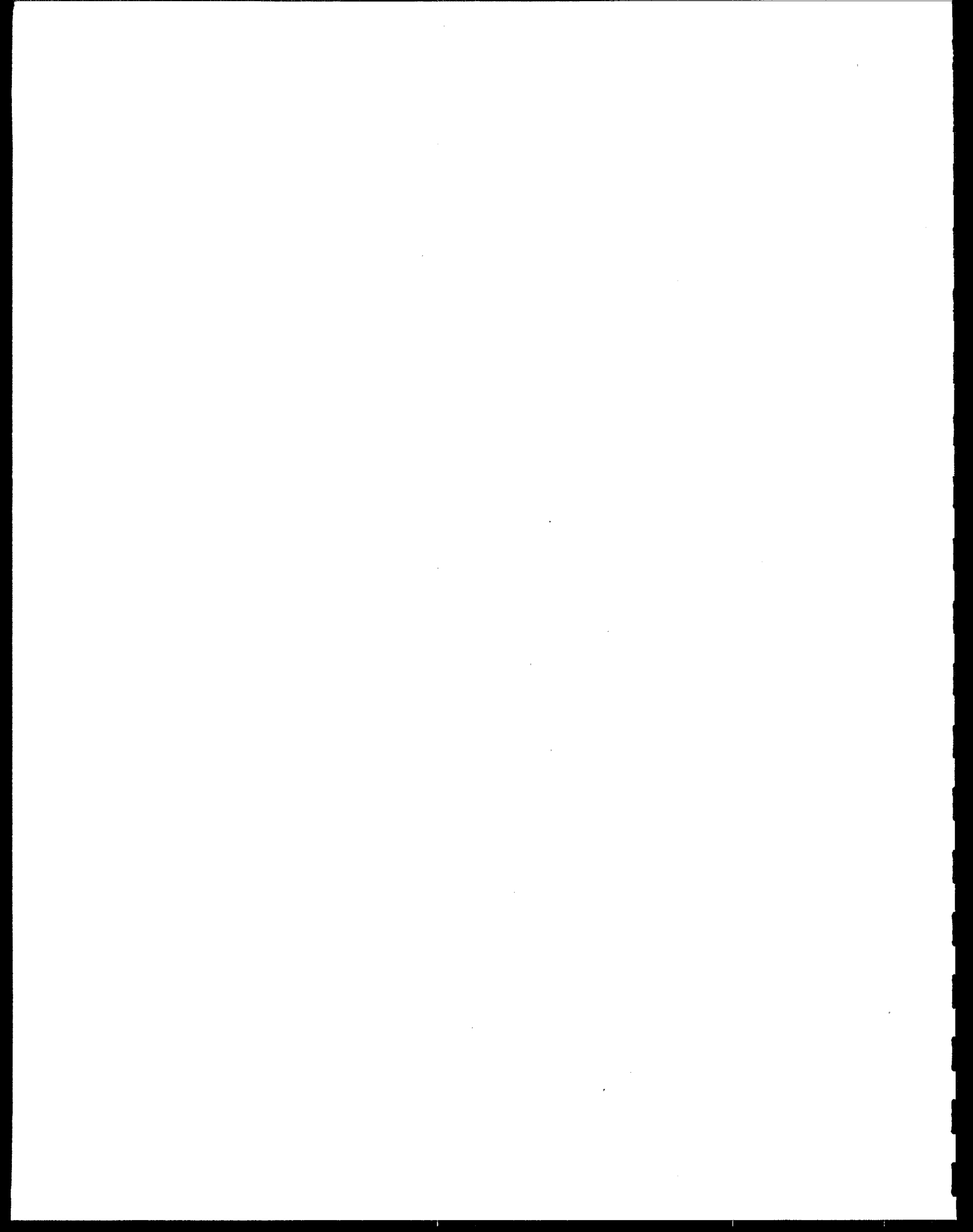
### **September 28, 1993**

- 11:00 AM    Registration
- 12:30 PM    Introductions - Barb Ryan, U.S. Geological Survey
- 12:40        *Organonitrogen Herbicides in Unregulated and Regulated Streams, in  
the Lower Kansas River Basin, Kansas and Nebraska*  
John Stamer, U.S. Geological Survey
- 1:20        *Impact of the Drinking Water Program on Nonpoint Source Activities*  
Ralph Langemeier, U.S. Environmental Protection Agency, Region  
VII
- 1:40        *Basic Principles of Pesticide Runoff*  
John Hickman, Kansas State University

### **OCCURRENCE IN SURFACE WATER AND GROUND WATER**

**Moderator: Ronald F. Hammerschmidt  
Division of Environment  
Kansas Department of Health and Environment**

- 2:00        *Occurrence and Transport of Pesticides in the Mississippi River Basin*  
Donald A. Goolsby and W.A. Battaglin, U.S. Geological Survey
- 2:20        *Missouri River Monitoring for Pesticides*  
Terry L. Gloriod and Paul W. Keck, St. Louis County Water Com-  
pany
- 2:40        BREAK



- 3:00      *Occurrence of Herbicides in Water from Rural Domestic Wells, Northwest and Northeast Missouri, July 1991 and July 1992*  
Donald H. Wilkison, U.S. Geological Survey, Randall D. Maley, Missouri Department of Health
- 3:20      *Pesticide Persistence in Two Impoundments in Northeastern Nebraska*  
Daniel D. Snow and Roy F. Spalding, University of Nebraska-Lincoln
- 3:40      *Determining the Age, Transport, and 3-Dimensional Distribution of Atrazine in a Reservoir by Immunoassay*  
James D. Fallon and E.M. Thurman, U.S. Geological Survey
- 4:00      *Occurrence and Control of Atrazine and its Degradation Products in Public Drinking Water Supplies*  
Stephen J. Randtke, University of Kansas
- 4:20      *Herbicide Distribution Beneath Nebraska MSEA Blocks*  
Roy F. Spalding and Thomas D. Papiernik, University of Nebraska-Lincoln
- 4:40      *A Natural Gradient Transport Study of Selected Herbicides*  
Sharon K. Widmer and R.F. Spalding, University of Nebraska-Lincoln
- 5:00      BREAK
- 5:15      Poster Session and Cash Bar
- 7:00      Adjourn

**September 29, 1993**

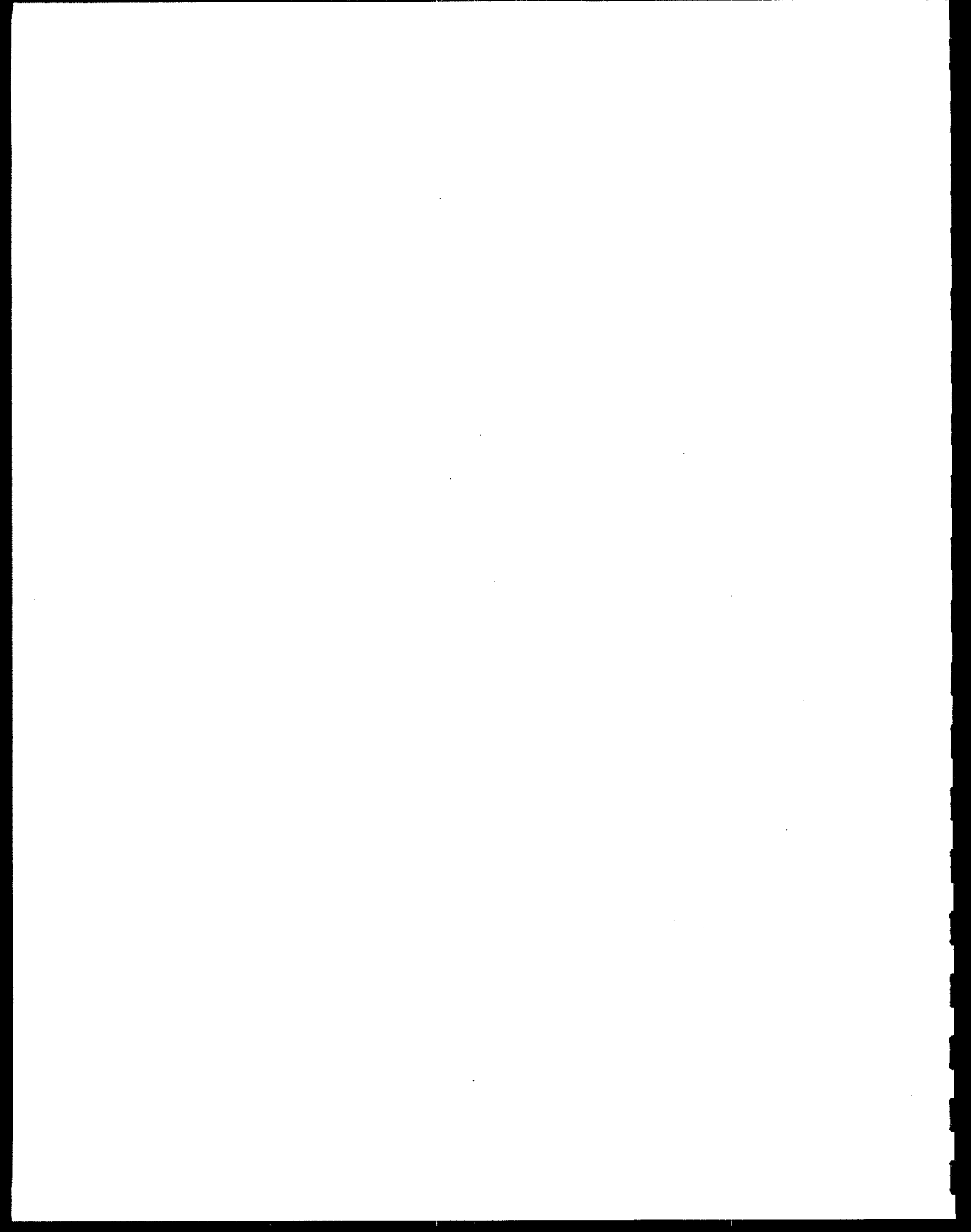
## **FATE AND TRANSPORT**

**Moderator: U. Gale Hutton**

**Water Quality Division**

**Nebraska Department of Environmental Quality**

- 8:00 AM      *Herbicide Transport and Degradation in a Pristine Watershed: The Fate of Herbicides Deposited by Precipitation*  
Aron E. Cromwell and E. Michael Thurman, U.S. Geological Survey



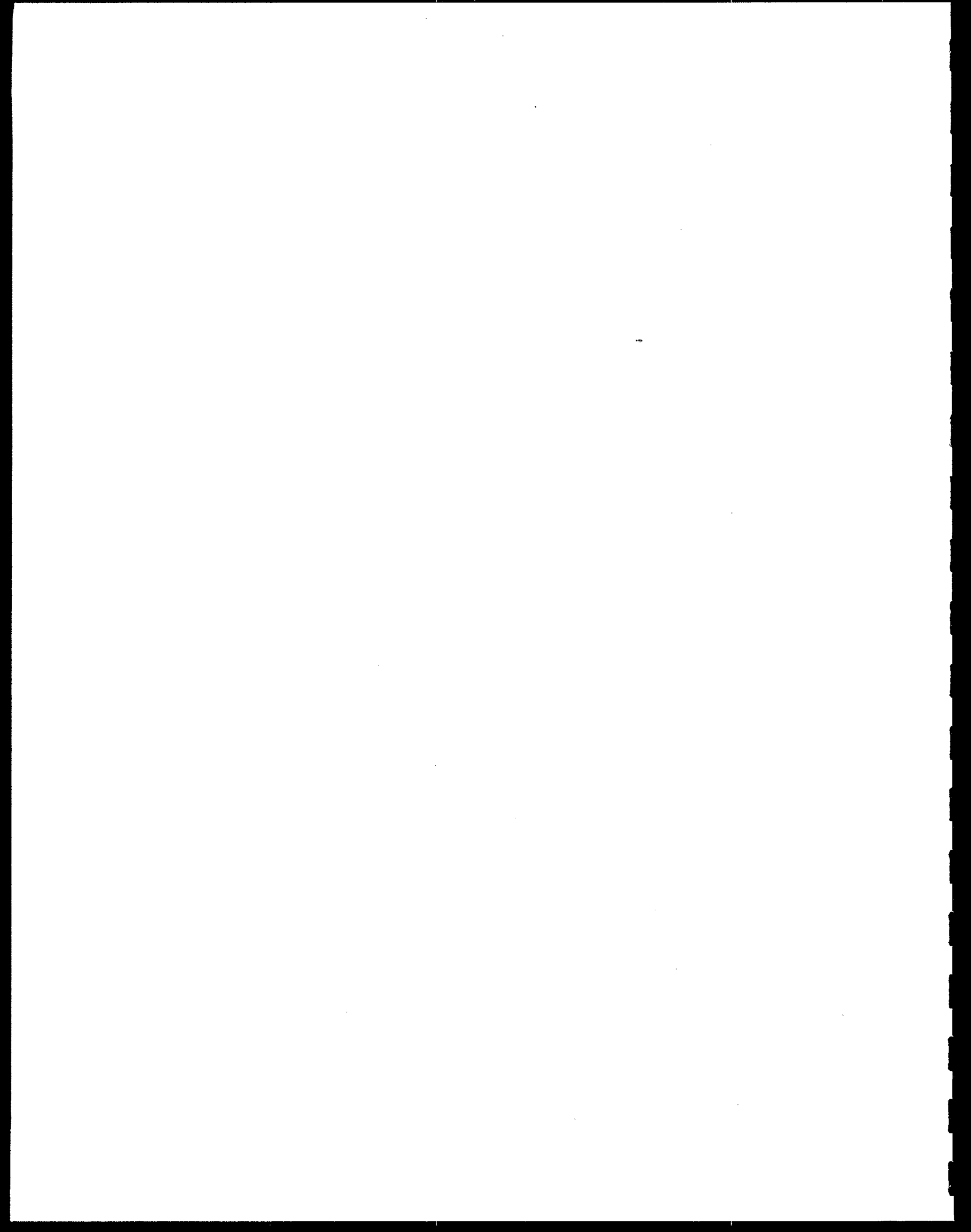


- 8:20      *A Comparison of Atrazine and Metolachlor Biological Assessment Data to Concentrations Reported in Precipitation Monitoring Studies*  
Philip A. Banks, MARATHON-Agricultural and Environmental Consulting, Inc., and Dennis P. Tierney, Ciba-Geigy Corporation
- 8:40      *Chemistry, Degradation, and Transport of Triazine Metabolites in Surface Water*  
E.M. Thurman, U.S. Geological Survey
- 9:00      *Nonequilibrium Adsorption and Degradation of Atrazine and Alachlor in Soil*  
Gerard J. Kluitenberg, Leticia S. Sonon, and A. Paul Schwab, Kansas State University
- 9:20      *Cyanazine Metabolites in Surface Water: The Transport and Degradation of Labile Herbicides*  
M.T. Meyer and E.M. Thurman, U.S. Geological Survey
- 9:40      *Biodegradation of Pesticides in Subsurface Samples from Three Midcontinent sites*  
James L. Sinclair and Tony R. Lee, Robert S. Kerr Environmental Research Laboratory
- 10:00      BREAK

## **HEALTH AND ECOLOGICAL EFFECTS**

**Moderator: Darrell McAllister**  
**Surface and Groundwater Protection Bureau**  
**Iowa Department of Natural Resources**

- 10:30      *Incidence of Certain Cancers and Exposure to Agricultural Herbicides: Measures to Reduce the Risk*  
Robert J. Robel, Kansas State University, Frederick F. Holmes and Cathy D. Boysen, University of Kansas Medical Center
- 10:50      *Hazard Assessment of Atrazine*  
Darrell D. Sumner, Charles B. Breckenridge, and James T. Stevens, Ciba-Geigy Corporation
- 11:10      *Ecological Impacts of Herbicides--A Review*  
Don Huggins, Director, Aquatic Ecotoxicology Program, Kansas Biological Survey
- 11:30      LUNCH



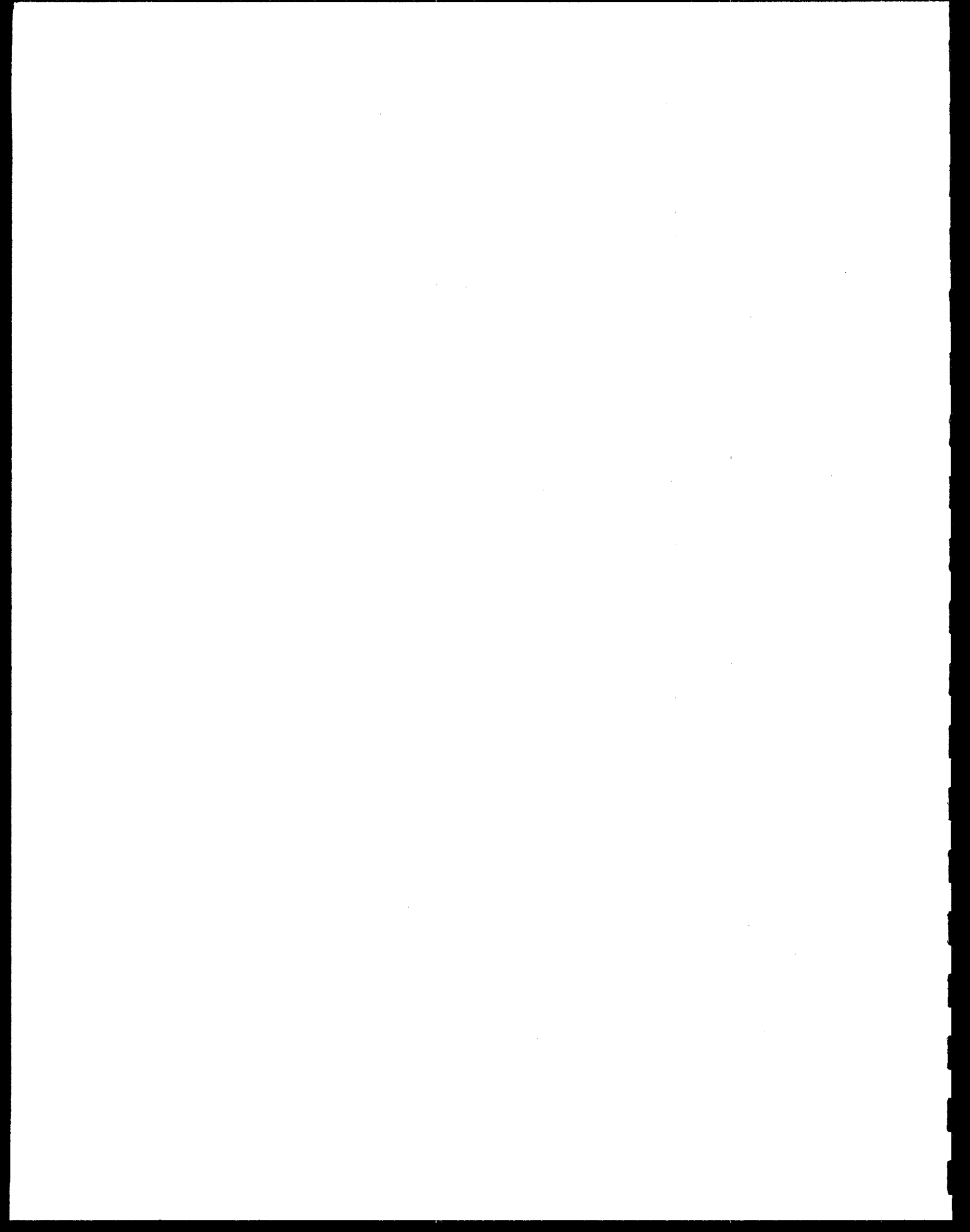
## **MANAGEMENT OPTIONS**

**Moderator: Nicholas A. Di Pasquale**  
**Water Pollution Control Program**  
**Missouri Department of Natural Resources**

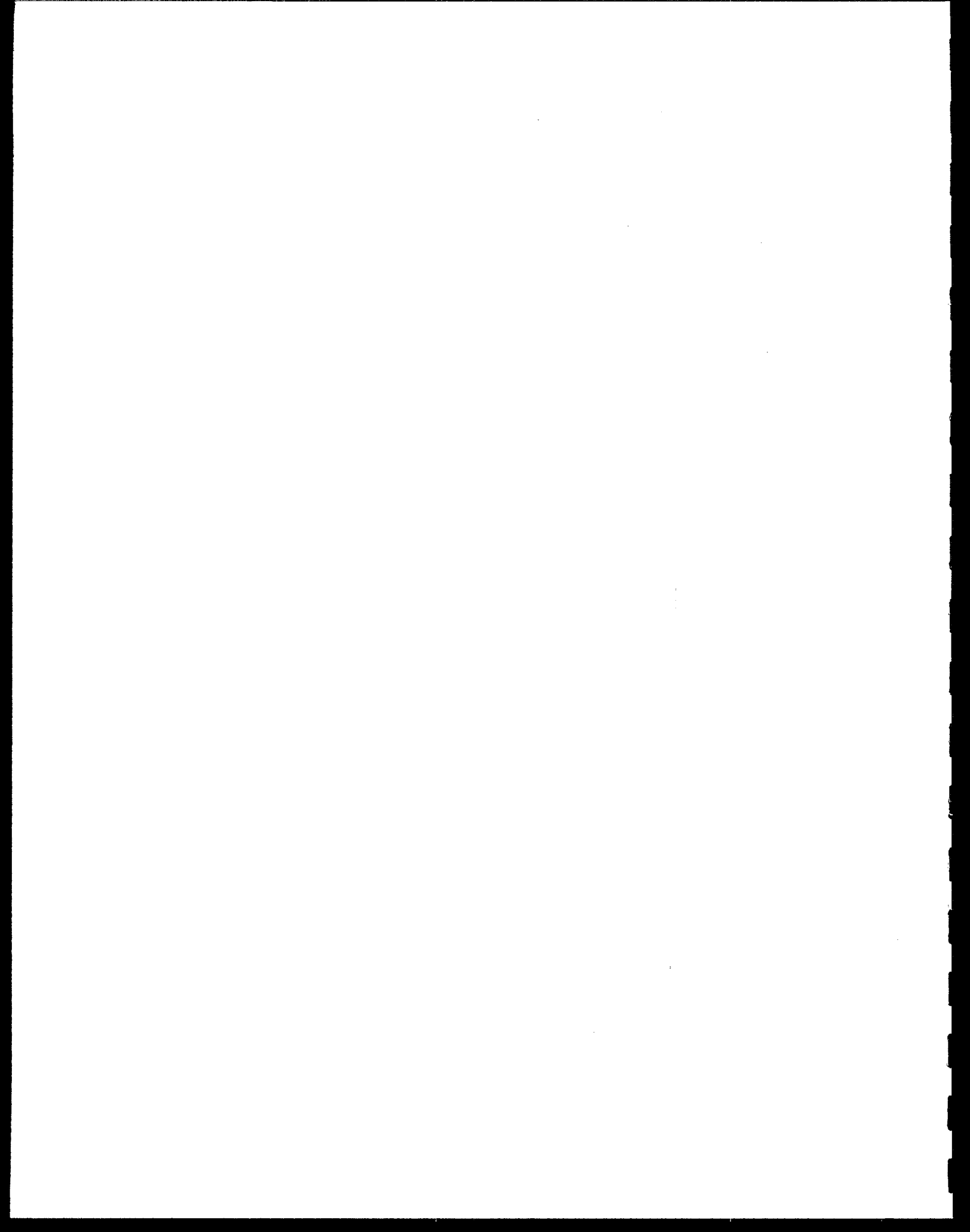
- 1:00 PM     *Weed Control Options for Reducing Atrazine Impact*  
David L. Regehr, Kansas State University
- 1:20     *Impact of Conservation Tillage Systems on Agricultural Runoff*  
Douglas W. Rushing, Monsanto Agricultural Company
- 1:40     *Pesticide Incorporation and Tillage Affects Atrazine and Alachlor Losses*  
James Steichen, Hirozumi Watanabe, Kansas State University,  
Elbert Dickey, David Shelton, Paul Jasa, and Nathan Watermeier,  
University of Nebraska-Lincoln
- 2:00     *Impact of Conservation Practices on Agricultural Nonpoint Contamination*  
Philip L. Barnes, Kansas State University, Mike Pope and Andy Foster, U.S. Geological Survey
- 2:20     *Federal, State, and Local Cooperation to Improve Surface Water and Groundwater Quality: The York Ground Water Recharge Project*  
Robert A. Dunlevy, U.S. Environmental Protection Agency, Region VII
- 2:40     BREAK

**Moderator: Dale Lambley**  
**Kansas State Board of Agriculture**

- 3:00     *Management of Herbicides in the Delaware River Basin*  
Jane Nieuwhues, Non Point Source Pollution Plan for the Delaware River Basin
- 3:20     *West Lake Water Quality Project*  
Alan Teel, ICM Coordinator, Iowa State University Extension Service, Osceola, Iowa
- 3:40     *Influence of Management Practices on Water Quality in Walnut Creek Watershed*  
J.L. Hatfield and D.B. Jaynes, U.S. Department of Agriculture,  
R.C. Buchmiller, P.J. Soenksen, U.S. Geological Survey



- 4:00      *Utilizing Fertilizer and Chemical Dealers to Manage Pesticides*  
Duane Sand, Director, Long Range Planning and Research,  
Iowa Natural Heritage Foundation
- 4:20      Open discussion, wrapup  
Larry Ferguson and Richard Herbert
- 5:00      Adjourn



# **ORGANONITROGEN HERBICIDES IN UNREGULATED AND REGULATED STREAMS IN THE LOWER KANSAS RIVER BASIN, KANSAS AND NEBRASKA**

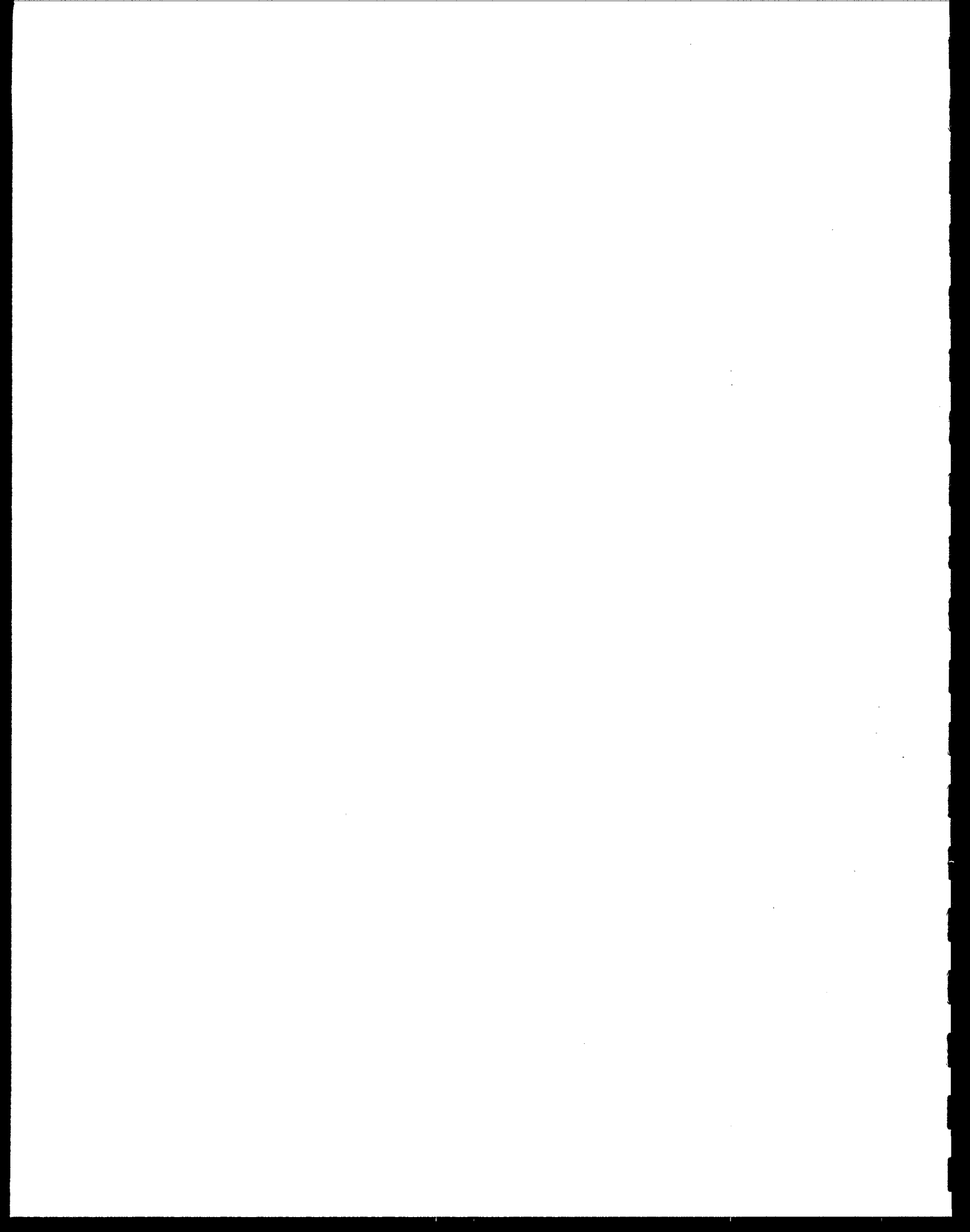
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**John K. Stamer, U.S. Geological Survey, Lawrence, Kansas**

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Atrazine has been the most extensively applied herbicide in the lower Kansas River Basin, which drains 39,627 square kilometers of predominantly agricultural land in northeast Kansas and southeast Nebraska. As part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program, the spatial and temporal distributions of organonitrogen herbicides in surface water were defined. Results indicated that, in principal streams of the basin, atrazine was the most frequently detected organonitrogen herbicide and occurred in the largest concentrations. The larger atrazine concentrations were measured in parts of the basin where the larger amounts of atrazine had been applied. Atrazine concentrations varied seasonally; the larger concentrations occurred in the spring and summer and the smaller in the fall and winter. Reservoirs decreased the seasonal variability of atrazine concentrations from that of inflowing streams.

Atrazine poses a problem for public-water supplies because it is water soluble, relatively persistent in the hydrologic system, and not effectively removed by conventional water-treatment practices. The U.S. Environmental Protection Agency has established a Maximum Contaminant Level (MCL) for atrazine 3.0 µg/L in finished public drinking-water supplies. The 1989 mean concentration of atrazine in the outflow of Perry Lake exceeded the MCL even though streamflows in the Delaware River during 1989 were only about 20% of the long-term mean. Results of the NAWQA study were used by the Kansas State Board of Agriculture as a basis for designating the Delaware River Basin as the Nation's first inland surface-water pesticide management area (PMA).





# IMPACT OF THE DRINKING WATER PROGRAM ON NONPOINT-SOURCE ACTIVITIES

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**Ralph N. Langemeier, U.S. Environmental Protection Agency, Kansas City, Kansas**

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**Phase II Rule** - On January 30, 1991, EPA promulgated regulations that established Maximum Contaminant Levels (MCLs) for a variety of pesticides and other contaminants, including a level of 3 µg/L for atrazine. This regulation went into effect in July of 1992. Public water systems are to conduct quarterly monitoring for atrazine and the other contaminants between January 1993 and December 1995. Systems are in compliance with these regulations if the annual average concentration is below the MCL.

Based on studies conducted by various water suppliers, State and Federal agencies prior to the start of the official monitoring, it is anticipated that many surface-water systems in the Midwest will have difficulty meeting the atrazine MCL without treatment. Public water supplies that rely on reservoirs are likely to have more problems meeting the atrazine MCL than those that take water directly from rivers. There are approximately 150 surface-water systems in EPA Region VII that use reservoirs.

**Phase V Rule** - The Phase V regulations promulgated on July 17, 1992, added 5 inorganic chemicals and 18 synthetic organic chemicals (SOCs) to the list of regulated contaminants. The list of 18 SOC's include such chemicals as Dinoseb, Diquat, Endothall, Glyphosate and Simazine. The Phase V monitoring coincides with the Phase II rule.

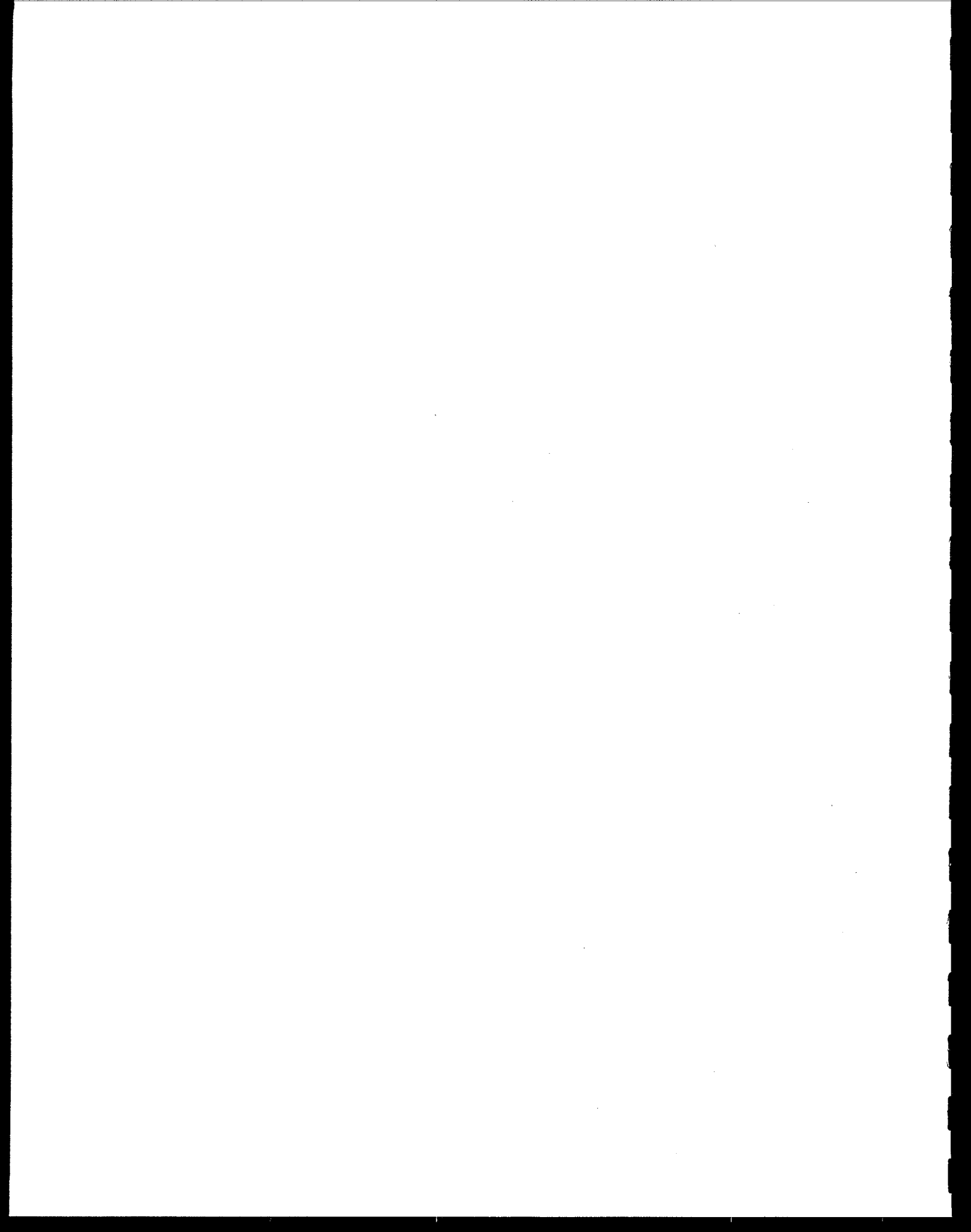
**Surface Water Treatment Rule** - The Surface Water Treatment Rule will also have an impact on nonpoint-source activities. It requires, among other things, that State primacy agencies determine if public water systems that are using ground water, e.g. wells and springs, are under the direct influence of surface water. For instance, does nearby surface water affect the quality of the well water? The State has until June of 1994 to make those decisions on community water systems. It is anticipated that many public water systems that use alluvial aquifer wells may be affected.

If a ground water source is determined to be under the influence of surface water, the public water system must provide the same level of treatment as traditional surface-water systems, which may include filtration and disinfection. Treatment must be in place within 18 months from the time the public water system is notified of the decision. Systems wishing to avoid expensive treatment may be required to implement watershed protection programs.

The secondary impact of these decisions is that a State may revise its ambient water-quality standards water-body designation for those surface waters that are influencing wells to include a public drinking-water supply use. This, in turn, could have a significant effect on the nonpoint-source program. For instance, the priorities for the State and Federally funded nonpoint-source projects could be altered, and the level and type of prevention/control activities could be affected.

Future Surface Water Treatment regulations being considered by EPA may require public water systems to do extensive evaluations of their source water, including the watershed, to identify and address potential sources of contamination. Of particular concern are microbiological contaminants, such as Giardia, Cryptosporidium, and E. Coli bacteria; all have links to agricultural activities.

The EPA Region VII office is involved in various activities to inform those involved with nonpoint-source pollution prevention and control activities about the drinking-water regulations and their impact. These outreach efforts will help States establish priorities in their nonpoint-source management programs.



## BASIC PRINCIPLES OF PESTICIDE RUNOFF

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**John S. Hickman, Kansas State University, Manhattan, Kansas**

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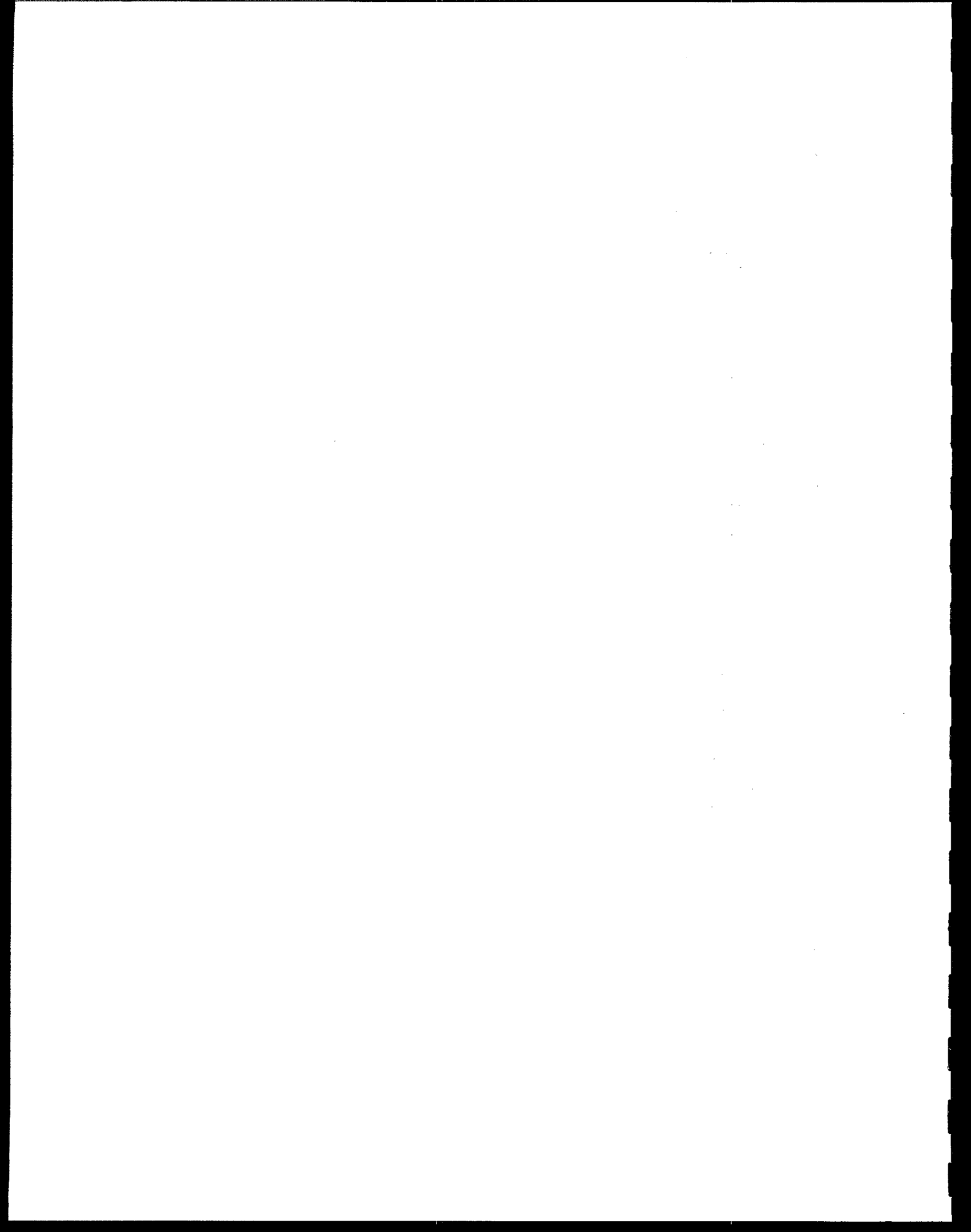
Understanding basic principles of pesticide runoff is key to designing and implementing management practices to reduce surface loss of pesticides. There are a variety of practices that can be used to reduce pesticide runoff; however, the effectiveness of these factors will vary from one site to another.

The amount of pesticides lost in surface runoff will vary depending on three key factors. The first factor is that most pesticides are partitioned into the adsorbed (sediment) and/or the solution (water) phase of runoff. Pesticides with a solubility of greater than 2 ppm are typically lost with the water leaving the field. Some exceptions to this rule are pesticides with both a high solubility and adsorption coefficient such as paraquat or Roundup. An even better rule of thumb is that pesticides with an adsorption coefficient ( $K_{oc}$ ) less than 1,000 are typically lost in the solution or water phase. Atrazine has a solubility of 33 ppm and  $K_{oc}$  of 100 and thus is lost in the water that leaves the field. In some recent modelling using the GLEAMS model, about 90 percent of 232 pesticides modelled were lost primarily in the solution phase of runoff. For most pesticides, controlling runoff that leaves the field is more important than sediment control for reducing loss in overland flow. Fortunately, some of the soil-erosion control practices used today also reduce runoff and thus are somewhat effective in reducing pesticide losses.

The second key factor is the concept of a "mixing zone," a zone where pesticide, soil, overland flow, and precipitation intermix to create runoff. This zone is at the soil surface and is very narrow, often less than one-third of an inch in thickness. The concentration of pesticide in the mixing zone often controls the amount lost in overland flow. Once the product moves below this depth, there is a much smaller chance for the pesticide to be lost in overland flow. Soils that are coarse-textured and/or have low amounts of organic matter often have lower pesticide concentrations in the mixing zone. Incorporation and reducing application rates will also reduce the pesticide concentration in the mixing zone. Incorporation will result in a 50 to 70% reduction in pesticide surface loss as compared to a surface application.

The third factor affecting pesticide runoff loss is the characteristic of the first precipitation/runoff event after application. Critical storms that have historically proven to have the largest pesticide runoff losses are those that occur within 2 weeks of application, have at least half an inch of rain, and have 50% runoff or greater. Storm patterns differ across the country. In Kansas, such storms are more likely to occur in May or June as compared to March or early April. Timing of application, therefore, can have a large effect on pesticide surface losses. Another important runoff-related factor is the time to runoff after rainfall begins. Any factor or practice that delays the time to runoff will help move the pesticide below the mixing zone and reduce runoff losses. Conservation tillage and contouring are examples of conservation practices which delay the time to runoff and reduce overland flow losses.

In summary, properties of the soil, pesticides, site, and climate as well as conservation and management practices will affect the amount of pesticide runoff. Management plans to reduce pesticide surface loss will vary from one site to another. Management practices, such as changing rate of application, timing, and placement, and conservation practices, such as conservation tillage and contouring, can all reduce pesticide surface loss.



# **OCCURRENCE AND TRANSPORT OF PESTICIDES IN THE MISSISSIPPI RIVER BASIN**

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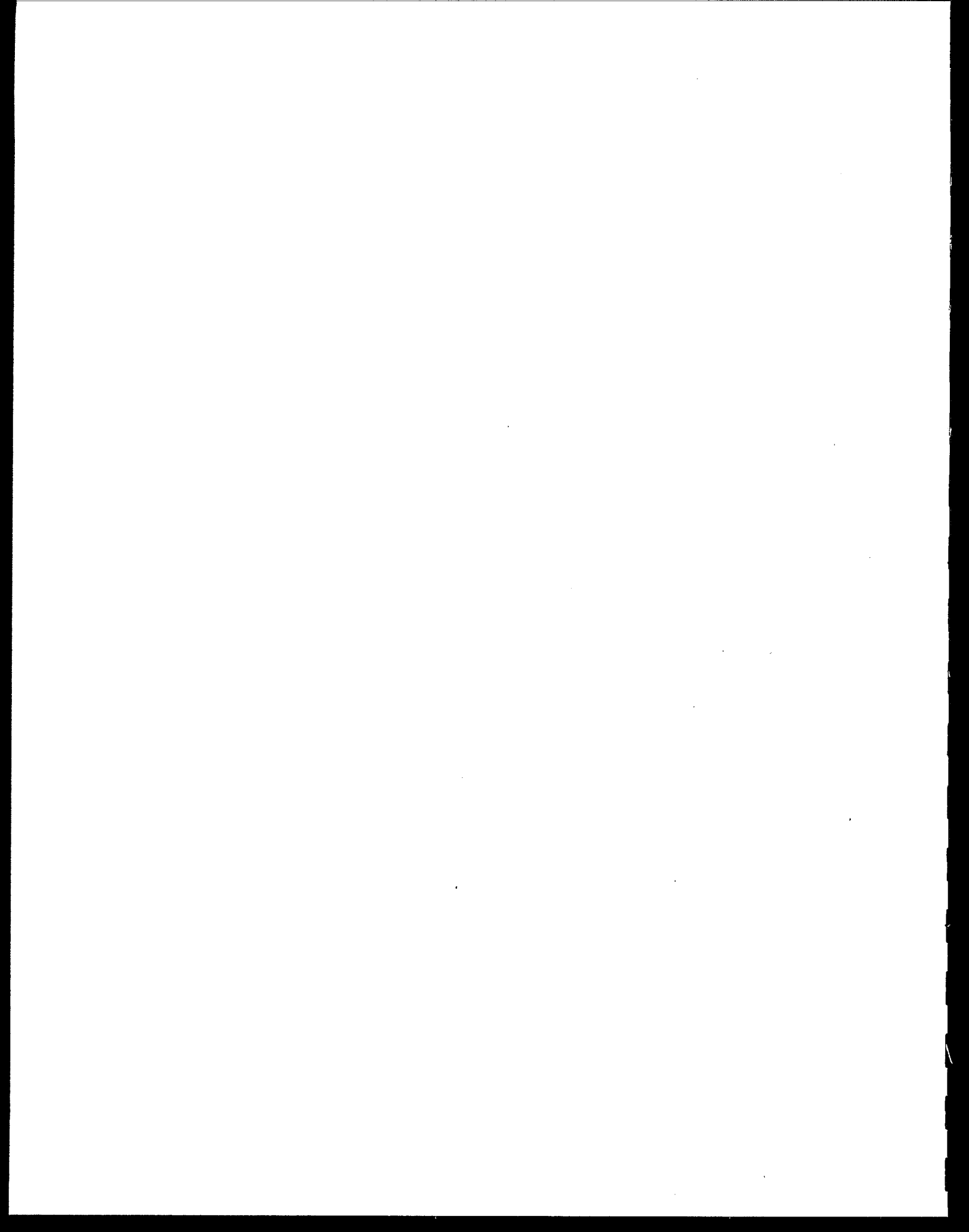
**D.A. Goolsby and W.A. Battaglin, U.S. Geological Survey, Lakewood, Colorado**

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The Mississippi River Basin contains the largest and most intensive agricultural region in the Nation. Large amounts of pesticides (herbicides, insecticides, and fungicides) are used in order to increase yields from the major crops grown in the basin (corn, soybeans, sorghum, wheat). About two-thirds of all pesticides used annually for agriculture in the United States are applied to cropland and pastureland in the Mississippi River Basin. Herbicides account for about three-fourths of the annual pesticide use and are the most frequently detected pesticides in streams throughout the basin.

Recent regional-scale studies by the U.S. Geological Survey have shown that significant amounts of herbicides are flushed into streams by late spring and summer rainfall following application of herbicides to cropland. These amounts are large enough to produce high concentrations of several herbicides in streams for a few weeks to several months during periods of storm runoff. Concentrations of herbicides in some small streams may briefly exceed 50  $\mu\text{g/L}$ , and annual average concentrations may exceed drinking-water standards established under the Safe Drinking Act. Flow from these small streams, in turn, transports significant amounts of pesticides into large rivers such as the Missouri, Ohio, and Mississippi, and eventually to the Gulf of Mexico. During 1991 and 1992, more than 40 pesticides and pesticide degradation products were detected in the main stem of the Mississippi River, although most of these were detected in very low concentrations (less than 0.5  $\mu\text{g/L}$ ). Maximum concentrations of the most extensively used herbicides such as alachlor, atrazine, cyanazine, and metolachlor, in the Missouri, Ohio, and Mississippi Rivers ranged from 3 to 10  $\mu\text{g/L}$  and exceeded health-based limits for drinking water for periods as long as one month at some locations. However, the annual average herbicide concentrations in these large rivers were far below health-based limits, and concentrations did not violate the Safe Drinking Water Act. Low concentrations (0.005 to 0.2  $\mu\text{g/L}$ ) of atrazine, cyanazine, and metolachlor were detected throughout the year in the Mississippi River due, in part, to storage and subsequent discharge of these compounds from lakes, reservoirs, and aquifers.

The total mass of pesticides discharged annually from the Mississippi River represents a small fraction of the total amounts applied to cropland in the basin. The atrazine and cyanazine discharged to the Gulf of Mexico during April 1991 through March 1992 was equivalent to about 1.6% of the amounts applied annually in the basin. The quantities of several other herbicides discharged annually from the basin, expressed as a percentage of the amount applied, were: metolachlor, 0.8%; alachlor, 0.2%; and simazine, 2.7%. Most of the herbicide transport occurs during May, June, and July. More than one-half of the total quantity of pesticides transported annually by the Mississippi River originates in small streams draining Iowa, Illinois, and parts of Missouri and Minnesota, an area that constitutes only about 22% of the Mississippi River drainage basin.



## MISSOURI RIVER MONITORING FOR PESTICIDES

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**T.L. Gloriod and P.W. Keck, St. Louis County Water Company, St. Louis, Missouri**

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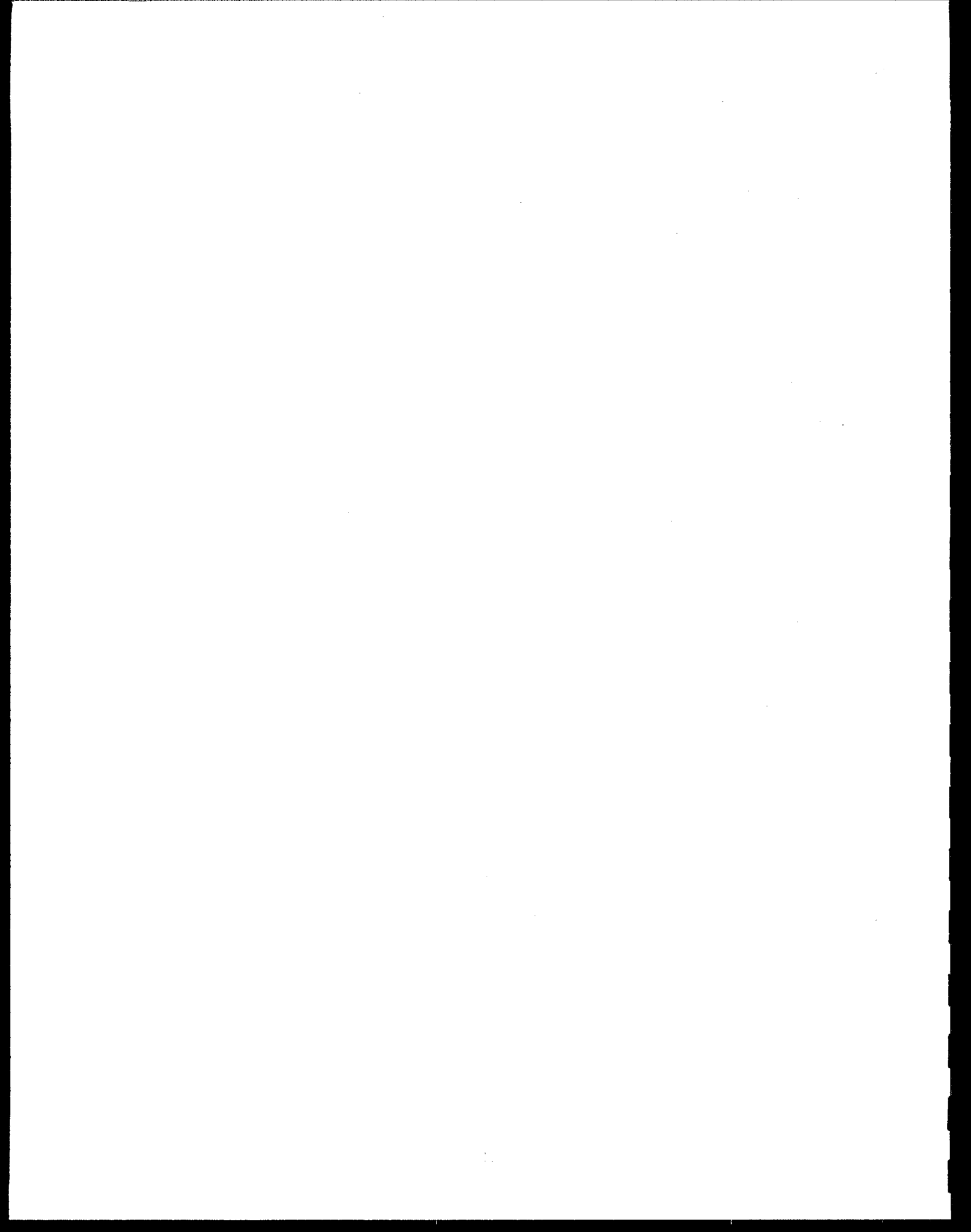
During the 1980's, laboratory improvements in instrumentation and methods provided the means for reliable measurement of many pesticides/herbicides in water. Subsequent monitoring by water utilities on the Missouri River during spring and summer runoff periods identified four commonly occurring compounds; atrazine, alachlor, metolachlor, and cyanazine. A 1990 study by the St. Louis County Water Company analyzed atrazine levels each day during May, June, and July at a single location on the Missouri River.

In January 1991, the USEPA finalized drinking-water standards for atrazine and alachlor. During the spring and summer of that year, the Missouri River Public Water Supplies Association (MRPWSA) conducted a comprehensive monitoring study on the Missouri River to determine the occurrence, range of concentrations, and regional contribution of these two pesticides. Atrazine and alachlor concentrations were measured in daily samples from seven sites that were near Corps of Engineers gaging stations. The study report presents the occurrence pattern at each site, and the mass of pesticide contributed by major tributary regions. The study was repeated in 1992, using fewer sampling sites.

While the concentration of atrazine can vary widely from day to day, the total amount of atrazine discharged from the Missouri River did not change dramatically during the 3 years of study. During 1990, 118,456 pounds of atrazine were discharged from the Missouri; during 1991, 106,230 pounds; and in 1992, 88,363 pounds.

The occurrence data collected by the MRPWSA members are important in assessing the potential impact on water systems who must comply with the drinking-water standards that have been established.

Conventional water-treatment plants on the Missouri River are only marginally effective in reducing pesticide levels in river water. Drinking-water compliance monitoring using quarterly samples, has a high probability of producing average levels that exceed the drinking-water standards especially in lower volume tributaries. Granular activated carbon, if required for treatment of pesticides, will dramatically increase water pricing for consumers.





# **OCCURRENCE OF HERBICIDES IN WATER FROM RURAL DOMESTIC WELLS, NORTHWEST AND NORTHEAST MISSOURI, JULY 1991 AND JULY 1992**

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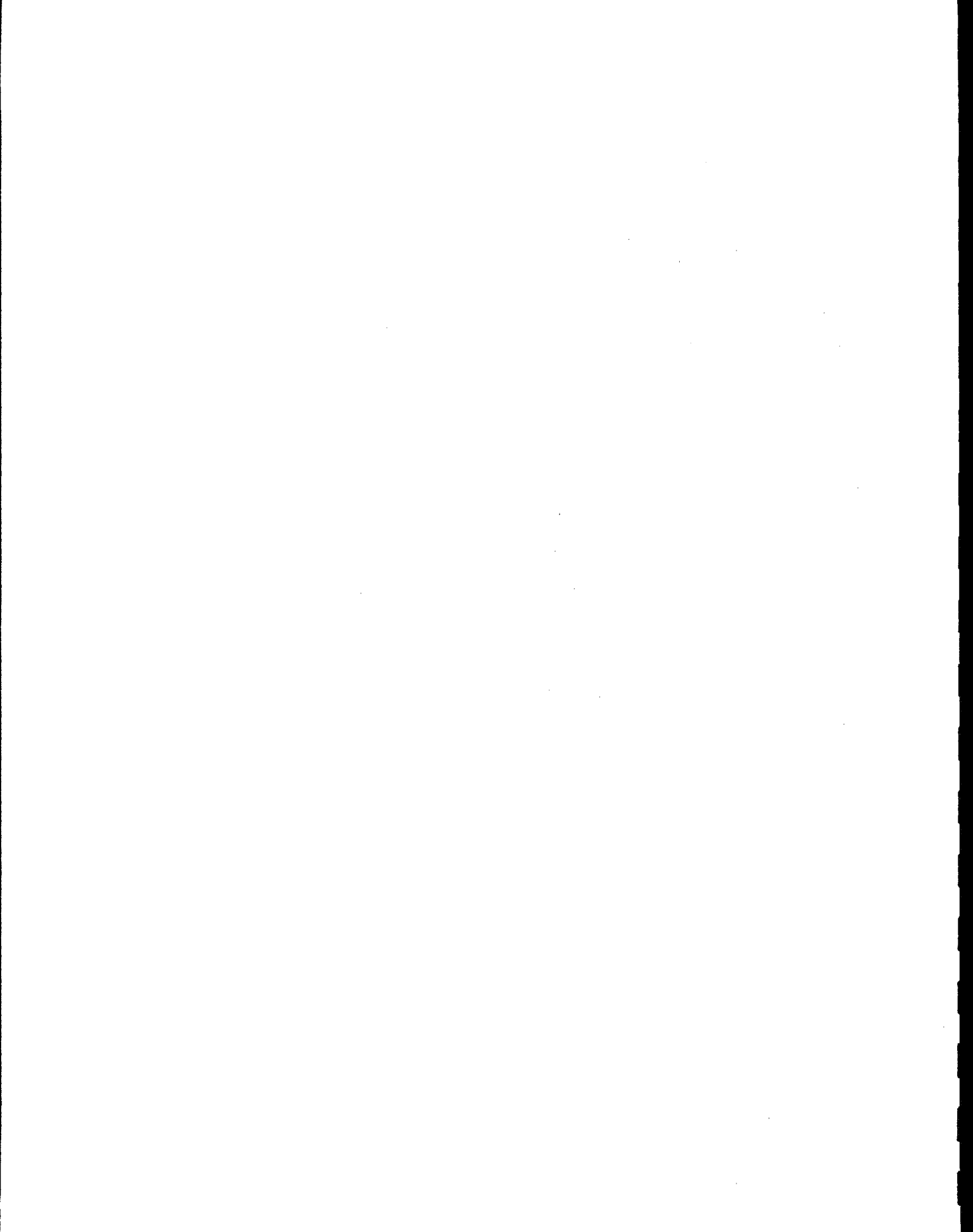
**Donald H. Wilkison, U.S. Geological Survey, Independence, Missouri, and  
Randall D. Maley, Missouri Department of Health, Jefferson City, Missouri**

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In July 1991, the U.S. Geological Survey and the Missouri Department of Health sampled water from 130 rural domestic wells in Caldwell, Clinton, Daviess, Gentry, and Nodaway Counties in northwest Missouri. These water samples were analyzed for the presence of triazine and C1-acetamide herbicides using enzyme-linked immunosorbent assays. Triazine or C1-acetamide herbicides were detected at concentrations higher than 0.05 µg/L in one-third of all samples. Samples from 79 wells were analyzed using gas-chromatograph/mass spectrometry methods. One or more of the herbicides alachlor, atrazine, cyanazine, metribuzin, metolachlor, and trifluralin were detected at concentrations greater than or equal to 0.05 µg/L in samples from 19 of the 79 wells. Atrazine was detected in samples from 16 of the wells in concentrations that ranged from 0.05 to 9.6 µg/L. Atrazine concentrations exceeded 3.0 µg/L in only one sample.

In July 1992, water samples were collected from 147 wells in Audrain, Clark, Lewis, Monroe, Scotland, and Shelby Counties in northeast Missouri. Alachlor, atrazine, cyanazine, metribuzin, and metolachlor were detected at concentrations greater than 0.10 µg/L in water samples from 19 of the 147 wells sampled. Atrazine was detected in water from 18 of the 19 wells with detectable herbicide concentrations. Atrazine concentrations exceeded 3.0 µg/L in two of the samples.

Well depth, well diameter, and geology were significant factors in the occurrence of herbicides in water from wells sampled in northeast Missouri. For wells with detectable concentrations of herbicides in the water samples, well depths ranged from 12 to 220 feet, and averaged 58.9 feet. For wells with no detectable concentrations of herbicides, well depths ranged from 15 to 740 feet, and averaged 211 feet. The diameter of wells with detectable concentrations of herbicides in the water samples ranged from 1.5 to 144 inches, and averaged 33.2 inches. For wells with no detectable herbicide concentrations in the water samples, the well diameter ranged from 1.5 to 72 inches, and averaged 14.7 inches. Although only 21% of the 147 wells sampled during July 1992 were screened in rocks of Pennsylvanian age of the Cherokee Group, these wells accounted for 60% of the wells with detectable concentrations of herbicides in the water samples. The rest of the wells sampled were screened in Ordovician- or Mississippian-age rocks, alluvium of the Des Moines or Mississippi Rivers, or glacial till.



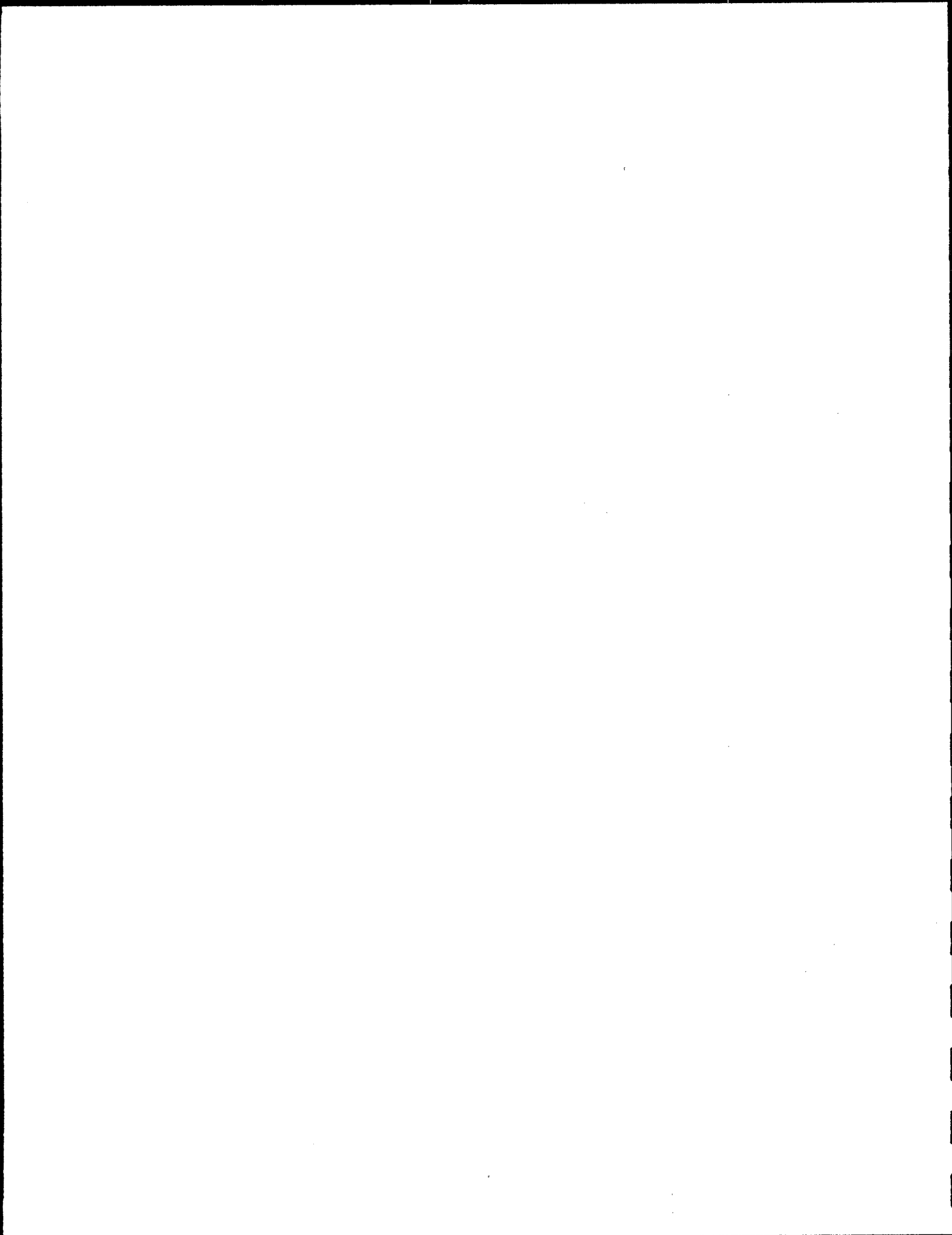
## PESTICIDE PERSISTENCE IN TWO IMPOUNDMENTS IN NORTHEAST NEBRASKA

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Daniel D. Snow and Roy F. Spalding, University of Nebraska-Lincoln, Lincoln, Nebraska

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Dissolved pesticide concentrations in 108 water samples collected from two closely spaced lakes between early May 1990 and mid-June 1991 indicated large differences in impacts from watershed nonpoint-source inputs. Pesticide levels in Maskenthine Lake, a small impoundment of only 34 hectares, increased dramatically in response to spring and early summer runoff events. Fifteen pesticides (atrazine, alachlor, metolachlor, cyanazine, EPTC, butylate, propachlor, trifluralin, simazine, prometon, propazine, fonofos, disulfoton, metribuzin, and terbufos) and two atrazine metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA), were detected. Atrazine, cyanazine, DEA, and DIA levels were greater than  $1 \mu\text{g/L}^{-1}$ . Atrazine remained above the Maximum Contaminant Level for potable water of  $3 \mu\text{g L}^{-1}$  throughout the period of investigation. The pesticide response to spring and summer runoff events was much less dramatic at Willow Lake, a 284-hectare impoundment. All of the 15 pesticides and two metabolites detected in Maskenthine Lake, except terbufos and disulfoton, were detected in Willow Lake. However, the concentrations were lower and did not exceed  $1 \mu\text{g L}^{-1}$ . In months following the maximum flush of pesticides in May and June there was a significant decrease in pesticide residues that appeared to follow first-order kinetics. Apparent half-lives were calculated from the observed decrease. Atrazine was the most persistent agrichemical ( $t^{1/2} = 133$ ,  $t^{1/2} = 148$ ) introduced in the spring runoff events. Extracted pesticide levels were also higher in bottom cores from Maskenthine Lake. Differences in pesticide levels in the two lakes were related to watershed slope, soil-drainage capacity, land use, and rainfall.



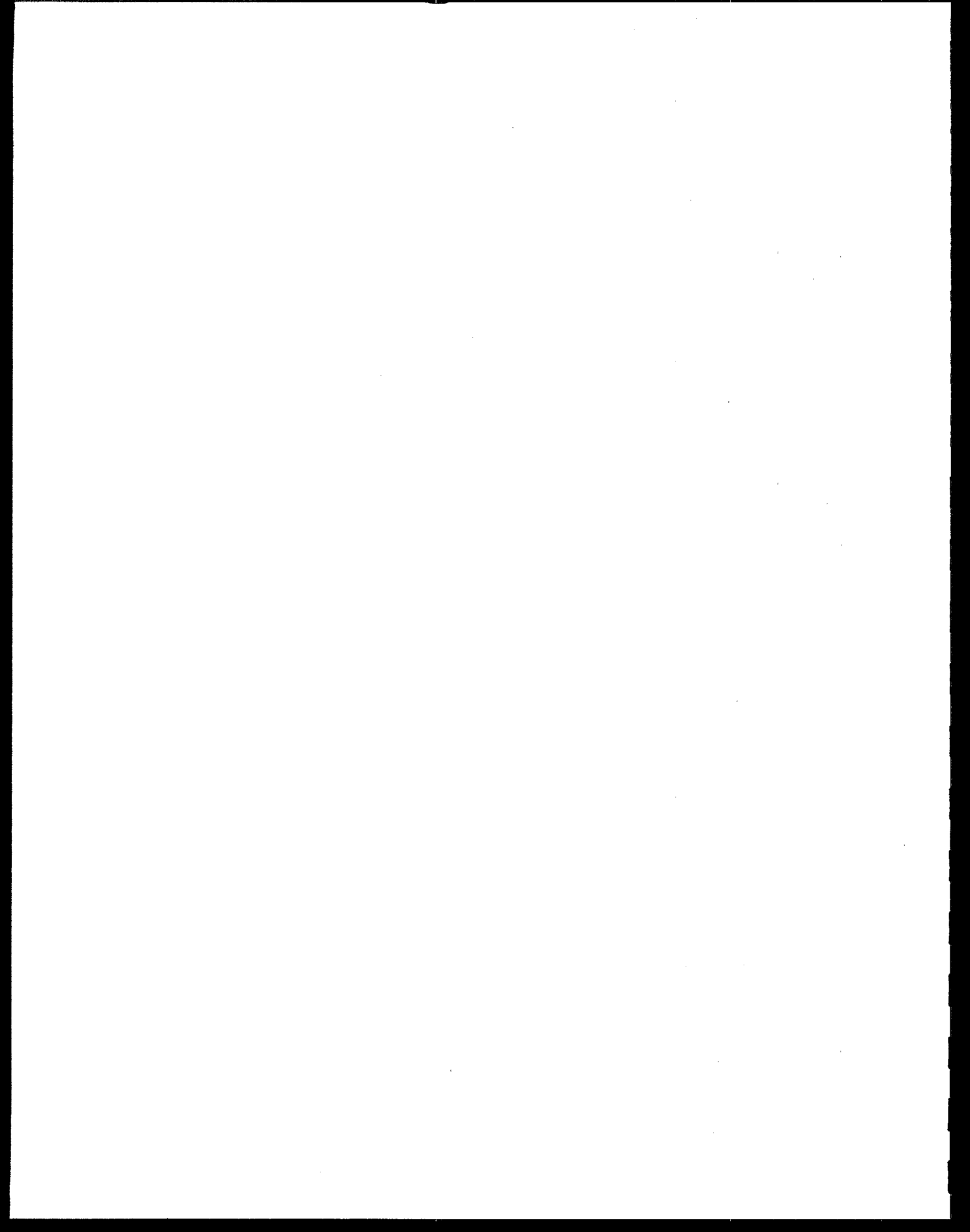
# **DETERMINING THE AGE, TRANSPORT, AND 3-DIMENSIONAL DISTRIBUTION OF ATRAZINE IN A RESERVOIR BY IMMUNOASSAY**

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**James D. Fallon and E.M. Thurman, U.S. Geological Survey, Lawrence, Kansas**

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The age, transport, and distribution of atrazine in a reservoir were determined using enzyme-linked immunosorbent assay. A pulse of stormwater runoff containing atrazine concentrations as much as nine times larger than the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) for drinking water (the MCL for atrazine is based on an annual average concentration of 3.0 µg/L) was monitored as it moved through Perry Lake, northeastern Kansas, during the 1992 growing season. The drainage basin of Perry Lake is the first Pesticide Management Area designated by the State of Kansas. The leading edge of the pulse marked the boundary and mixing zone between old atrazine applied in previous years and freshly applied atrazine. Deethylatrazine-to-atrazine ratios (DAR) further defined the age of atrazine in the reservoir. Runoff entering the reservoir immediately after herbicide application was identified by its small DAR values (0.09 to 0.13). Water with increasing DAR values (0.14 to 0.25) entered the reservoir as the year progressed and gradually displaced water with smaller DAR values. Four hundred and twenty (420) samples from four detailed reservoir surveys (pre-application, post-application, summer, and autumn) were analyzed by immunoassay to determine the distribution of herbicide concentrations in the reservoir. Also, weekly samples were collected from four fixed sites located upstream, within, and downstream of the reservoir. One hundred (100) of these samples were analyzed by gas chromatography/mass spectrometry to confirm immunoassay results and to determine deethylatrazine and deisopropylatrazine concentrations. A combination of immunoassay and DAR values could prove useful in developing reservoir-release strategies to mitigate atrazine concentrations in reservoirs and their outflows.



# OCCURRENCE AND CONTROL OF ATRAZINE AND ITS DEGRADATION PRODUCTS IN PUBLIC DRINKING WATER SUPPLIES

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**Stephen J. Randtke, University of Kansas, Lawrence, Kansas**

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Atrazine is frequently detected in municipal water supplies, at times above the Maximum Contaminant Level (MCL) of 3 µg/L promulgated by the U.S. EPA. Atrazine's degradation products have toxicological properties similar to those of atrazine and may eventually be regulated. Little is known regarding the occurrence of these compounds in drinking water, the possibility of their formation during treatment, or methods for their removal.

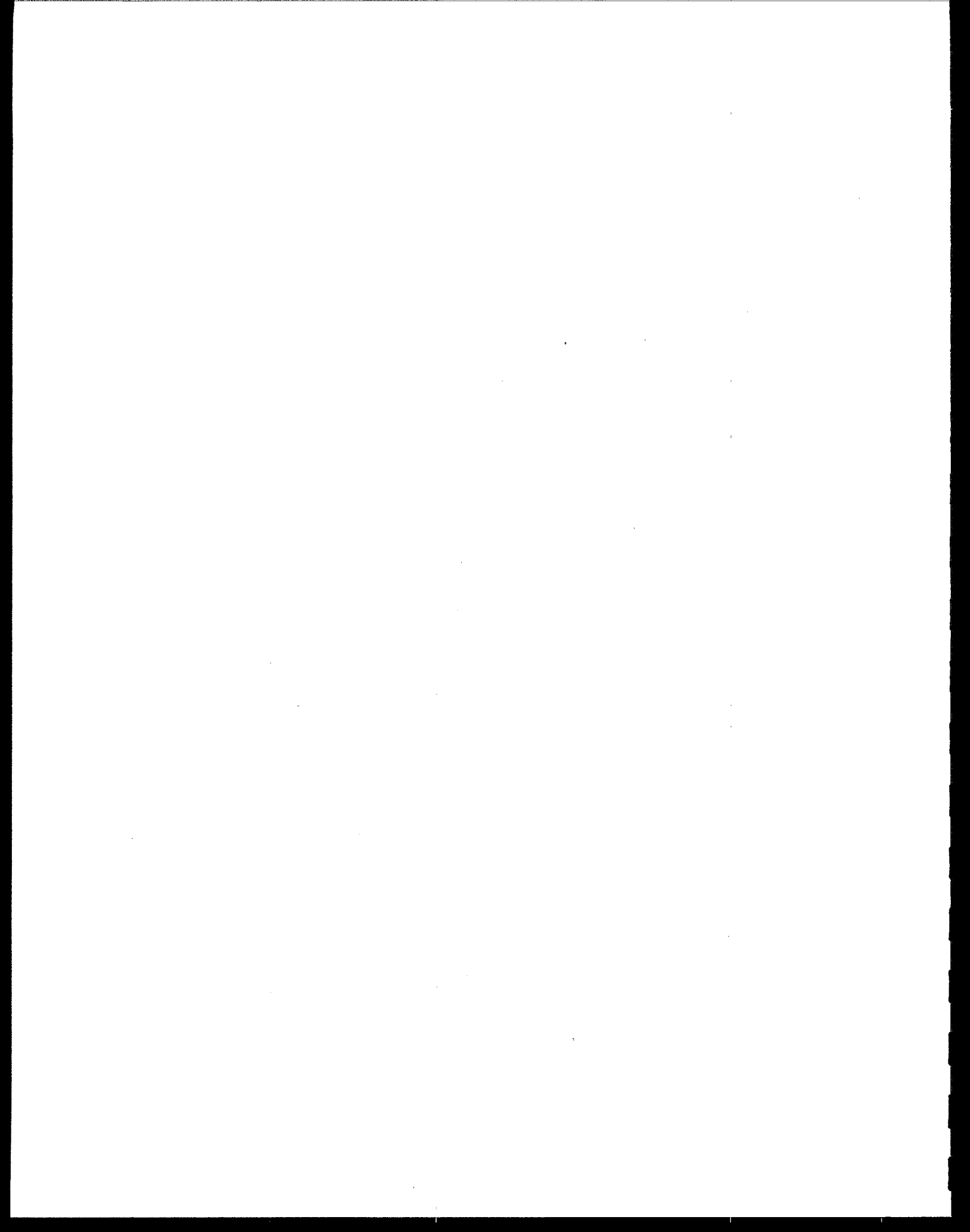
This presentation will summarize the results of a 2-year study that focused on the types and concentrations of atrazine degradation products present in raw and treated drinking-water samples collected from seven treatment facilities located in the midwestern United States. Treatment processes studied included adsorption on powdered and granular activated carbon (PAC and GAC), oxidation (using ozone, potassium permanganate, chlorine, or chlorine dioxide), and ion exchange. Point-of-use activated carbon filters were also evaluated. Atrazine and its major degradation products were determined using solid-phase extraction and high-pressure liquid chromatography.

Atrazine concentrations in water supplies drawn from streams peaked in late spring to early summer; those in supplies drawn from lakes or reservoirs were relatively constant. The concentrations of degradation products in streams were less variable and significantly lower than those of the parent compound. Hydroxyatrazine was the most abundant degradation product detected, averaging about 1 µg/L (versus about 3 µg/L for atrazine). Deethylatrazine and deisopropylatrazine were routinely detected, but at concentrations averaging only 0.7 and 0.3 µg/L, respectively. Didealkylatrazine and the deethylated hydroxanalogues were not detected.

Conventional treatment processes did not achieve substantial removal or alteration of atrazine or its degradation products. PAC addition resulted in substantial removal of atrazine and its degradation products; i.e., about 30 to 90%, depending on the dosage applied. At the Rathbun, Iowa, treatment facility, a 2-foot cap of GAC removed 24% of the influent atrazine and between 9 and 31% of the atrazine degradation products. At Perry Lake, Kansas, a GAC system installed by the U.S. Army Corps of Engineers achieved complete removal of atrazine and its degradation products during April through September of its first year in service. Some point-of-use GAC systems effectively removed atrazine and its degradation products from tap water throughout the stated life of the unit; others experienced premature breakthrough, and breakthrough of atrazine correlated with breakthrough of residual chlorine.

Potassium permanganate reacts too slowly with atrazine and its major degradation products to cause a significant change in their concentration under typical water-treatment conditions. Atrazine and its major degradation products were adsorbed by a strong-acid cation-exchange resin, but they were chromatographically displaced by calcium.

The concentrations of atrazine and its degradation products in surface-water supplies are variable, which has significant implications for both monitoring and control. Fortunately, it appears that the degradation products occur at lower concentrations than the parent compound and that their removal by most non-oxidative processes is similar to that of atrazine. However, oxidative processes tend to convert atrazine to uncleaved degradation products that may be no less toxic to humans. Adsorption, especially on PAC, appears to be the best means of control based on the information now available.





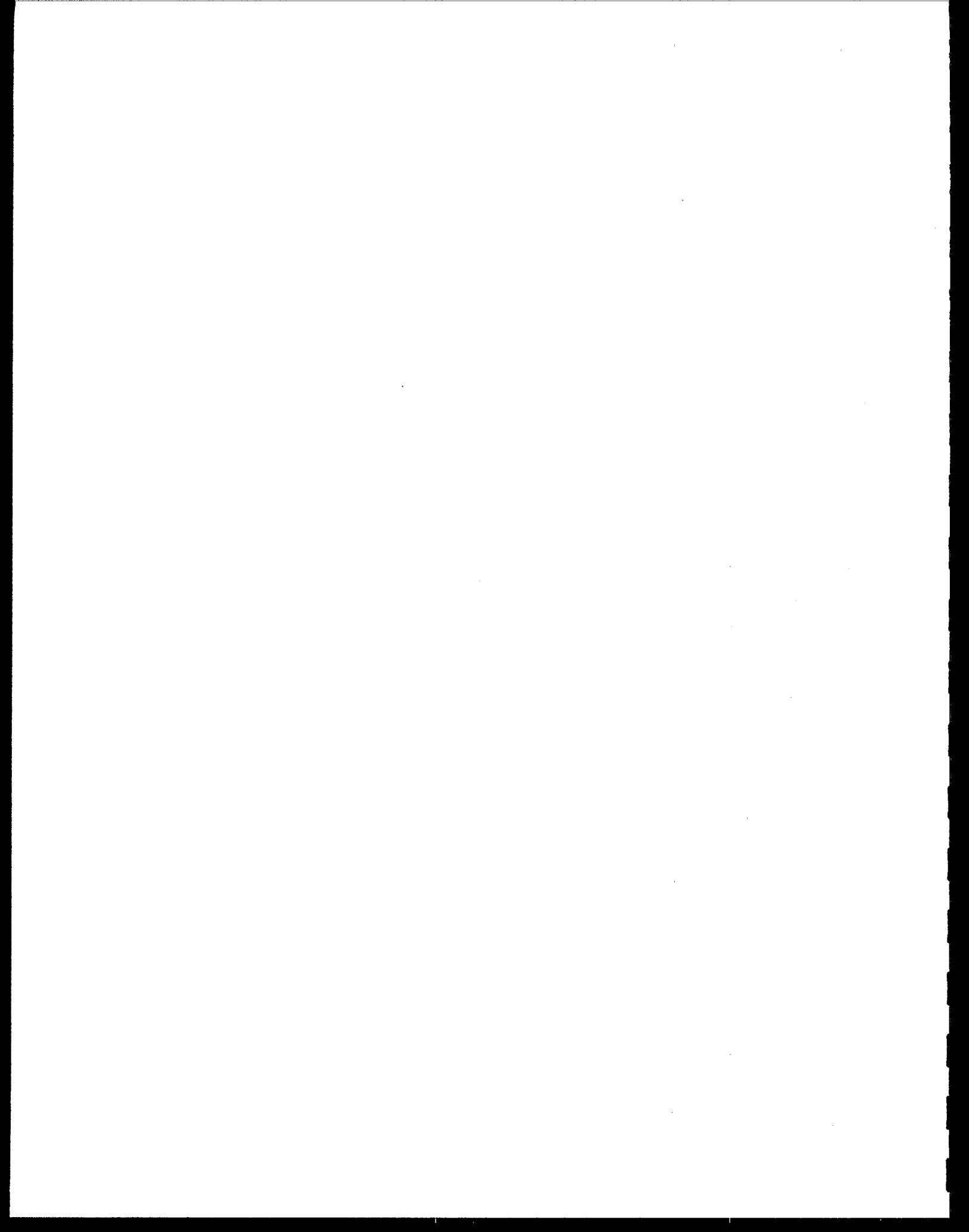
## HERBICIDE DISTRIBUTION BENEATH NEBRASKA MSEA BLOCKS

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Roy F. Spalding and Thomas D. Papiernik, University of Nebraska-Lincoln,  
Lincoln, Nebraska

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Sampling of 41 multilevel sampler installations occurred in early spring, summer, and fall and represents times of maximum and minimum water levels. From July 1991 to October 1992, a total of 2,200 discrete samplings for nitrate and atrazine and its degradates were used to calculate average concentrations at each depth. Initially, nitrate-N concentrations in pore water beneath the root zone (unsaturated zone) to the bottom of the primary aquifer were invariant with depth. Atrazine concentrations were stratified with average concentrations of  $\sim 3 \mu\text{g/L}$  in the shallow water and  $\sim 1 \mu\text{g/L}$  at depth. Both deethyl- and deisopropylatrazine decrease at almost the same rates as the parent compound, suggesting that hydrolysis is the primary process controlling atrazine concentrations. Deethylatrazine concentrations are about 30% higher than atrazine concentrations throughout the profiles.  $^3\text{H}/^3\text{He}$  dates suggest that the ground water at the bottom of the primary aquifer to be from 10-20 years old. Irrigation water is drawn primarily from the lower part of the primary aquifer because the irrigation wells are screened in the lower one-third of the aquifer. Through the October 1992 sampling, water-table fluctuations of 1.5 meters (5 feet) occurred annually, and declines from irrigation were normally compensated by recharge in the winter and spring. A decrease in aquifer  $\text{NO}_3\text{-N}$  concentration was not noted until the spring 1993 sampling. High recharge rates during a very wet spring and early summer of 1993 have aided the remediation of the upper portions of the primary aquifer.



# A NATURAL GRADIENT TRANSPORT STUDY OF SELECTED HERBICIDES

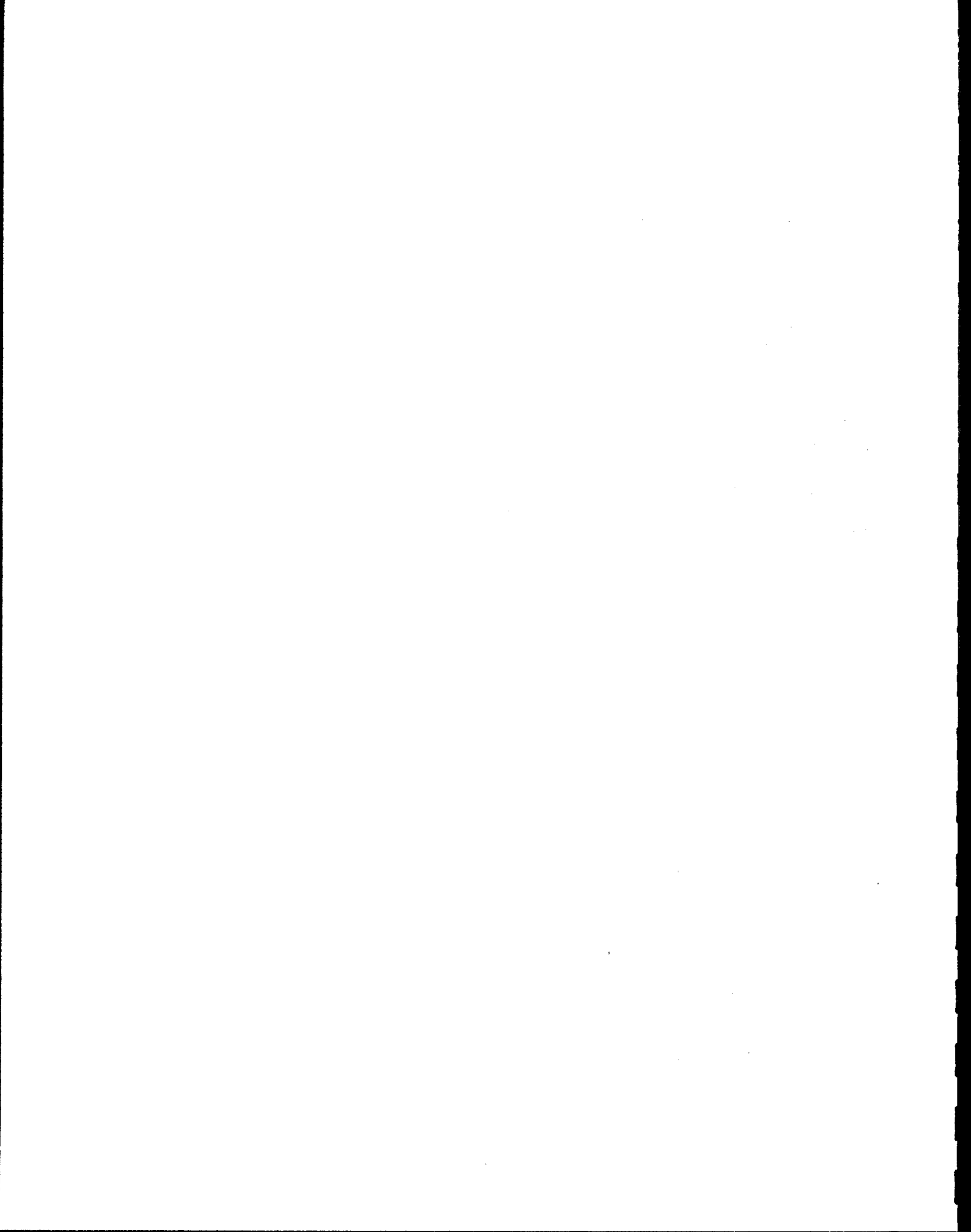
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S.K. Widmer and R.F. Spalding, Water Center, University of Nebraska, Lincoln

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An investigation of the behavior of commonly detected herbicides and herbicide degradates under aquifer conditions was conducted in a shallow sand and gravel aquifer near Fremont, Nebraska. Approximately 950 liters (250 gallons) of 3 ppb atrazine, 2 ppb alachlor, 10 ppb cyanazine, 10 ppb metolachlor, 1 ppb butachlor, 3 ppb deethylatrazine (DEA), and 3 ppb deisopropylatrazine (DIA) and a conservative tracer (sodium bromide) were injected into the aquifer in two experiments. The plumes were monitored over several months. A system of multilevel samplers (MLS) was used to delineate the solute plume. Fences of MLSs were arranged in arcs, such that eight arcs were longitudinally located within the 7.3 meters (24 feet) monitored. The measured average rate of ground-water flow at the study site was  $15 \text{ cm day}^{-1}$  ( $0.5 \text{ feet day}^{-1}$ ). Samples were collected at 0.30-meter (1-foot) depth intervals.

A retardation factor (R) was determined for each pesticide by comparing its concentration profile to that of the conservation tracer at a given distance. The triazines (atrazine and cyanazine,  $R=1.2$ ) were slightly less mobile than the acetanilides (alachlor and metolachlor,  $R=1.1$ ). DEA ( $R=1.1$ ) was more mobile than the atrazine, while DIA ( $R=1.3$ ) was less mobile. Persistence of atrazine, cyanazine, metolachlor, DEA, and DIA was verified by lack of loss of parent compounds and, in the case of atrazine, static levels of the degradates. Alachlor and butachlor exhibited losses of approximately 30 and 60%, respectively, while the conservative tracer showed a decrease of less than 15%.



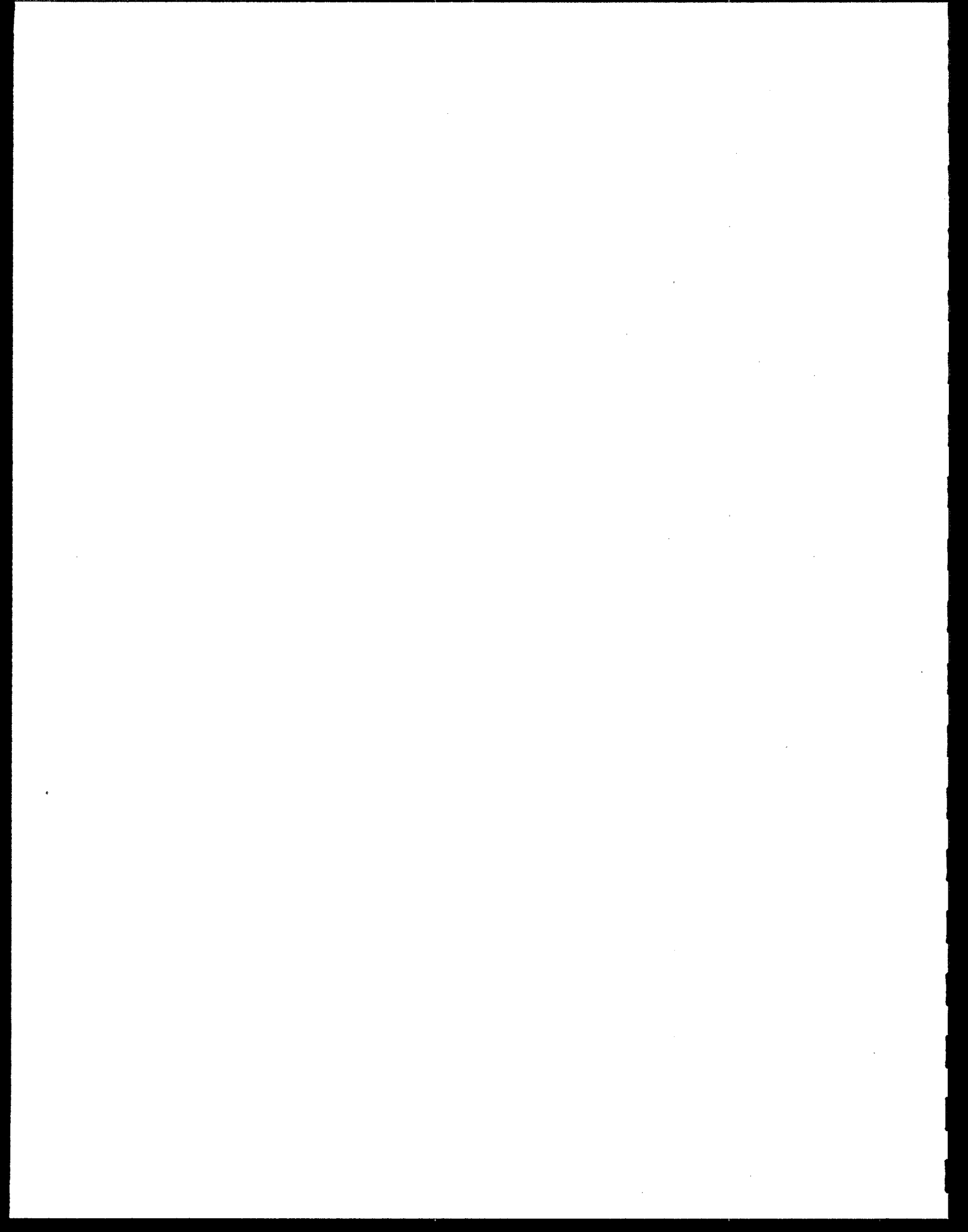
# HERBICIDE TRANSPORT AND DEGRADATION IN A PRISTINE WATERSHED: THE FATE OF HERBICIDES DEPOSITED BY PRECIPITATION

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Aron E. Cromwell and E. Michael Thurman, U.S. Geological Survey, Lawrence, Kansas

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Herbicides used in agricultural areas are being transported atmospherically and deposited by precipitation onto pristine watersheds. The fate of these herbicides was studied at Isle Royale National Park, an island park located in Lake Superior on the United States-Canadian border. Rainfall, soil water, surface water, and soils were analyzed by combining solid-phase extraction (SPE) with enzyme-linked immunosorbent assay (ELISA). This combination enabled the onsite analysis of samples in which the concentrations of herbicides were as little as 5 ng/L. The SPE-ELISA results were confirmed using gas chromatography/mass spectrometry (GC/MS) with isotope dilution. Herbicides detected at Isle Royale included the triazine herbicides atrazine and cyanazine, as well as two triazine metabolites, deethylatrazine and deisopropylatrazine. Maximum atrazine and cyanazine concentrations in rainfall occurred in late spring, approaching or exceeding the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) of 3.0 µg/L for atrazine, and the health advisory (HA) of 1.0 µg/L for cyanazine. By mid-summer, rainfall concentrations of the herbicides decreased to less than detection levels. Atrazine was detected in small concentrations in water from all lakes that were sampled. Field data and soil-column and lake-water degradation experiments indicate that atrazine degrades rapidly in soil environments, but more slowly in aquatic environments. This slow degradation rate in water has important implications for the quality of lakes in pristine areas receiving herbicide-contaminated rainfall because the potential exists for the accumulation of herbicides to levels harmful to aquatic life.



## **A COMPARISON OF ATRAZINE AND METOLACHLOR BIOLOGICAL ASSESSMENT DATA TO CONCENTRATIONS REPORTED IN PRECIPITATION MONITORING STUDIES**

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**Philip A. Banks, MARATHON-Agricultural and Environmental Consulting, Inc., Las Cruces, New Mexico, and Dennis P. Tierney, Ciba Plant Protection, Greensboro, North Carolina**

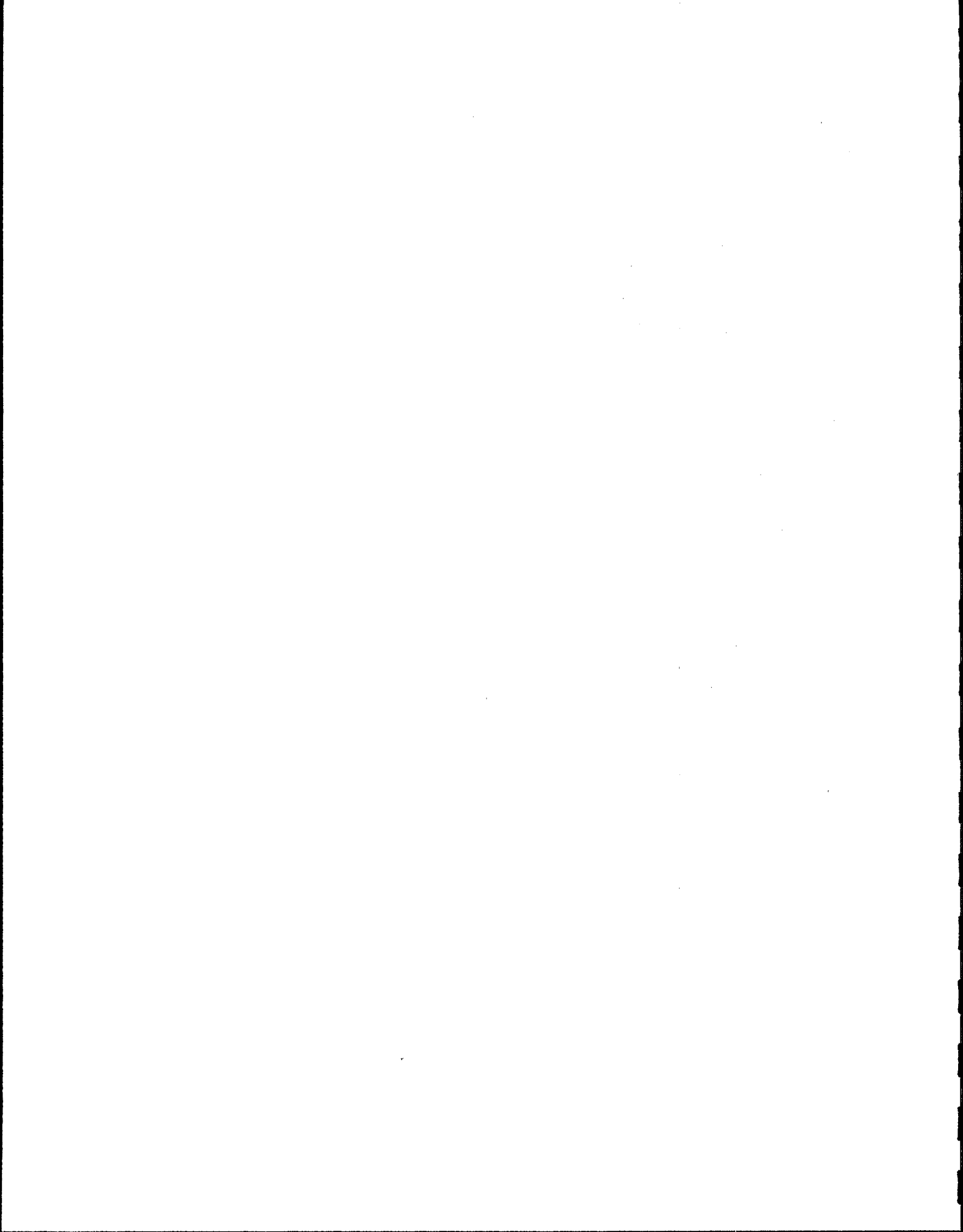
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Several pesticides have recently been reported in precipitation, including the herbicides atrazine and metolachlor. While data are limited on how these herbicides get into the atmosphere, it appears that volatilization and particle erosion following application are the primary contributors. Atrazine and metolachlor presence in precipitation is seasonal with the highest concentrations and most detections occurring during and shortly after the peak application period in the spring. From published reports, five for atrazine and three for metolachlor, atrazine was detected in approximately 50% of the samples collected and metolachlor in approximately 20% of the samples. For both herbicides, over 90% of the precipitation samples contained concentrations of less than 1 ppb (atrazine = 94% and metolachlor = 97%).

A biological risk assessment evaluated the significance of atrazine and metolachlor concentrations in rainfall on various terrestrial and aquatic plants and animals. For atrazine, various algae species were reported to have lowest observable response levels (LOEL) that ranged from 10 to 565 ppb in a variety of aquatic studies. Most terrestrial plants were more tolerant of atrazine, with cucumber and cabbage having no observable effect levels (NOEL) of 12 and 6 ppb, respectively. In general, aquatic and terrestrial plants were more tolerant of metolachlor than atrazine. Based upon measured concentrations of each herbicide in rainfall, atrazine and metolachlor do not pose an ecological risk.

Additionally, a human exposure assessment evaluated the potential health effects of atrazine and metolachlor in rainfall relative to the Federal Safe Drinking Water Act and the Environmental Protection Agency Health Advisory criteria. A dermal risk assessment is also provided. No adverse health effects are expected due to drinking water or dermal exposure routes.

While historical data on atrazine and metolachlor presence in precipitation is limited to only five published reports, two were in the atrazine and metolachlor high-use areas of the Midwest. Data from these areas can be used to provide perspective on data from future studies.





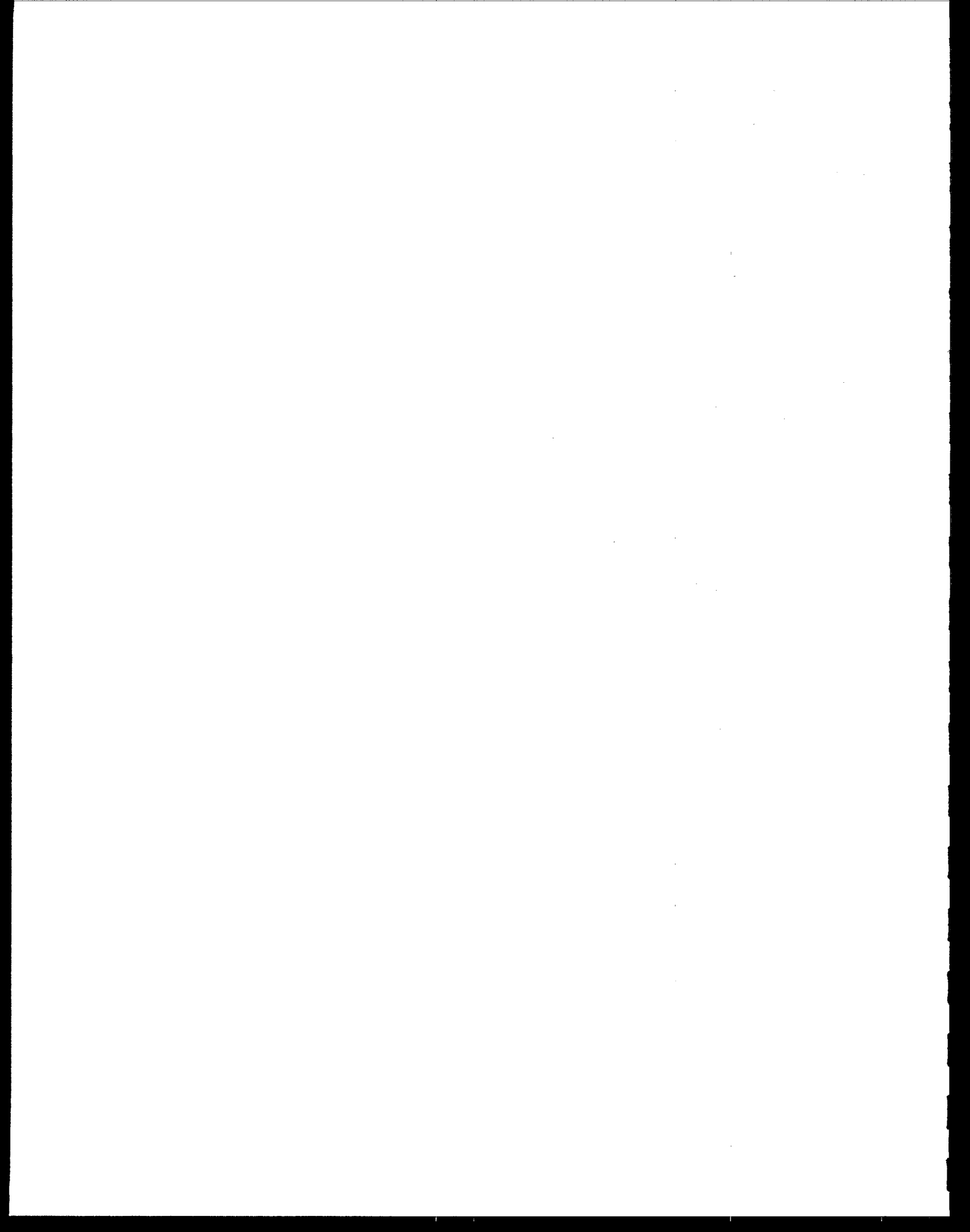
## CHEMISTRY, DEGRADATION, AND TRANSPORT OF TRIAZINE METABOLITES IN SURFACE WATER

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E.M. Thurman, U.S. Geological Survey, Lawrence, Kansas

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Atrazine, one of the most extensively used herbicides in the midwestern United States, degrades in soil to several important metabolites (principally deethylatrazine and deisopropylatrazine). Atrazine field-dissipation studies show that only deethylatrazine persists in soil and is transported to ground water through the unsaturated zone. In soil, deisopropylatrazine rapidly degrades further to didealkylatrazine; consequently, deisopropylatrazine is found in only trace amounts relative to atrazine and deethylatrazine (approximately one-tenth the concentration or less). Alternatively, deisopropylatrazine is more stable in surface water and is present at concentrations equal to one-third the concentration of deethylatrazine. In areas where atrazine is the only parent compound for these metabolites, the dichotomy in degradation rates makes the two atrazine metabolites suitable indicators of surface- and ground-water interactions in the Corn Belt (a 12-state region in the midwestern United States). The ratio of concentrations of each degradation product to the parent compound may be used to distinguish ground-water flow paths, such as streambank infiltration into ground water, ground-water contribution to streams during base flow, and point-source contamination of an aquifer (such as a spill at a poorly constructed well). Other herbicides that commonly occur with atrazine use also may be indicators of flow path. These herbicides include cyanazine, propazine, and simazine. They degrade in soil to metabolites that may be identical to atrazine metabolites and also may be indicators of surface- and ground-water interactions in the Corn Belt.



# NONEQUILIBRIUM ADSORPTION AND DEGRADATION OF ATRAZINE AND ALACHLOR IN SOIL

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Gerard J. Kluitenberg, Leticia S. Sonon, and A. Paul Schwab, Department of Agronomy,  
Kansas State University, Manhattan Kansas

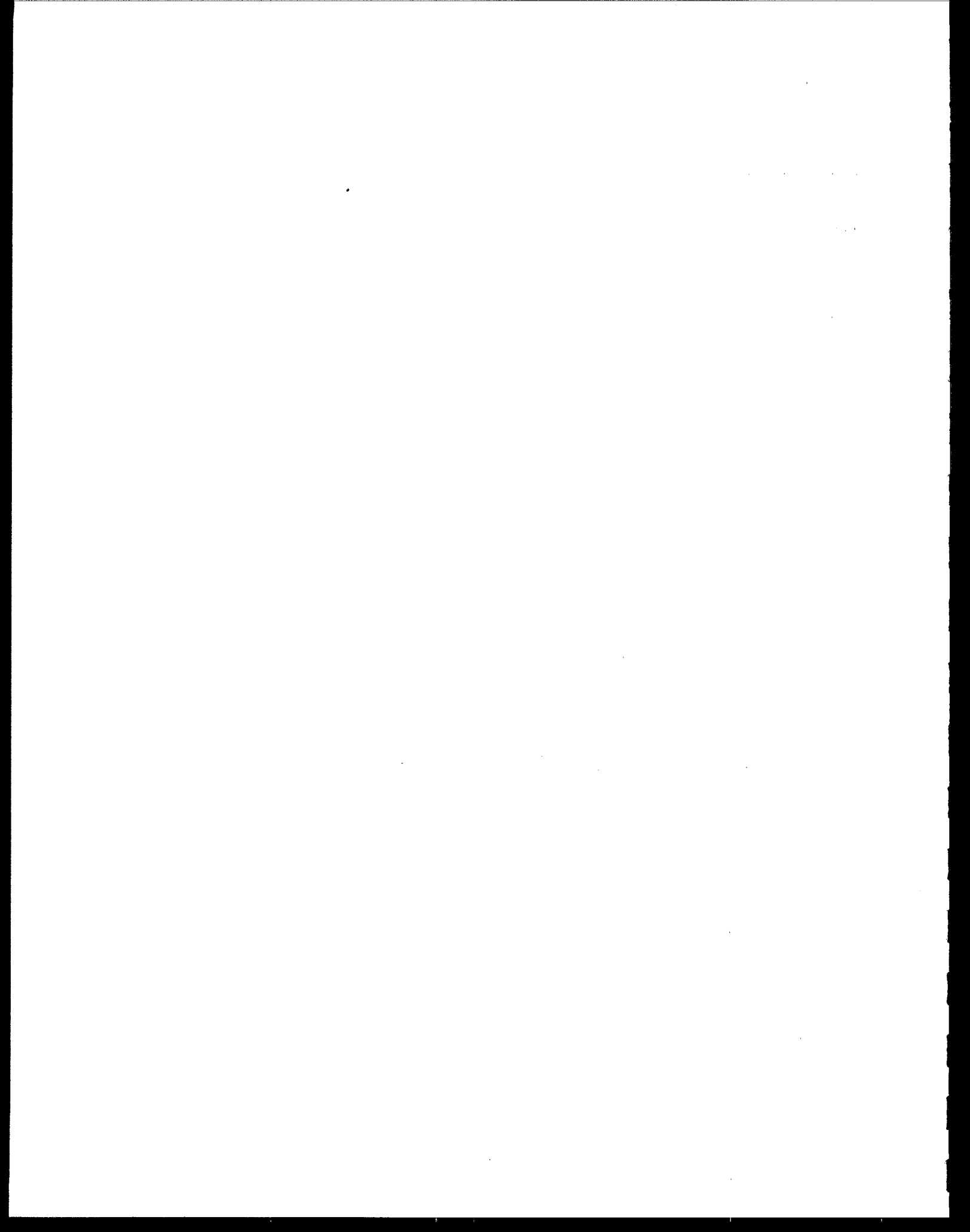
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Atrazine and alachlor are chemically and biologically degraded during transport through soil. Degradation of atrazine produces daughter products such as hydroxyatrazine, deethylatrazine, and deisopropylatrazine. Both herbicides are also sorbed to soil particles during transport. This research was conducted to provide insight into the mechanisms of atrazine and alachlor adsorption and degradation.

Laboratory leaching experiments were conducted by using 1.1 meter-long undisturbed soil columns from four soils varying in texture, pH, and organic carbon content. Atrazine, alachlor, and bromide were added at the soil surface at a rate similar to recommended rates. Solute application was followed by steady-state water applications of 2.6 and 0.2 inches per day, respectively, for the saturated and unsaturated flow conditions. Soil-water potential was set to approximately -0.3 bar at the bottom of the unsaturated columns. Column effluent was collected at regular time intervals and used to plot effluent breakthrough curves (BTC's).

Results from experiments with Pratt loamy fine sand will be presented. This soil was collected at the Sandyland Experiment Field near St. John, Kansas, which overlies the Great Bend aquifer. Mass recovery of atrazine at the conclusion of the experiments was 50 and 9%, respectively, for the saturated and unsaturated leaching experiments. Greater degradation in the unsaturated flow experiment was mainly a result of the greater solute residence time within the soil. Under saturated conditions, deisopropylatrazine and deethylatrazine were present in the column effluents at or below detection limits; however, effluents collected from the unsaturated experiments contained relatively high concentrations of the degradation products. Mass recovery of alachlor was 10% for the saturated leaching experiments, and alachlor was not detected in the effluent from the unsaturated flow experiments. Thus, degradation rates for alachlor were significantly higher than atrazine degradation rates.

The results of batch adsorption experiments were used to calculate atrazine retardation factors of 7.7 and 12.5 for the saturated and unsaturated flow regimes, respectively. Atrazine BTC's would be centered at 7.7 and 12.5 pore volumes if equilibrium adsorption prevailed during transport. Measured centers of mass of the atrazine BTC's were located between 2 and 3 pore volumes. The leftward shift of the BTC's indicates that nonequilibrium adsorption significantly enhanced the mobility of atrazine under both saturated and unsaturated flow conditions. Atrazine and its degradation products ranked in order of decreasing mobility: deethylatrazine > atrazine > deisopropylatrazine. Alachlor was found to be less mobile than atrazine, a result opposite from that expected based on batch adsorption data. Thus, nonequilibrium adsorption also enhanced alachlor movement but to a lesser extent. Modeling of the bromide BTC's with the advection-dispersion equation yielded dispersivities of 1-2 centimeters. This indicates that nonequilibrium due to the chemical kinetics of adsorption was more important than physical causes of nonequilibrium.



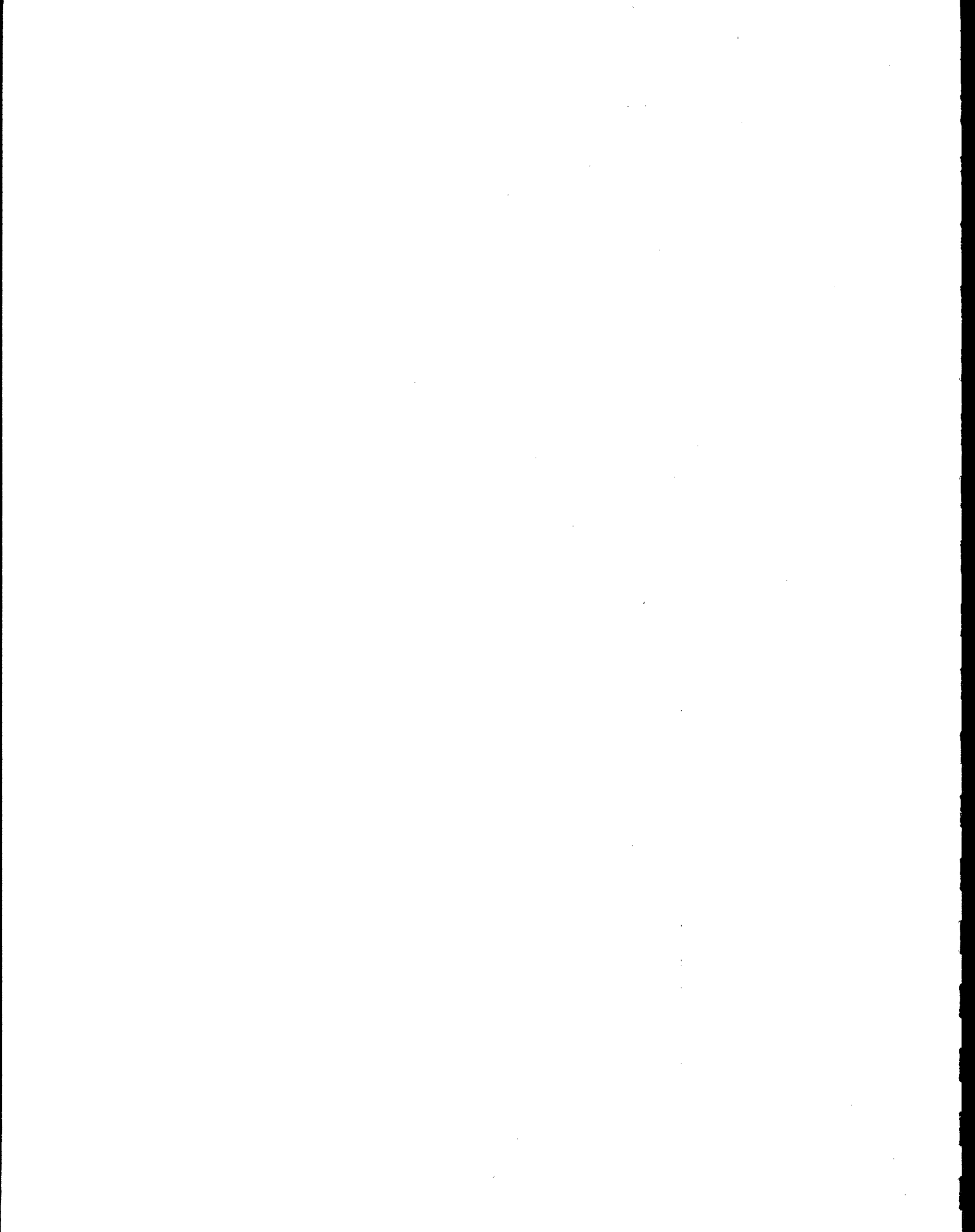
# CYANAZINE METABOLITES IN SURFACE WATER: THE TRANSPORT AND DEGRADATION OF LABILE HERBICIDES

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M.T. Meyer and E.M. Thurman, U.S. Geological Survey, Lawrence, Kansas

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Cyanazine (2-chloro-4-(ethylamino)-6-(1-cyano-1-methylamino)-S-triazine) is one of the five most extensively used herbicides in the United States and is more labile than atrazine; however, there are few studies of the fate and transport of cyanazine metabolites in surface water. A field-dissipation study showed that cyanazine degrades to a common atrazine metabolite, deisopropylatrazine. Analysis of samples collected from several stream sites during storm runoff throughout the spring and early summer demonstrates that the ratio of deisopropylatrazine to deethylatrazine ( $D^2R$ ) is an indicator of the quantity of cyanazine relative to atrazine. Cyanazine was detected in 73%, cyanazine amide in 63%, deethylcyanazine in 36%, and deisopropylatrazine in 52% of the samples collected during the first storm runoff after herbicide application in a reconnaissance study of stream water from 150 sites in the midwestern United States. Except for deisopropylatrazine, these compounds were detected in 5 to 30% of the samples collected in the spring before planting and in the fall during low streamflow. In addition, both the storm-runoff and herbicide reconnaissance studies show that the cyanazine amide-to-cyanazine ratio (CA/CR) increased throughout the summer, indicating that the cyanazine amide is more stable than cyanazine. Finally, the CA/CR may be an indicator of the length of time cyanazine resided in the soil relative to its application in the spring.



# BIODEGRADATION OF PESTICIDES IN SUBSURFACE SAMPLES FROM THREE MIDCONTINENT SITES

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**James L. Sinclair and Tony R. Lee, ManTech Environmental Technology, Inc.,  
Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma**

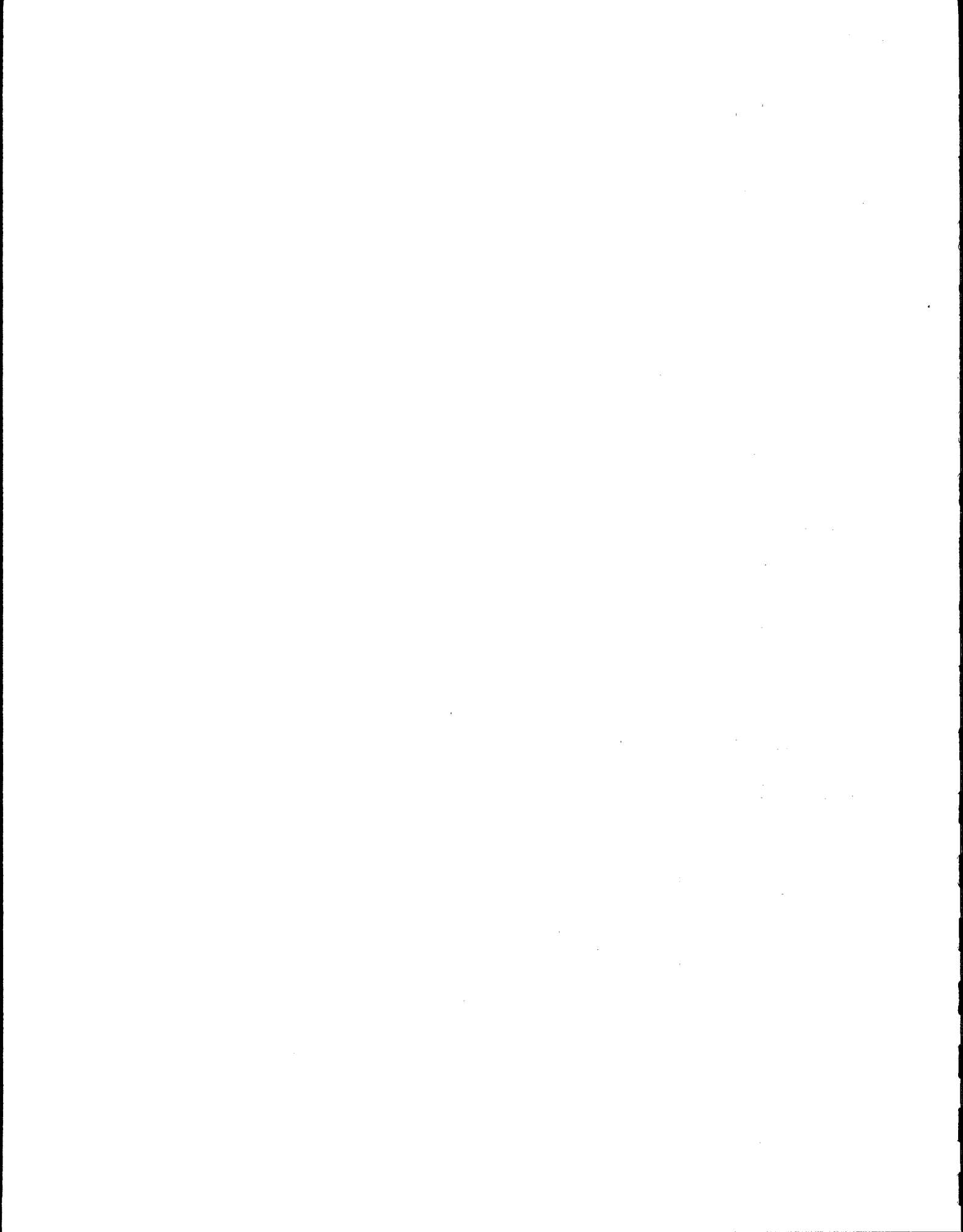
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Little information is currently available concerning the biodegradability of pesticide contaminants in the subsurface. Pesticide contamination of ground water is a particular problem in the midcontinent region of the United States. To investigate pesticide biodegradation in soil and sediments from this region, subsurface drill core samples were obtained from agricultural fields which had received applications of pesticides near Iowa City, Iowa, Princeton, Minnesota, and south-central Ohio. Cores were handled with aseptic technique to minimize microbial contamination. Samples were taken from the surface to slightly below the water table from the Iowa and Minnesota sites, and only from below the water table from the Iowa and Minnesota sites, and only from below the water table at the Ohio site. Microcosms were made from the sediments and spiked with 100 ppb  $^{14}\text{C}$ -ring labeled atrazine, alachlor, carbofuran or 2,4-D. Experiments were run on the mineralization of the four pesticides and on the breakdown of atrazine and formation of atrazine breakdown products.

Preliminary results indicate that the rate of mineralization of pesticides followed patterns based on the type of pesticide, the nature of the soil or sediment used, and the different sites that sediments were obtained from. Generally, 2,4-D was mineralized much more readily than the other pesticides with 25 to 50% of the amount added being mineralized after 146 days of incubation. More 2,4-D was mineralized in the saturated zone sediment microcosms from both the Iowa and Minnesota sites than was mineralized in the surface soil or the unsaturated zone sediments. Usually about 10 to 15% of added carbofuran was mineralized in most sediments by day 146 of the experiment. The greatest amount of carbofuran mineralization occurred in the Iowa surface soil, and slightly more mineralization occurred in the saturated zone than in the unsaturated zone sediments. For most samples, about 5 to slightly more than 10% of added alachlor was mineralized by 146 days. The largest amount of alachlor mineralization observed in this experiment, 21.8% of the added alachlor, occurred in the saturated zone sediments from the Iowa site. More alachlor mineralization occurred in the saturated zone sediments of the Iowa and Minnesota sites than in the unsaturated zone sediments or even the surface soil. Atrazine was mineralized the least of any of the four pesticides tested. About 4 to 15% of the amount of added atrazine was mineralized in the different soils or sediments tested by 146 days of incubation. As with the other pesticides, more atrazine mineralization occurred in the saturated zone sediments than in the unsaturated zone sediments. Slightly more atrazine was mineralized in the surface soil than in the saturated zone sediments of the Iowa site, but more atrazine was mineralized in the saturated zone sediments than in the surface soil of the Minnesota site.

The distribution of  $^{14}\text{C}$  activity between water soluble, chloroform extractable, and bound residue fractions varied with the chemical nature of the different pesticides. Generally, the largest amount of  $^{14}\text{C}$  activity occurred in the soil bound fraction. Most sediment types yielded a mass balance of the total of all  $^{14}\text{C}$  activity from all fractions of 70% or more of the  $^{14}\text{C}$  activity added to the microcosms.

This work demonstrated that significant biodegradation of pesticides can occur in subsurface sediments. It also showed that differences occur between subsurface sediment types and between sites at different geographical locations.





## **INCIDENCE OF CERTAIN CANCERS AND EXPOSURE TO AGRICULTURAL HERBICIDES: MEASURES TO REDUCE THE RISK**

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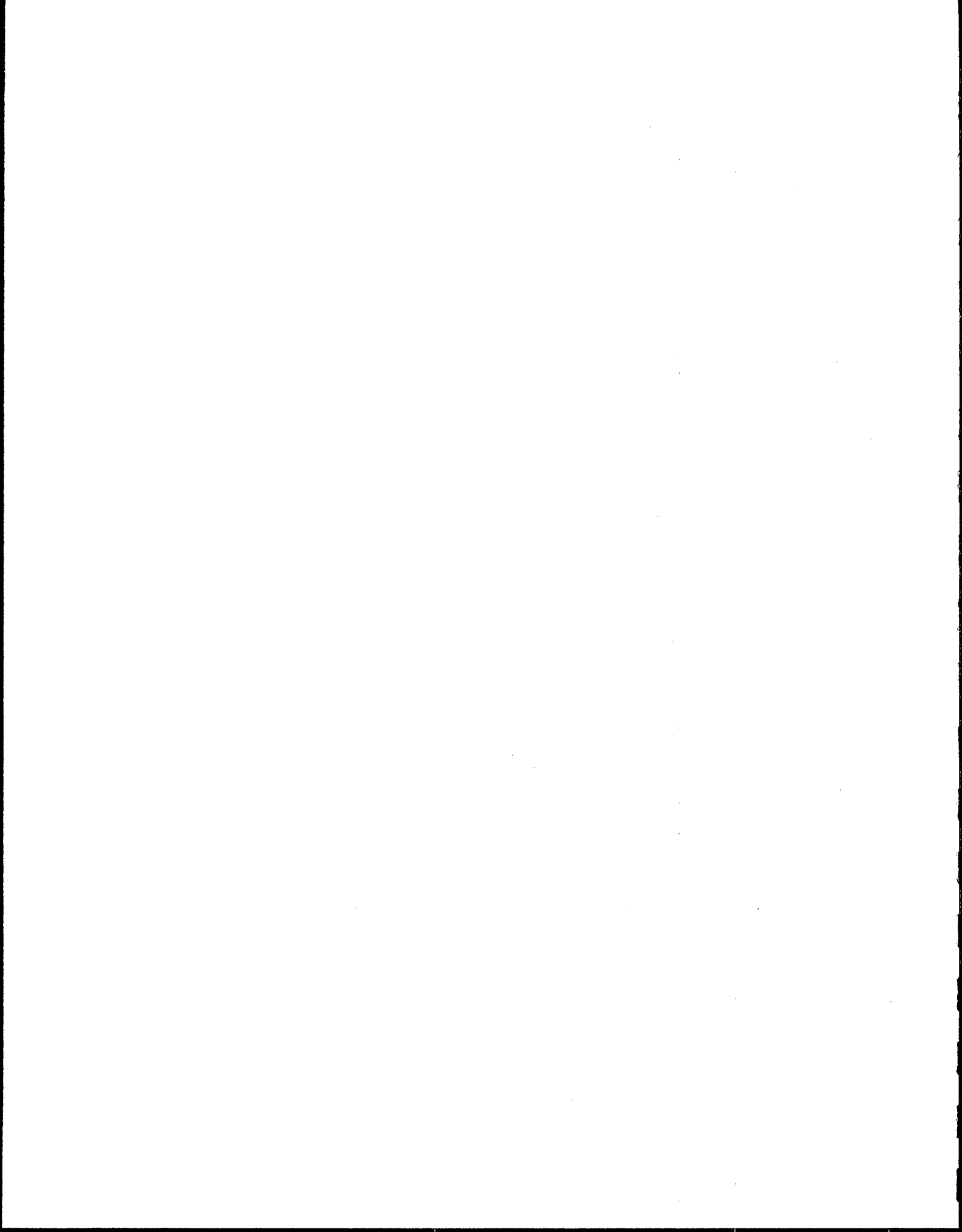
**Robert J. Robel, Kansas State University Division of Biology, Manhattan, Kansas,  
Frederick F. Holmes and Cathy D. Boysen, University of Kansas Medical Center,  
Kansas City, Kansas**

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A case-control study in Kansas of soft-tissue sarcoma, Hodgkin's disease, and non-Hodgkin's lymphoma found farm herbicide use associated with the incidence of non-Hodgkin's lymphoma, but not soft-tissue sarcoma or Hodgkin's disease. Cases were newly diagnosed white males over 20 years of age with soft-tissue sarcoma, Hodgkin's disease, or non-Hodgkin's lymphoma, whereas controls were white males from the general Kansas population matched to each case by age and vital status. The incidence of non-Hodgkin's lymphoma increased significantly with days of reported herbicide exposure per year and years of exposure. Male farmers exposed to herbicides more than 20 days per year had a sixfold increase in the risk of non-Hodgkin's lymphoma compared to nonfarmers. Farmers who used herbicides frequently and mixed or applied the herbicides themselves had an eightfold increased risk compared to nonfarmers. Exposure data were more abundant for phenoxyacetic acids (2,4-D, and 2,4,5-T), triazines (atrazine, cyanazine, propazine, etc.), and uracils than for amides, benzoics, carbamates, and trifluralin. All herbicides showed significant increased risk of non-Hodgkin's lymphoma except the uracils; however, the assessments of risk were stronger for the phenoxyacetic acids and triazines because of the number of cases involved. Farmers using protective equipment (rubber gloves, masks, etc.) had a lower risk than those who did not.

A follow-up case-control study in eastern Nebraska looked at additional types of cancer (multiple myeloma and chronic lymphocyte leukemia) and included women as well. Cases were white males and females over 20 years old with various cancers, whereas control subjects were residents of the same area matched to the cases by age, sex, and vital statistics. As in the Kansas study, the Nebraska study also showed increased risk of non-Hodgkin's lymphoma associated with 2,4-D exposure for males aged 20 years or older. Men who mixed or applied 2,4-D had an additional increased risk of non-Hodgkin's lymphoma, and that risk increased further with time spent in contaminated clothing.

Results from these two studies provide justification for reducing human exposure to agricultural herbicides and suggest possible ways of doing so.



## HAZARD ASSESSMENT OF ATRAZINE

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**Darrell D. Sumner, Charles B. Breckenridge, and James T. Stevens, Ciba Plant Protection, Greensboro, North Carolina**

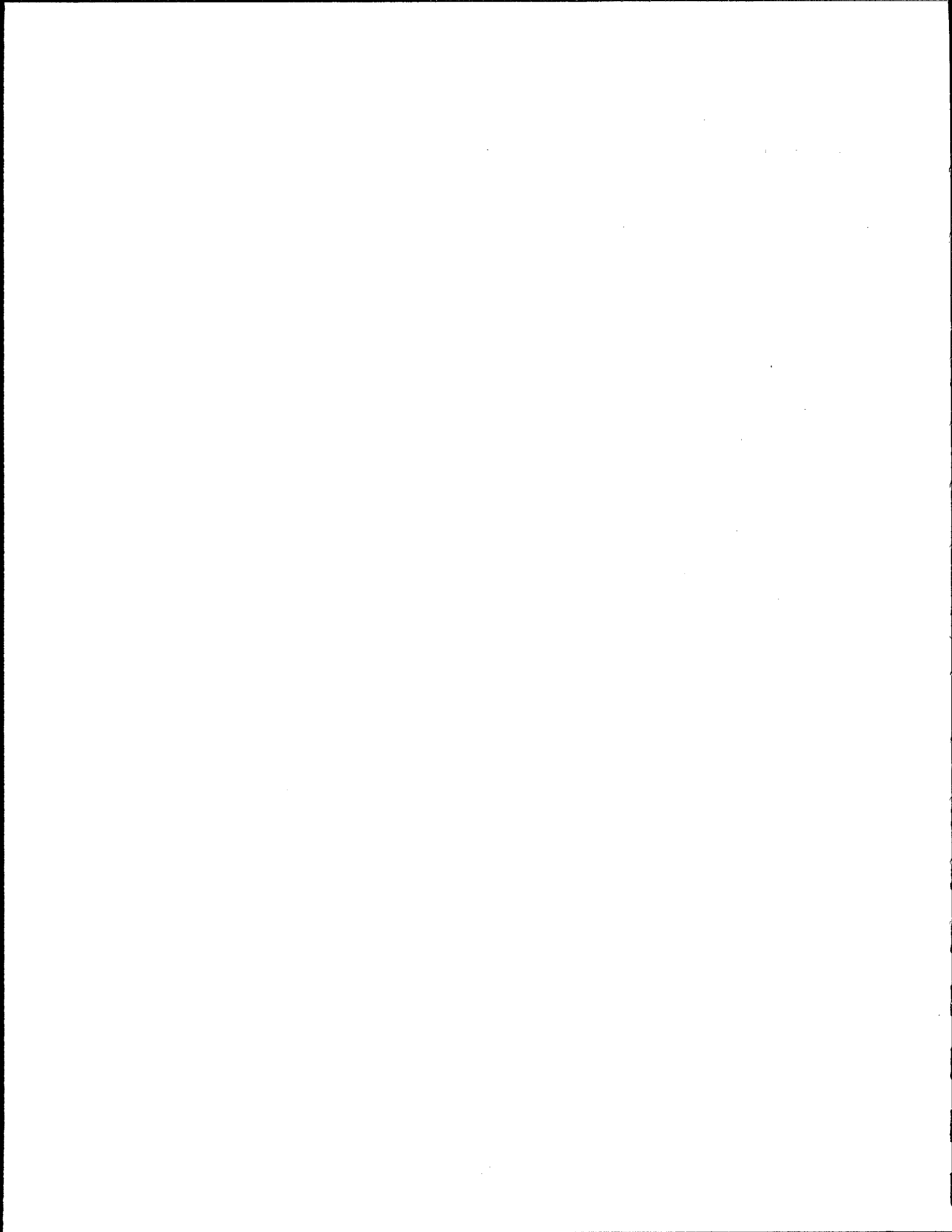
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Atrazine is a chloro-s-triazine herbicide that has been used for weed control in corn for over three decades. It exerts herbicidal activity by inhibition of photosynthesis. It is not particularly toxic in acute administration to animals ( $LD_{50}$  in rats about 3,000 mg/kg). Atrazine is not a reproductive toxin, not a teratogen, not a mutagen (evaluated in over 50 tests), and probably not a carcinogenic in humans. Evidence indicates that a carcinogenic response in female Sprague-Dawley rats is a strain and species specific response. Therefore, low-level exposures do not constitute unreasonable risk to humans.

Atrazine was not carcinogenic to three strains of mice in three different studies, not carcinogenic in Fischer-344 rats, and not carcinogenic to male Sprague-Dawley rats. But, female Sprague-Dawley rats fed atrazine in their diet showed an increased incidence and/or earlier onset of mammary tumors, this was the only tumor response observed in these studies. This response was manifest as an increase in the incidence of mammary tumors, which is highly spontaneous in this strain of rat (incidence ranging to as high as 70% of aged females). Female Sprague-Dawley rats have an estrogen-dependent hormone cycle that is progressively unstable with age. Increased estrogen is thought to lead to the biological processes that produce tumors in these animals.

Ciba has conducted numerous special studies with atrazine. These studies have confirmed that large doses atrazine (100 mg/kg) administered for short intervals (2 weeks) or lower feeding levels (400 ppm or about 20 mg/kg/day) for a period of several months results in a prolongation of the duration of estrous cycle in the female Sprague-Dawley rat. This response is accompanied by more days in estrus (tissue under estrogen influence) as well as an elevation of circulatory estrogen levels. This enhanced exposure to estrogen establishes an environment for appearance of these already highly spontaneous mammary tumors in this strain of rat.

The mechanism by which atrazine affects the estrus cycle in Sprague-Dawley rats is thought to be associated with its ability to interfere with estrogen binding and to exert an anti-estrogenic response. This effect interferes with the normal control mechanisms for the estrus cycle. Receptor binding studies, *in vivo* and *in vitro*, have revealed that the overwhelming concentrations of triazine must be available at unoccupied estrogen receptor sites before the interferences can occur. Binding constants indicate that the concentration of atrazine required to interfere with the estrogen receptor is 10,000 - 100,000 times more than that of estrogen. Analysis of the mammary tumor responses for the six studies conducted in female Sprague-Dawley rats suggests that lifetime exposure to feeding levels in excess of 400 ppm would be required for tumor production. In addition, the mechanism by which this highly varied strain and species-specific response is produced has a receptor-mediated threshold; therefore; risk assessment for this tumor should be conducted using the traditionally safety factor approach.



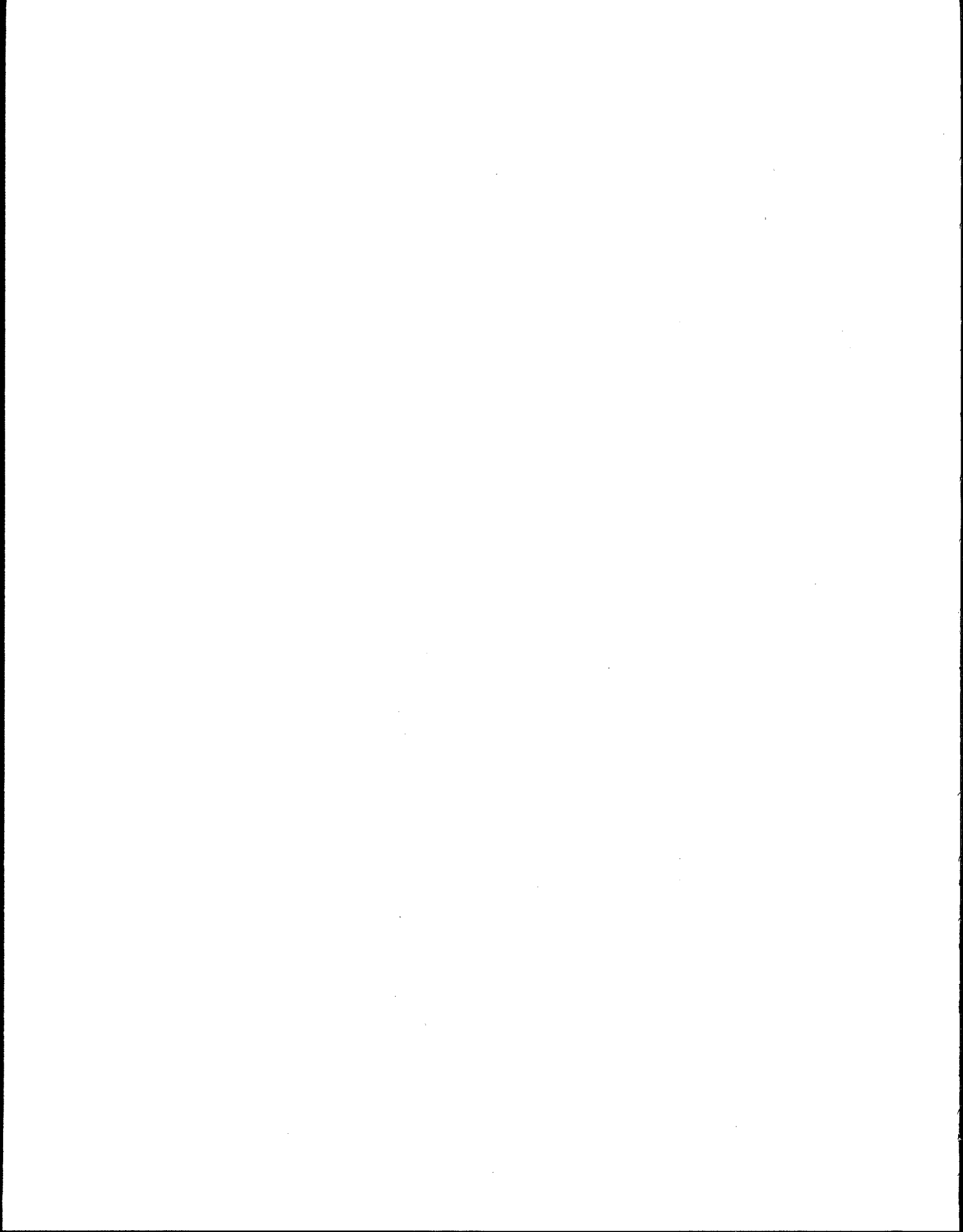
## **ECOLOGICAL IMPACTS OF HERBICIDES--A REVIEW**

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**Donald Huggins, Aquatic Ecotoxicology Program, Kansas Biological Survey,  
Lawrence, Kansas**

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(Abstract not received in time for publication)



## **WEED-CONTROL OPTIONS FOR REDUCING ATRAZINE IMPACT**

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**David L. Regehr, Kansas State University, Manhattan, Kansas**

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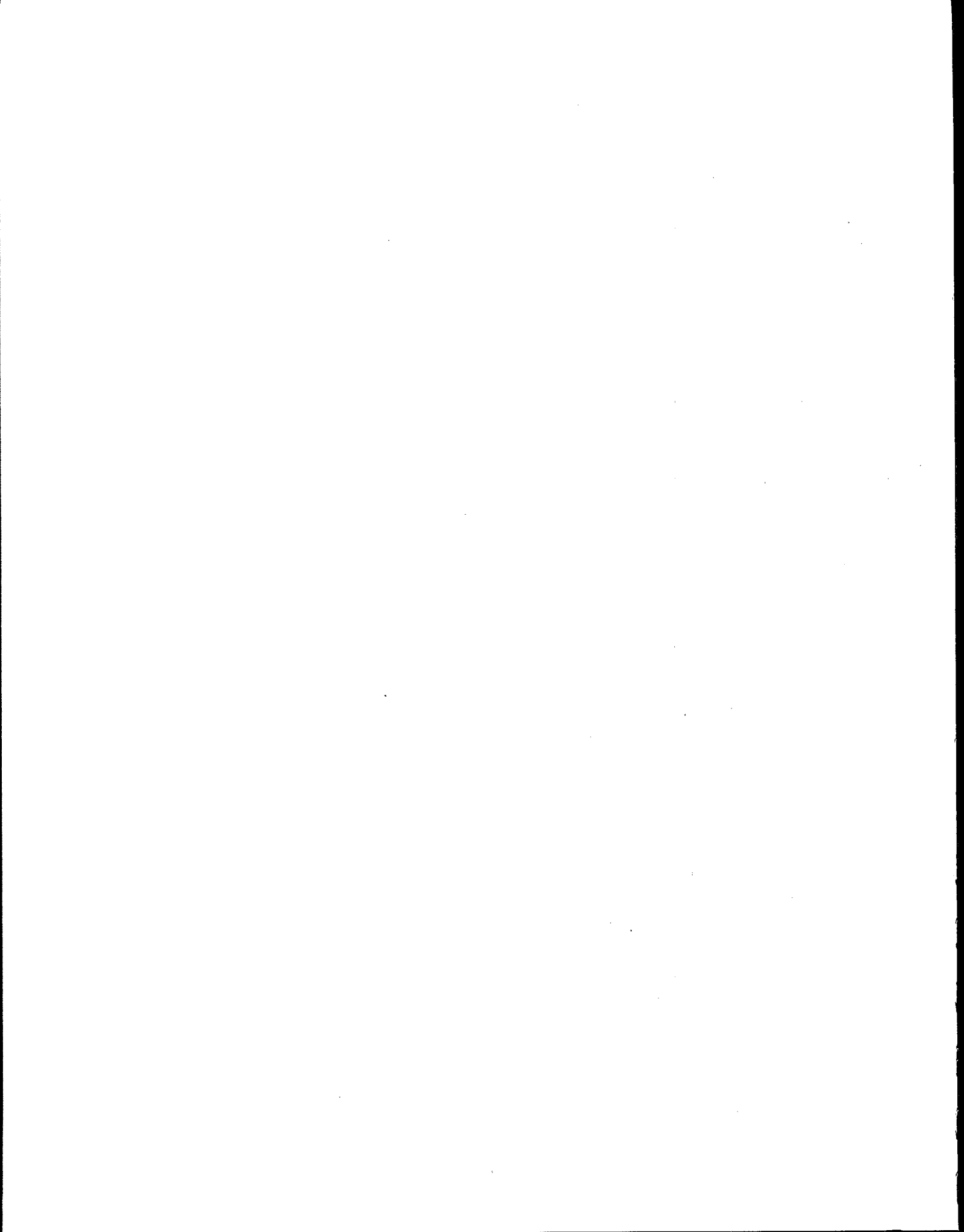
Atrazine herbicide remains an important component of weed management in Kansas, where it is applied to 71 and 74% of sorghum and corn acres, respectively. This widespread use reflects the efficacy, favorable economics, and risk avoidance that corn and sorghum producers seek for weed management.

Vulnerability of atrazine to field loss via surface-water runoff is a function of the field's erosion potential and plant-residue cover. In environmentally vulnerable areas, we recommend switching from higher rates of soil-applied atrazine, to rates of 1 lb/acre or less soil-applied, followed by foliar-applied herbicides that contain about 0.5 lb/acre atrazine. This atrazine use provides superior control of tough broadleaf weeds like velvetleaf, cocklebur, and sunflower and has been adopted by many corn and sorghum producers. It does require field scouting to determine weed pressure and size, and additional application and herbicide costs.

Recent changes in the atrazine label prohibit application in certain "set-back" areas where field-surface runoff enters streams, ponds, and tile-outlet terraces. Crop producers who want to continue atrazine use near those areas are encouraged to establish vegetated buffer zones that delay entry of field runoff into drainage ways. Or, producers may choose to rely more heavily on alternatives to atrazine for weed control.

Dicamba and 2,4-D have limited potential as substitutes for atrazine because of their potential for sorghum and corn injury. Several new herbicide alternatives to atrazine are being developed by the agrichemical industry. These compounds appear to be environmentally benign but are based on a mode of action that appears highly vulnerable to selection of resistant weed biotypes.

A key to reducing dependence on atrazine is integrated weed management where crop rotation, highly competitive crops, and a vigorous weed-management effort, including tillage and herbicides, combine to reduce weed pressure. Once weed pressure is reduced, low rates of foliar-applied atrazine and band-applying herbicides at planting and cultivation become more attractive options.





## **IMPACT OF CONSERVATION TILLAGE SYSTEMS ON AGRICULTURAL RUNOFF**

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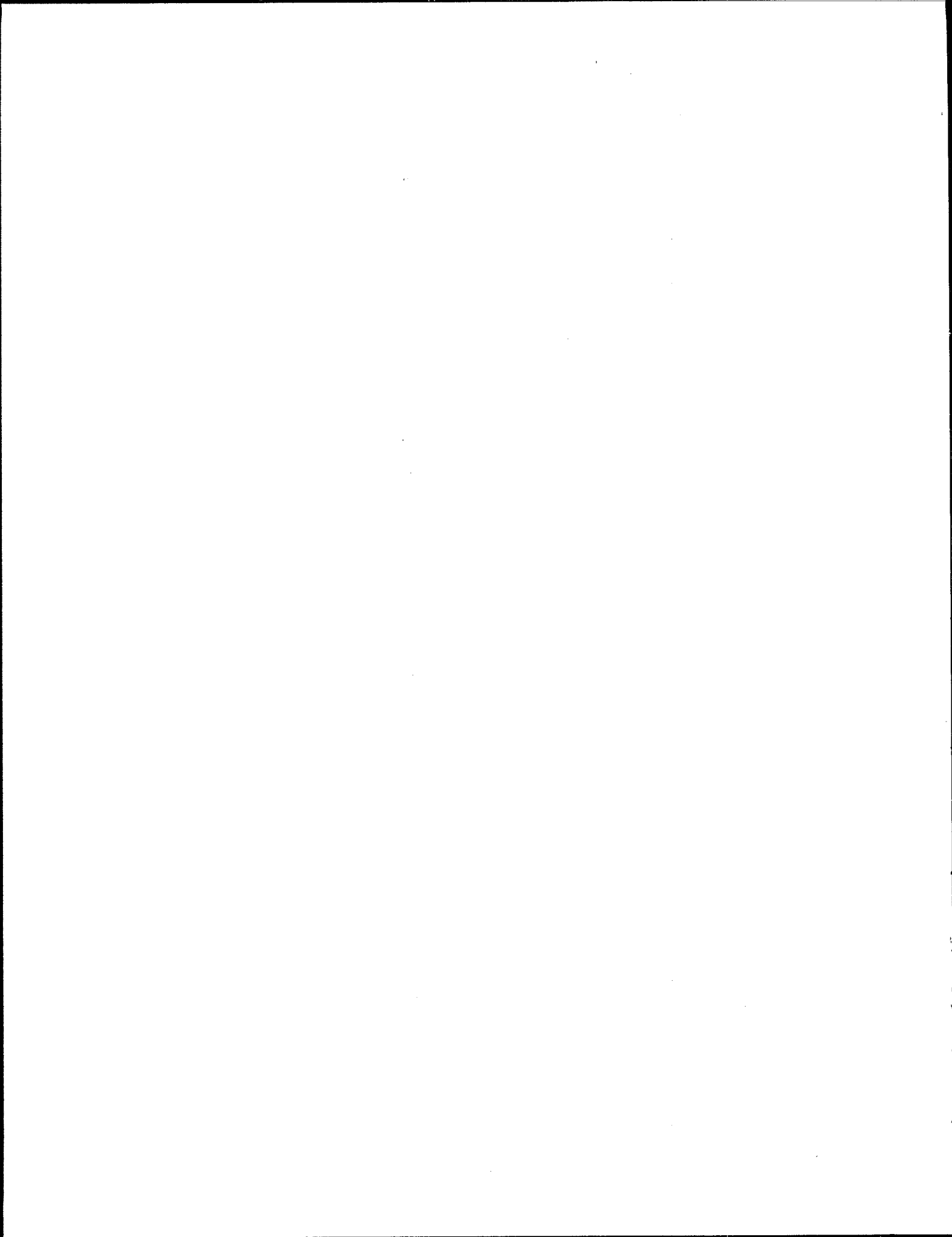
**D.W. Rushing, Monsanto Agricultural Company, Des Moines, Iowa**

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During the past several years, ground water has received most of the attention when the issue of water quality has been discussed. However, surface water is actually far more vulnerable and often more contaminated. More than half of the U.S. population drinks surface water, including many larger cities. Wells contaminated by herbicides have often been traced to point sources at mixing and disposal sites or from accidental spills. But contamination of surface water is largely a nonpoint-source problem. As soil erodes and water runs off fields, herbicides are carried with it, either adsorbed to the soil particles or dissolved in the water. Some commonly used soil-applied herbicides runoff with water rather than attaching to soil sediment. Reducing soil erosion alone will not entirely solve the problem of surface-water contamination. Most soil conservation practices slow or reduce water runoff, explaining why herbicide detections are reduced by practices such as conservation tillage, filter strips, and waterways.

Midwestern university results indicate conservation tillage significantly reduces herbicide runoff. Long-term no-tillage sometimes totally eliminated water and herbicide runoff by allowing greater water infiltration. Averaging all natural rainfall studies, no-till reduced herbicide runoff by 70%. Ridge till and chisel plowing also reduced runoff. Reducing soil erosion will often protect surface-water supplies from herbicide runoff. A 15-foot wide grass filter strip reduced atrazine runoff from a conventionally tilled field by 78% compared to a tilled field without a filter strip. Other best-management practices currently in place should also aid in protecting water supplies. These include "no spray zones" around points of entry into water bodies and tile inlet drains, limits on early preplant applications, application restrictions near lakes and reservoirs, and herbicide rate reductions.

There are a number of Federal, State, and industry supported programs that encourage farmer adoption of best-management practices. One such program is Monsanto's Operation Green Stripe, which, along with local FFA chapters, provides incentives for farmers to establish vegetative filter strips along streams, rivers, lakes, and around sinkholes. The project will involve over 500 farmers in seven states in 1993.



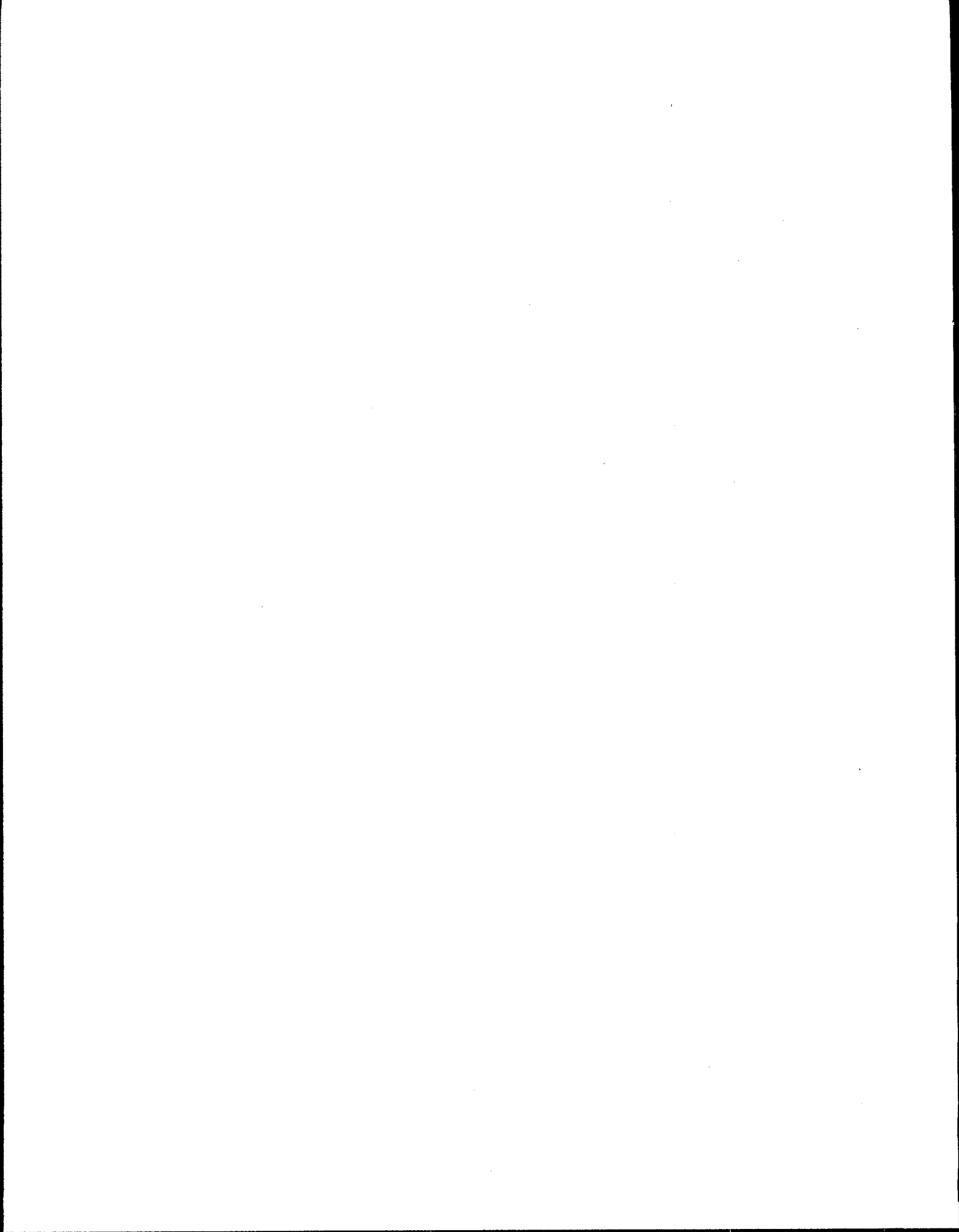
## PESTICIDE INCORPORATION AND TILLAGE AFFECTS ATRAZINE AND ALACHLOR LOSSES

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James Steichen, Philip Barnes, Hirozumi Watanabe, Kansas State University, Manhattan, Kansas, Elbert Dickey, David Shelton, Paul Jasa, and Nathan Watermeier, University of Nebraska-Lincoln, Lincoln, Nebraska

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The effect of tillage practice and the method of chemical application on atrazine and alachlor losses through runoff and erosion were evaluated on five treatments--no-till and pre-emergent (N.P), disk and pre-emergent (D.P), plow and pre-emergent (P.P), disk and pre-plant incorporated (D.I), and plow and pre-plant incorporated (P.I) treatments. A rainfall simulator was used to create 63.5 mmhr<sup>-1</sup> for 15 minutes. Rainfall simulation occurred 24-36 hours after chemical application. The concentration of herbicides in the water decreased with time. No-till treatments had the highest concentration, and disk treatments were higher than plow treatments. The pre-emergent treatment showed higher concentration than incorporated. Total herbicide loss of atrazine ranged from 0.08 kg ha<sup>-1</sup> (5.2% of applied mass for N.P treatment) to 0.007 kg ha<sup>-1</sup> (0.4% of applied mass for P.I treatment) and that of alachlor ranged from 0.14 kg ha<sup>-1</sup> (6.1% of applied mass for N.P treatment) to 0.01 kg ha<sup>-1</sup> (0.4% of applied mass for D.I treatment). No-till, pre-emergent treatments had the highest loss. For no-till, 98% of atrazine loss and 97% of alachlor loss occurred in the runoff water. Reducing both runoff and erosion contributes to reducing herbicide losses.



# **IMPACT OF CONSERVATION PRACTICES ON AGRICULTURAL NONPOINT CONTAMINATION**

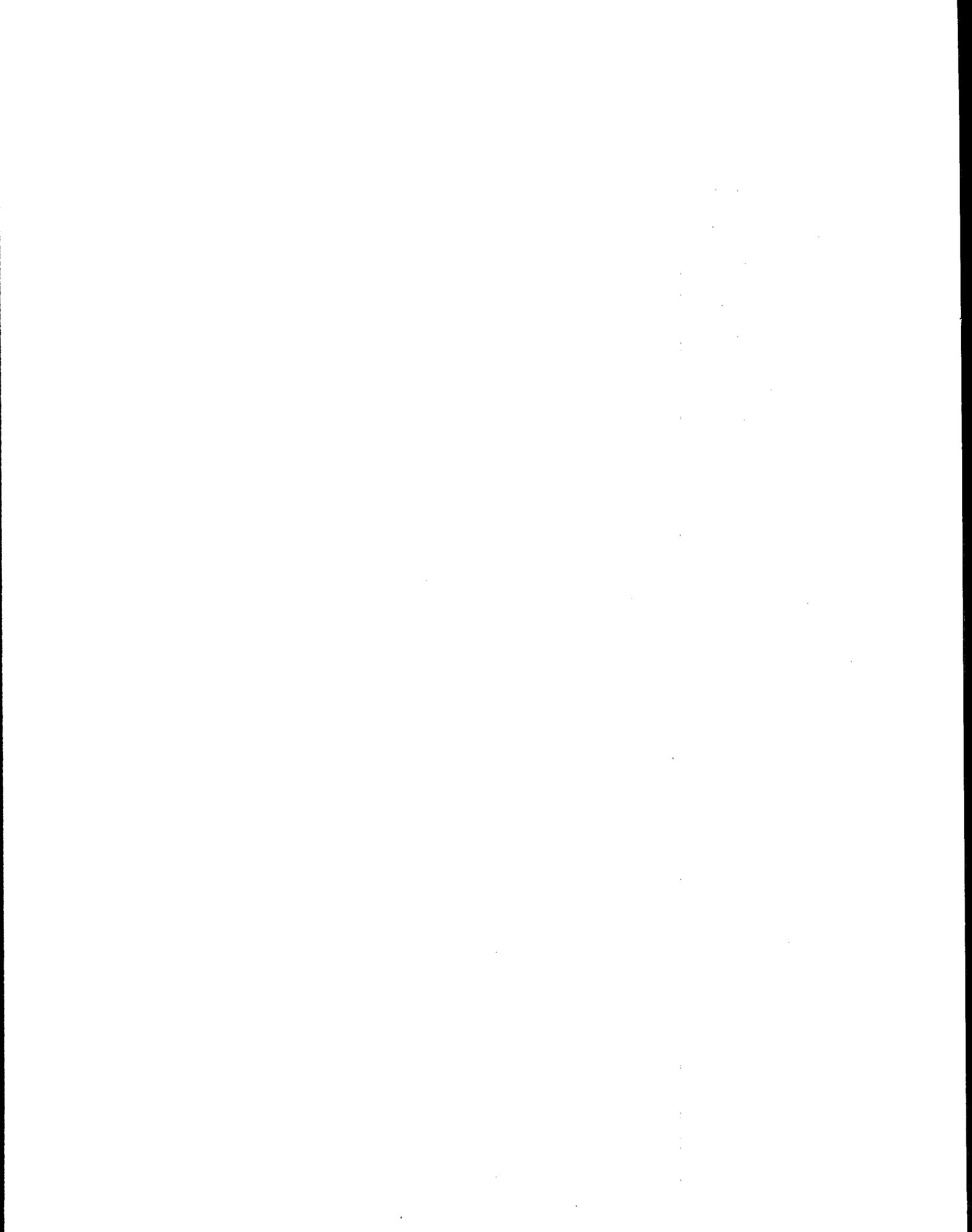
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**Philip L. Barnes, Kansas State University, Topeka, Kansas Mike Pope, and Andy Foster,  
U.S. Geological Survey, Lawrence, Kansas**

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The U.S. Department of Agriculture has developed conservation practices to reduce soil loss to surface runoff. The practices include terracing, crop-residue management, and contour farming. During the development and testing of terrace designs, the water that was caught by the terrace was moved off the field by grassed waterways. It was felt that if erosion could be reduced that nutrient and pesticide losses would also be reduced. Recent government programs have allowed the grass waterways used to channel water away from terraces to be replaced by tile outlets. These tile outlets hold the water in the terrace channel long enough to deposit sediments and then the water is rapidly transported off the field through the tile.

A majority of the herbicides used today are relatively soluble in water. When rainfall causes surface runoff from fields, it is carrying both sediments and herbicides. In the past, terraces drained into grass waterways that filtered the herbicides in the runoff water. Research would indicate that the tile-outlet terrace system may be a new source of nonpoint contamination.



# **FEDERAL, STATE, AND LOCAL COOPERATION TO IMPROVE SURFACE-WATER AND GROUND-WATER QUALITY: A CASE STUDY FROM RECHARGE LAKE IN YORK COUNTY, NEBRASKA**

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**Robert A. Dunlevy, U.S. Environmental Protection Agency,  
Kansas City, Kansas**

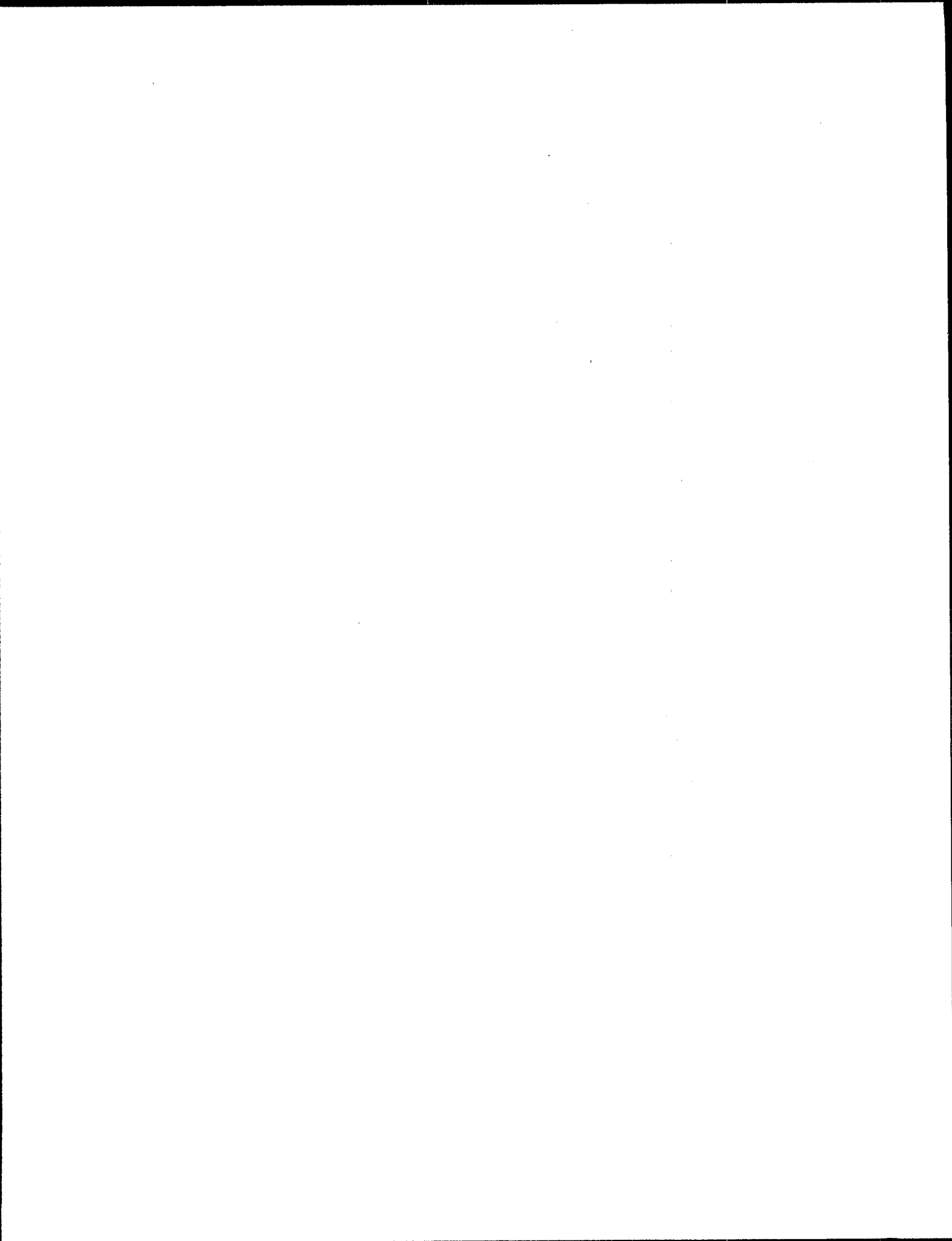
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Several Federal, State, and substate water-resource agencies are working together to reduce the impact of pesticide residue on ground-water quality at the York Groundwater Recharge Demonstration Project near York, Nebraska. This work is being performed while continuing to demonstrate the feasibility of recharging the ground water. The York Project is one of the Bureau of Reclamation's original 21 projects in the High Plains States Groundwater Recharge Demonstration Program.

Recharge Lake, a reservoir constructed to provide a supply of active and passive recharge water, is surrounded by ground-water monitoring wells. The monitoring wells are used to evaluate the success of the ground-water recharge efforts through the measurement of the ground-water elevations and to sample the ground-water quality.

Sampling of the lake water following 1991 and 1992 spring storm-runoff events indicated several pesticides, particularly atrazine, exceeded their Maximum Contaminant Level (MCL) in the reservoir. Samples from the ground-water monitoring wells also indicated higher pesticides levels, several above their MCL. Currently, there are no recharge activities at the project; any pesticides entering the ground water is from the seepage through the lake bottom.

The concern is that the lake is recharging the ground water with pesticides, and this process may be occurring in other impoundments throughout the Midwest and could affect the beneficial uses of ground water. Federal, State, and substate agencies along with private industry are combining their efforts and resources to study the surface and subsurface hydrodynamics. The information gathered will be used to develop a plan to reduce the pesticides in the surface runoff and subsequently the ground water.





## **MANAGEMENT OF HERBICIDES IN THE DELAWARE RIVER BASIN**

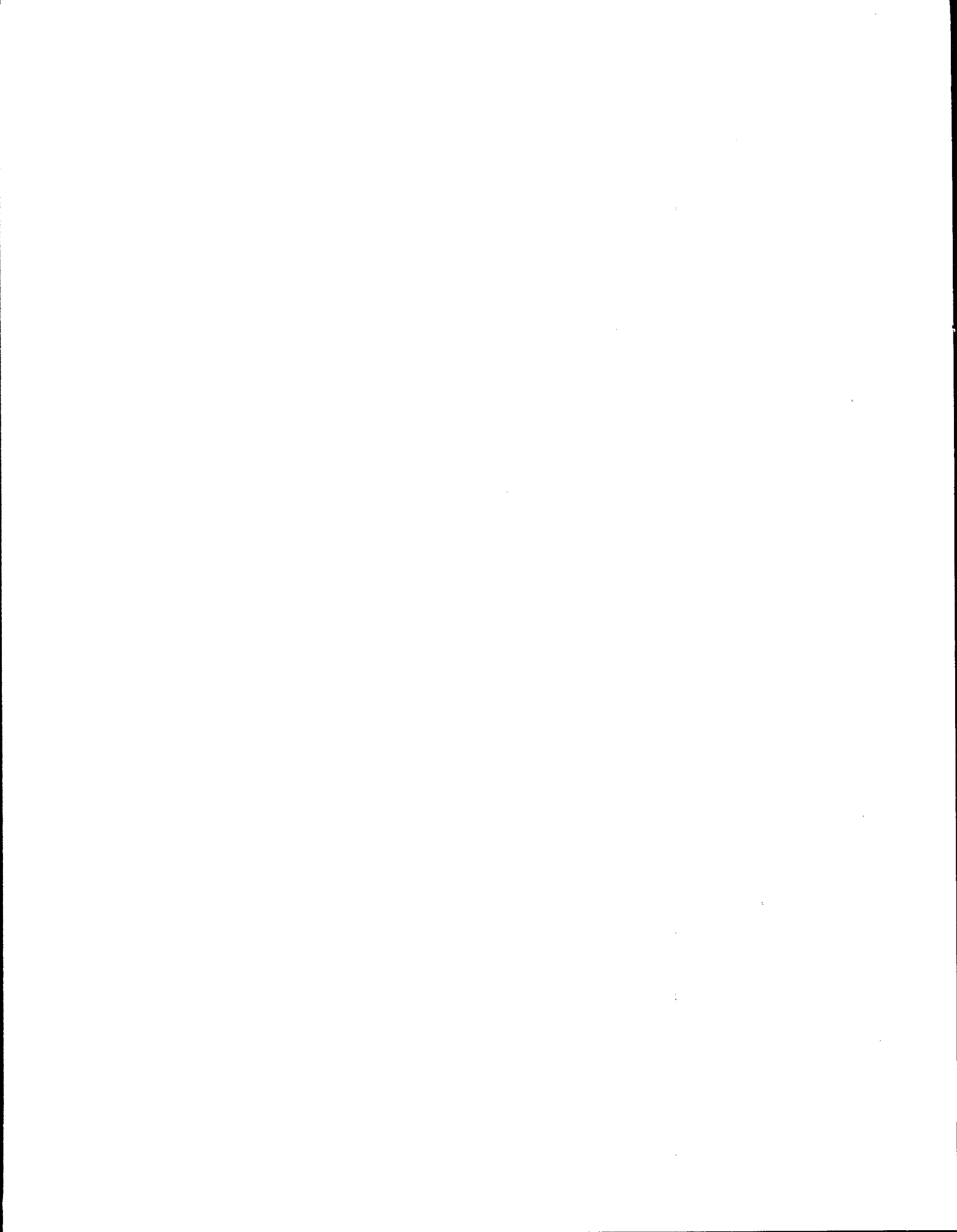
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**Jane Niehues, Steering Committee for the Non Point Pollution Plan for the Delaware River Basin, Goff, Kansas**

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Atrazine concentrations in Perry Lake, a reservoir within the Delaware River drainage basin, have become a concern to farmers, water suppliers, and regulators. As a result, a Pesticide Management Area was formed and a Non Point Source Pollution Plan has been developed. The committee that developed the plan consists of one member of each Conservation District Board from Nemaha, Brown, Atchison, Jefferson, and Jackson Counties, and a representative from the Kansas Rural Center. The effort is being coordinated by the Glacial Hills RC&D.

This presentation will describe the atrazine problem within the Delaware Drainage Area, the formation of the Pesticide Management Area, and discuss the Non Point Source Pollution Plan. The discussion will include proposed methods to decrease atrazine runoff, such as: terraces, waterways, contouring farming, conservation tillage, integrated crop management, watershed dams, and application methods. A monitoring program is now in place and development of a proposed geographic information system also will be discussed.



## **WEST LAKE WATER QUALITY PROJECT**

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**Alan Teel, Iowa State University of Science and Technology, Osceola, Iowa**

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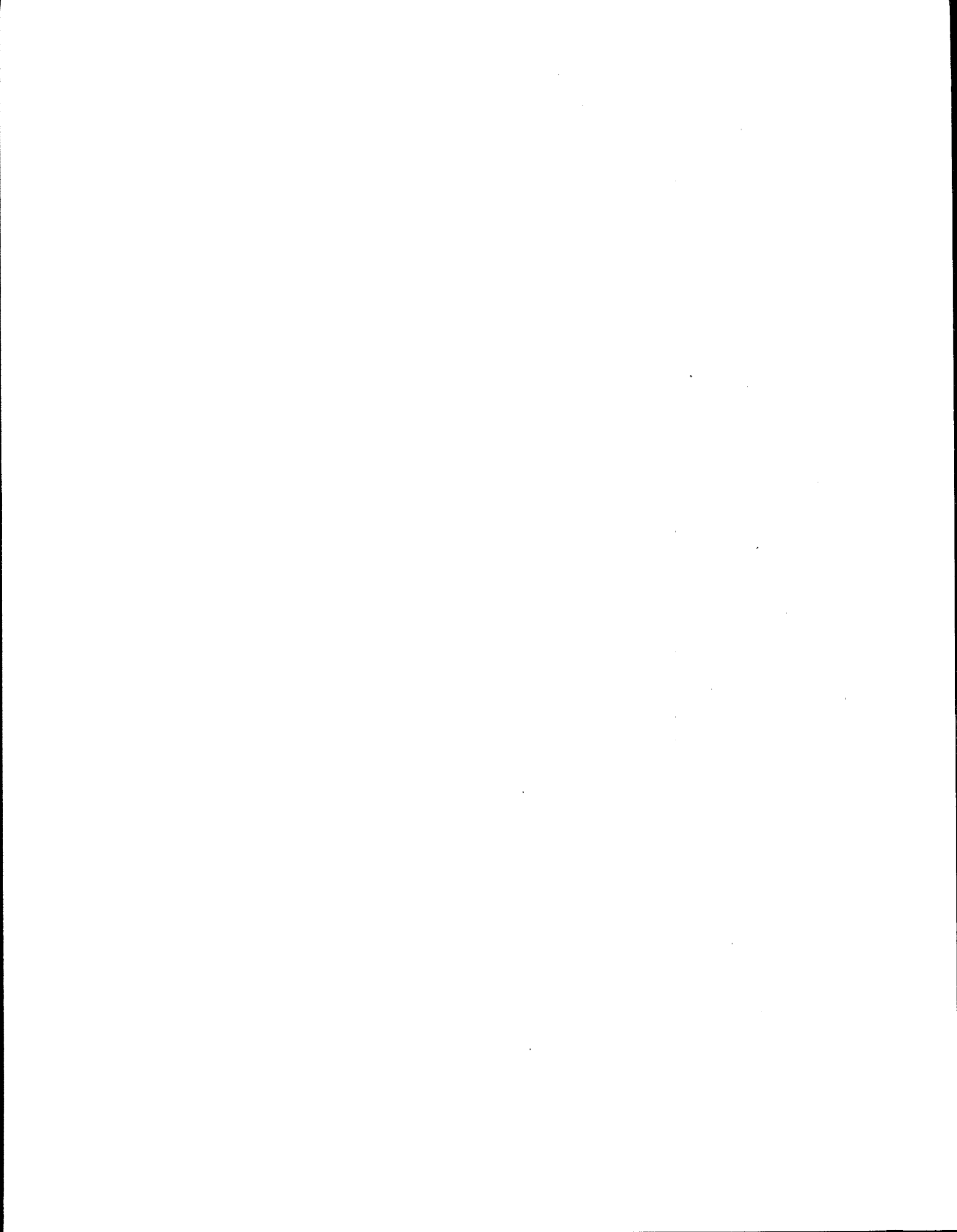
The West Lake Water Quality Protection Project began in November of 1990 and will continue until the fall of 1995. Planning for the project started in 1988. Funding for the project is through the U.S. Environmental Protection Agency section 319 funding. Cooperating agencies are the Iowa Department of Agriculture and Land Stewardship, Division of Soil Conservation; the U.S. Environmental Protection Agency; the Clark County Soil and Water Conservation District; and the Iowa State University Extension Service.

The West Lake Water Quality Project's primary objective is to preserve, protect, and improve the West Lake reservoir for use as a municipal, industrial, and rural water supply, and as a fish, wildlife, and recreational resource. Additionally, we want to achieve a level of project participation and practice adoption that will result in significant water-quality protection within the 5-year project period and to demonstrate the technical and economic feasibility and the effectiveness of the resource management practices being used as part of this project in hope that these practices will be adopted as permanent practices in the cooperator's farming operation.

The project will market pre-packaged basic conservation systems that reduce soil loss to "T." Financial incentives paid up-front to producers who enter into a 5-year compliance agreement will help to secure producer participation. An integrated crop-management program will be provided for each cooperating producer. Additionally, an informational program will be put in place to include field days and educational meetings.

Eleven hundred and thirty-six (1,136) acres are now under contract agreement, and an additional 575 acres have been designated as "volunteer compliance" acres. These volunteer compliance acres are being managed in compliance with project guidelines but are not under an agreement and are not receiving any payments. Thirteen educational classes have been conducted, 1 field day, 7 news articles, 1 television interview, and 15 radio programs have been generated via this project.

Providing "up front" funding for producers appears to be a viable way to attract the participation of producers in the West Lake watershed in soil conserving practices. The inclusion of Integrated Crop Management practices has helped in facilitating the soil conserving practices. Active informational and educational programs have increased the public's awareness of the project and have helped to support producers in the decision-making process.



# **INFLUENCE OF MANAGEMENT PRACTICES ON WATER QUALITY IN WALNUT CREEK WATERSHED**

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**J.L. Hatfield<sup>1</sup>, R.C. Buchmiller<sup>2</sup>, P.J. Soenksen<sup>2</sup>, and D.B. Jaynes<sup>1</sup>**

<sup>1</sup>**USDA - Agricultural Research Service, National Soil Tilth Laboratory, Ames, Iowa.**

<sup>2</sup>**U.S. Geological Survey, Iowa City, Iowa.**

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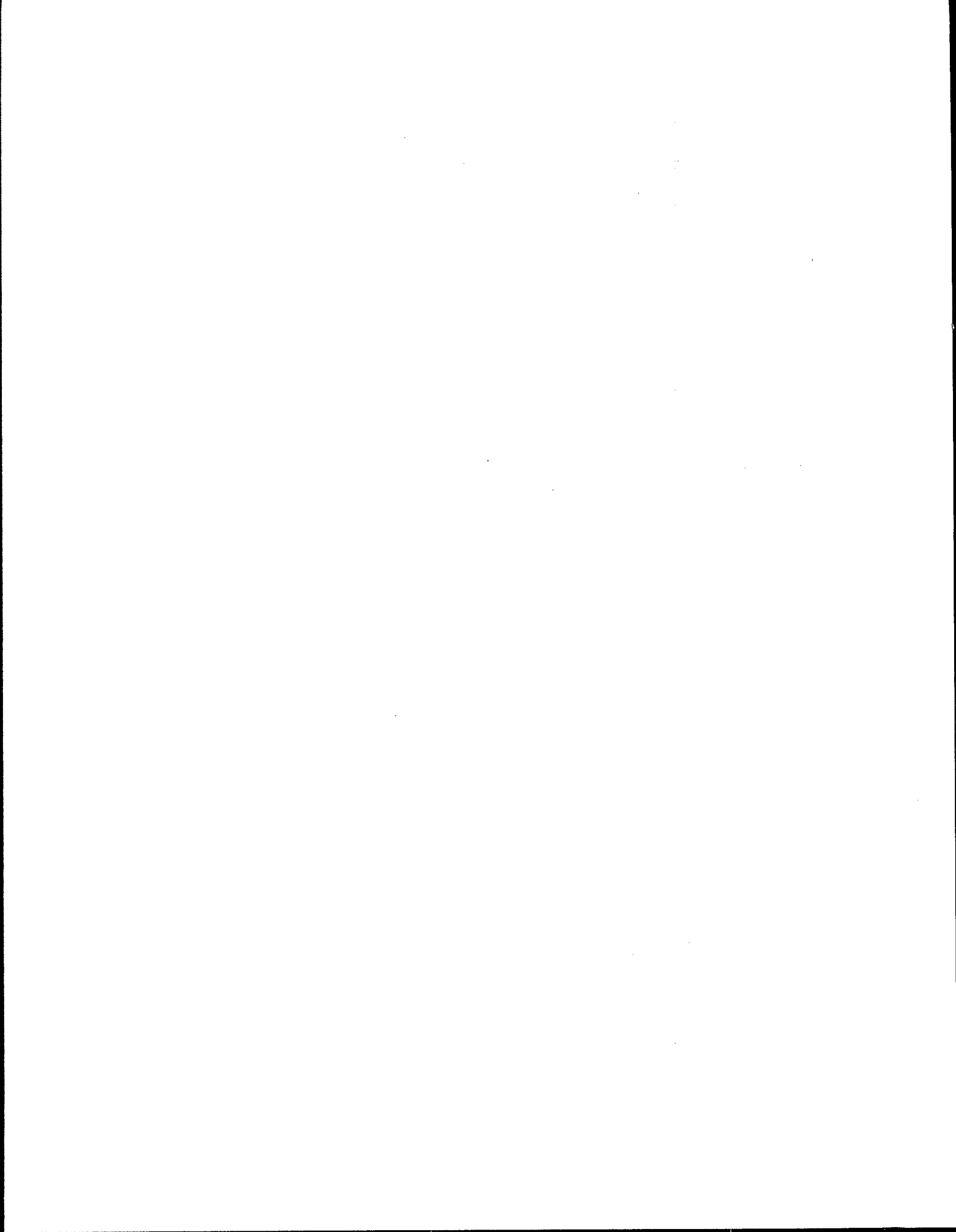
Influence of farming practices on both surface- and ground-water quality is difficult to quantify on a field and watershed scale; however, it is apparent that a linkage exists between different farming practices and their potential effect on water quality. To evaluate the impact of different farming practices, a study was designed in a large agricultural watershed to investigate the seasonal and positional variations in water quality.

Walnut Creek watershed is a 5,400-hectare watershed located south of Ames, Iowa, on the Des Moines landform region. This region is characterized by a relatively level surface with poorly defined surface-runoff features and an extensive number of prairie potholes. These potholes are poorly drained, and to remove the water from the soil profile, tile drain lines are placed throughout the watershed in a network. These drain lines remove water from the fields and route it to the stream. Walnut Creek as a stream empties into the Skunk River. There are a wide range of soils within the watershed ranging from moderately well-drained to poorly drained soils and a topography that varies from nearly level, e.g., less than 2% slope, to 5-7% slope in the lower reaches of the watershed.

The watershed is extensively farmed as a corn-soybean rotation system with field sizes that range from 20 to 150 hectares. Nearly 90% of the land area within the watershed is cultivated as a row crop. The inputs of chemical fertilizers and herbicides within the watershed are typical of the Corn Belt.

In 1991 a study began within the watershed to evaluate the current farming practices on water quality. Three stream-monitoring stations were installed to measure the stream discharge, water quality, and sediment load. Eight tile-monitoring locations were installed to measure both the discharge and the water quality. Surface-runoff flumes were installed in three fields. Over 40 well nests were placed around individual fields and subbasins to measure the quality of the ground water at depths from 2.5 to 15 meters. The agricultural chemicals being measured within the watershed include: atrazine, alachlor, cyanazine, metribuzin, metolachlor, and nitrate-nitrogen. These analytes are measured in stream, tile, well samples, and rainfall, as well as soil samples collected from individual fields.

There is a large seasonal variation in the concentrations of herbicides detected in the stream and tile drainage. This variation is related to the occurrence of surface runoff from the edge of fields or entry of surface water into the tile inlets. Base-flow concentrations in the tile and stream for the herbicides did not exceed the EPA limits. Nitrate-nitrogen values, however, ranged from 10 to 20 ppm throughout the year in the tile and surface water but did not exceed 5 ppm at well depths below 2.5 m. The seasonal variation in the nitrate-nitrogen concentrations is related to the rate of mineralization within these organically rich soils and has not shown an effect of the fertilizer application times. The different farming practices that are being examined will provide an insight into the loadings that are resulting from current practices and will be used to determine the extent to which improvements in water quality can be achieved.



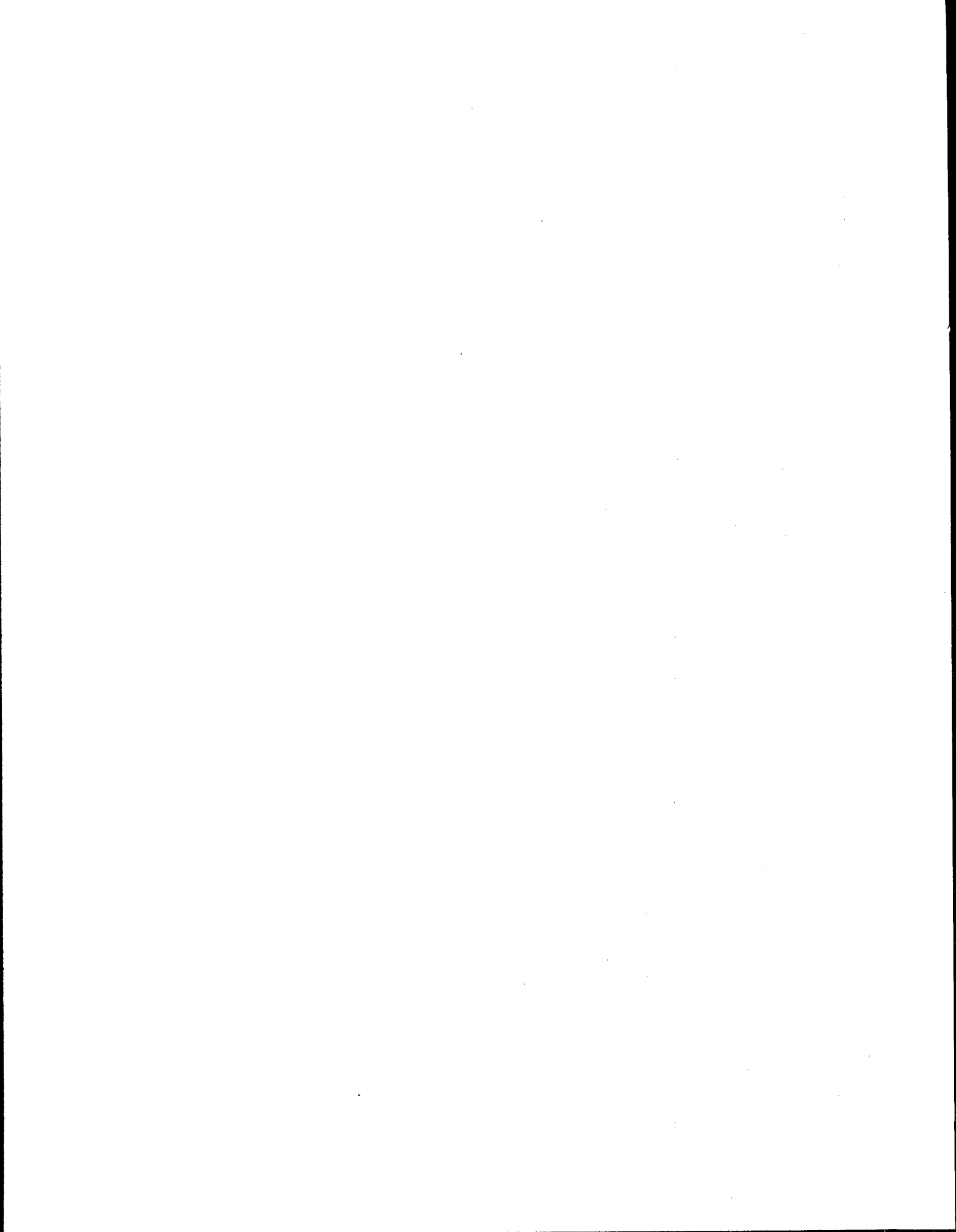
## **UTILIZING FERTILIZER AND CHEMICAL DEALERS TO MANAGE PESTICIDES**

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**Duane Sand, Director, Long Range Planning and Research, Iowa Natural Heritage  
Foundation**

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(Abstract not received in time for publication)





**Posters on Display during Tuesday Social Hour**  
**Coordinator: Hyde Jacobs, Kansas State University**

*Water-Quality Characteristics of Stormwater Runoff in Davenport, Iowa*

Bryan Schaap and Keith J. Lucey, U.S. Geological Survey

*Isocratic Separation of Alachlor Ethane Sulfonic Acid, Alachlor Oxacetic Acid, and Hydroxatrazine by Reversed-Phase Liquid Chromatography*

Michael L. Pomes and E.M. Thurman, U.S. Geological Survey

*Chromatographic Applications of Solid-Phase Extraction in Developing Immunoassay Methods for Herbicides and their Metabolites: An Example for Alachlor and Alachlor-Ethanesulfonic Acid*

Diana S. Aga and E.M. Thurman, U.S. Geological Survey

*Use of a Geographic Information System Procedure to Estimate Atrazine Impact*

John Hickman, Ray E. McDonald, H.L. Seyler, and Michel D. Ransom, Kansas State University

*Estimating Pollutant Soil Ratings*

John Hickman, P.R. Finnell, and R.L. Schlepp, Kansas State University and U.S. Soil Conservation Service

*Reconnaissance Data for Herbicides and their Metabolites in Surface Water of the Midwestern United States: Immunoassay and Gas Chromatography/Mass Spectrometry*

Elisabeth A. Scribner, E.M. Thurman, and Donald A. Goolsby, U.S. Geological Survey

*Atrazine Management to Meet Water-Quality Criteria*

David L. Regehr, Dallas E. Peterson, and John S. Hickman, Kansas State University

*Effects of Pore-Size Distribution and Saturation Cycles on Atrazine and Bromide Transport through Soil*

E.A. Smith, P.J. Shea, W.L. Powers, and D.R. Tupy, University of Nebraska-Lincoln

*Selected Herbicides in Bottom Sediments of Water-Supply Reservoirs in Iowa*

Stephen J. Kalkhoff, U.S. Geological Survey; Jack Kennedy, University of Iowa Hygienic Laboratory; Ubbo Agena, Iowa Dept. of Natural Resources; George Breuer, University of Iowa Hygienic Laboratory

*The Comprehensive Environmental Economic Policy Evaluation System: An Application to Atrazine and Water Quality*

Aziz Bouzaher, Center for Agricultural and Rural Development and Andrew Manale, U.S. Environmental Protection Agency



## **WATER-QUALITY CHARACTERISTICS OF STORMWATER RUNOFF IN DAVENPORT, IOWA**

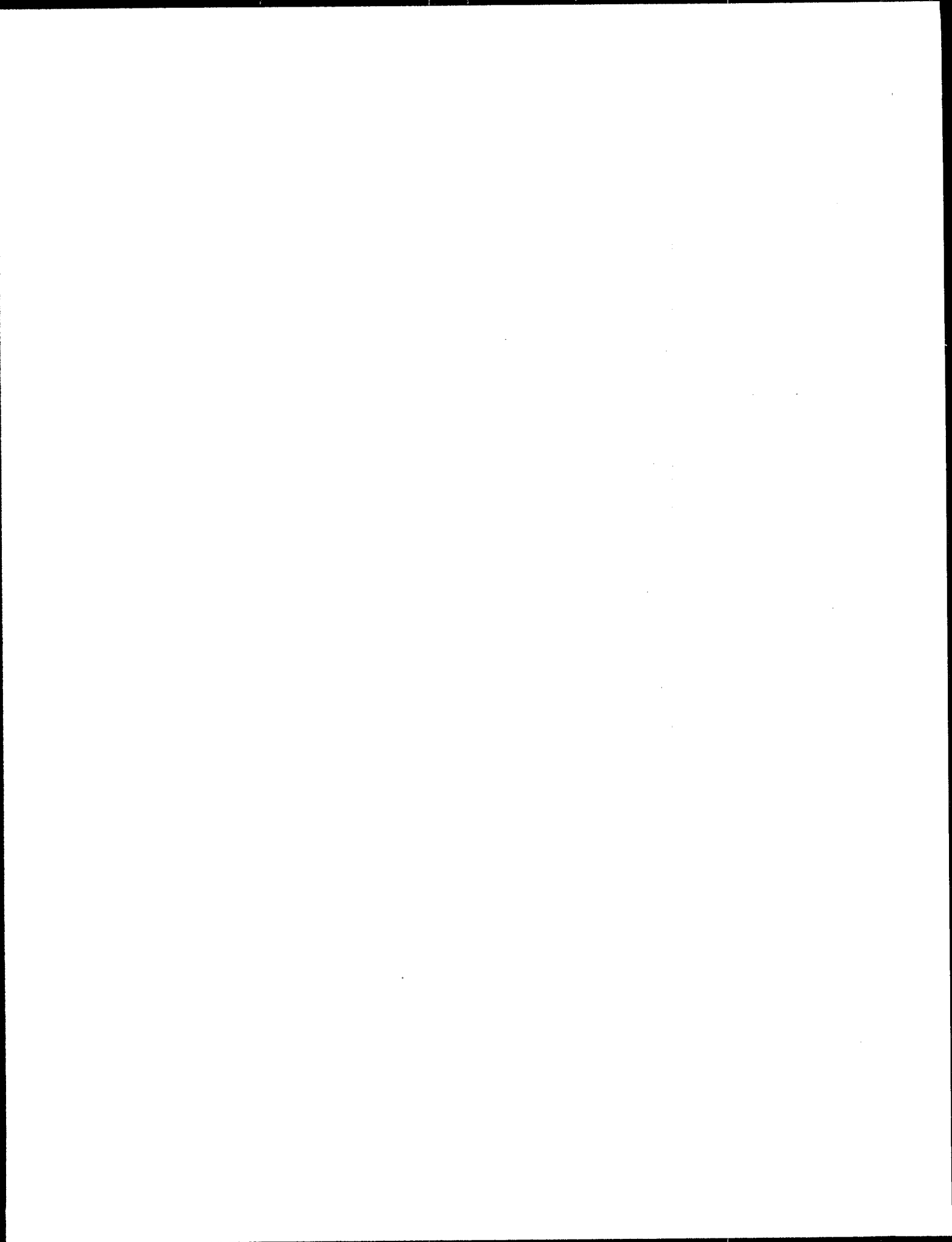
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**Bryan D. Schaap and Keith J. Lucey, U.S. Geological Survey, Iowa City, Iowa**

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To comply with U.S. Environmental Protection Agency (EPA) regulations to obtain a permit for stormwater discharges, the City of Davenport, Iowa, conducted an urban stormwater-runoff study in cooperation with the U.S. Geological Survey during the summer and fall of 1992. Five monitoring sites were selected to characterize the water quality of storm runoff from the following land-use types: agricultural, residential, commercial, industrial, and undeveloped areas. Three sets of stormwater-runoff samples were collected at each of the open-channel monitoring sites. Stormwater samples for a particular site were collected at least 30 days apart and after a 72-hour period had elapsed with less than 0.1 inch of rain. Rainfall totals for the events sampled varied from 0.09 to 0.48 inch from the beginning of the storm to the time the last sample was collected. Each set of samples consisted of both grab and composite samples. Grab samples were collected within the first hour of the runoff event and were analyzed for oil and grease, cyanide, bacteria, total phenols, and volatile organic carbons. Discrete samples, collected about every 15 minutes for the first 3 hours of the event, were used to produce flow-weighted composites that were analyzed for many constituents, including biochemical oxygen demand, chemical oxygen demand, total organic carbon, major ions, metals, acid/base-neutral organics, polyaromatic hydrocarbons, nutrients, and organo-chlorine pesticides.

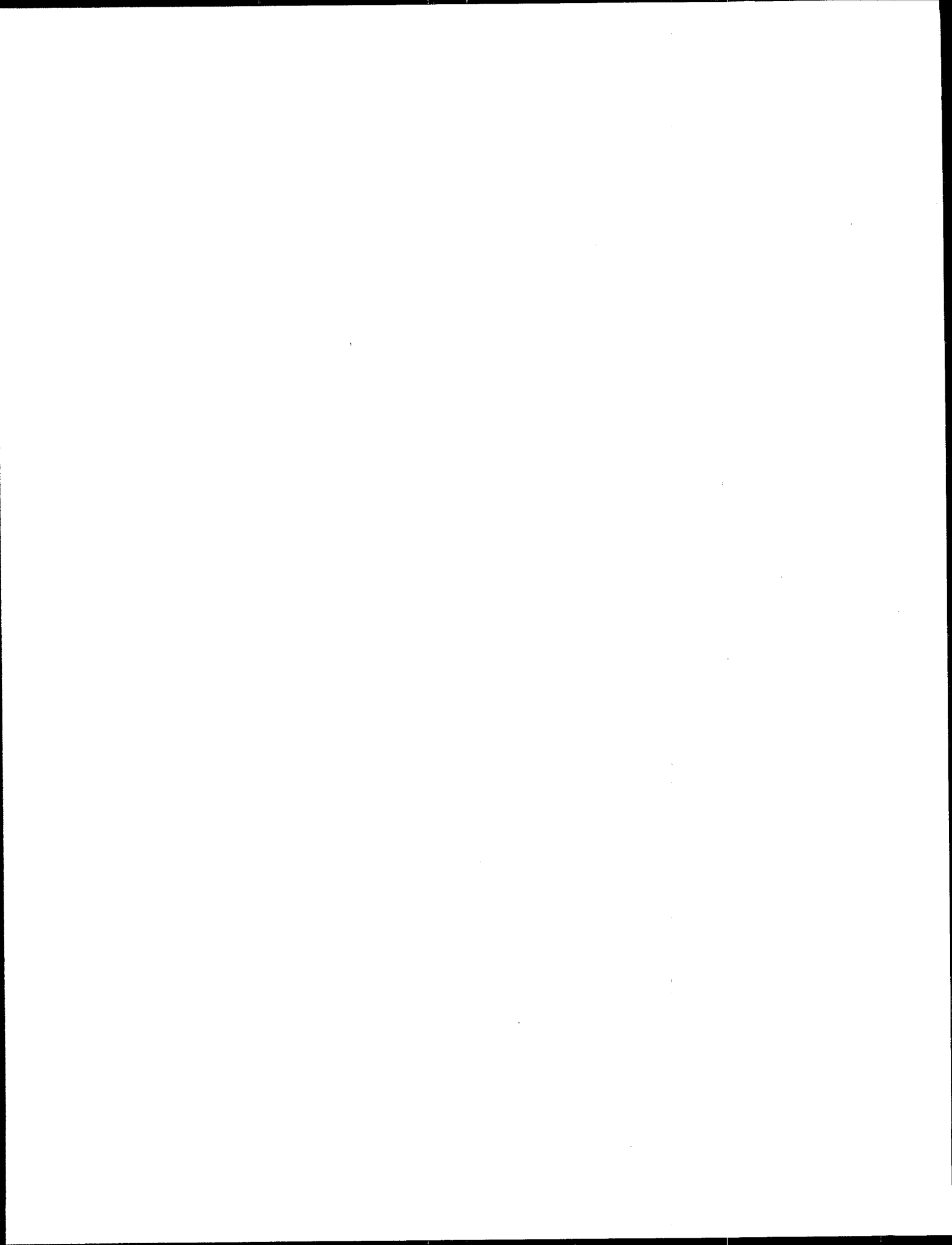
Total nitrogen and nitrate concentrations were greatest at the agricultural site. Metal concentrations (Ni, Pb, Zn) were greatest at the industrial site. Pesticide concentrations were less than the minimum reporting levels for single samples collected at the agricultural and residential sites and for two samples collected at the industrial site.



# ISOCRATIC SEPARATION OF ALACHLOR ETHANE SULFONIC ACID, ALACHLOR OXACETIC ACID, AND HYDROXYATRAZINE BY REVERSED-PHASE LIQUID CHROMATOGRAPHY

M.L. Pomes, D.F. Holub, and E.M. Thurman, U.S. Geological Survey, Lawrence, Kansas

The polar nature of two alachlor metabolites, alachlor ethane sulfonic acid and alachlor oxacetic acid, makes their detection by gas chromatography/mass spectrometry impossible without derivatization. Enzyme-linked immunosorbent-assay techniques cannot distinguish alachlor metabolites from alachlor; thus, reversed-phase high-pressure liquid chromatography with photodiode array detection is required for the separation and spectral detection of these analytes. Use of an isocratic methanol/10 mM (millimolar)  $\text{Na}_2\text{HPO}_4$  buffer mixture as the mobile phase with reversed-phase ( $\text{C}_{18}$ ) high-pressure liquid chromatography allows for the separation and detection of alachlor ethane sulfonic acid, alachlor oxoacetic acid, and hydroxyatrazine at concentrations greater to or equal to  $0.1 \mu\text{g/L}$  using 100-milliliter water samples. The buffer in the methanol mixture provides cations that ion pair with the alachlor metabolite anions to decrease polarity and promote nonpolar interactions between the analytes and the reversed-phase column. Enhanced chromatographic resolution results from injecting samples in a matrix that contains proportionally less methanol than the mobile phase. The disparity between methanol contents of the sample matrix and mobile phase focuses the analytes at the head of the chromatographic column to produce sharper peaks because the analytes are less soluble in the sample matrix than in the mobile phase. Results by reversed-phase high-pressure liquid chromatography show that alachlor ethane sulfonic acid is frequently found in surface water, with lesser concentrations of alachlor oxoacetic acid and hydroxatrazine.



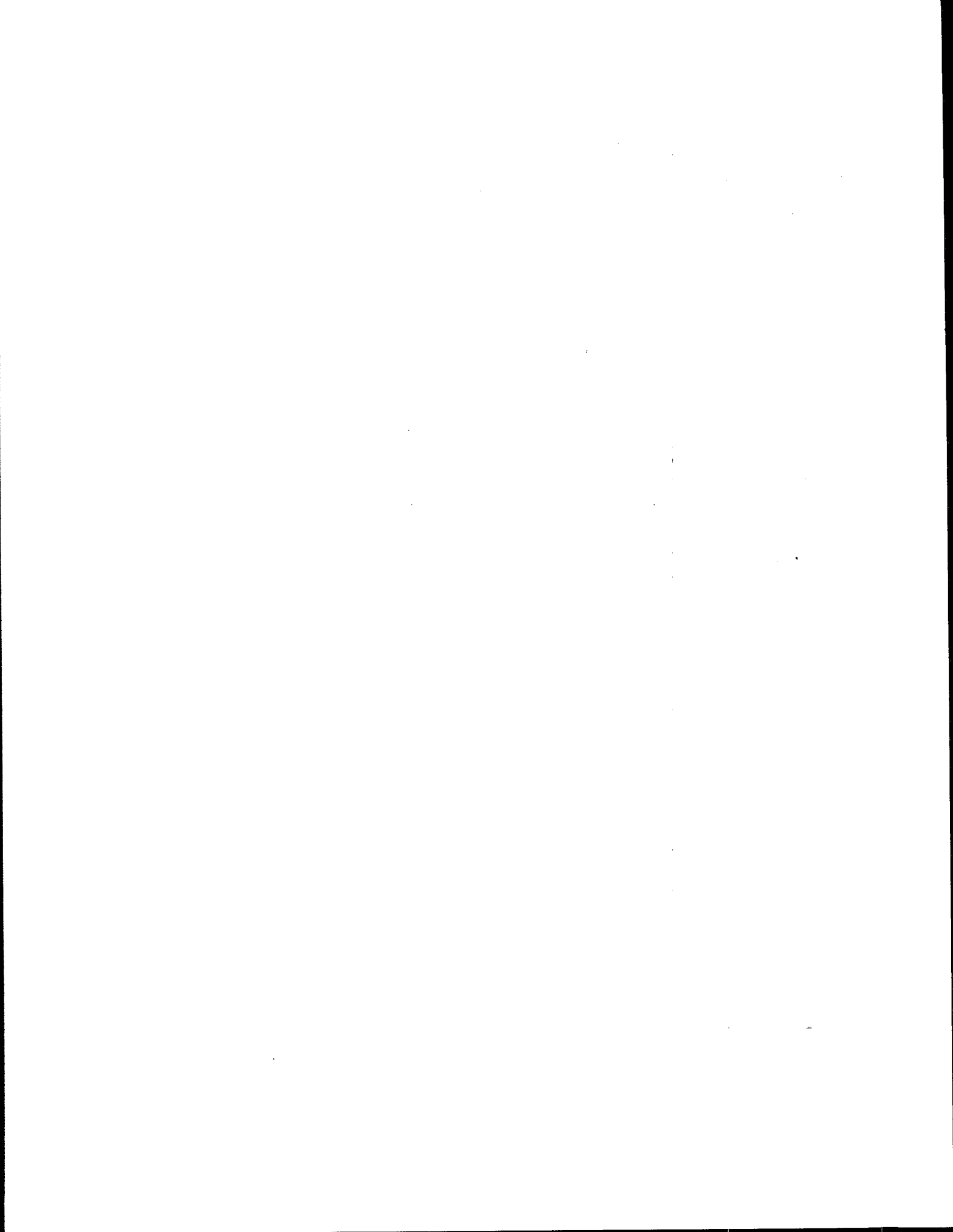
# **CHROMATOGRAPHIC APPLICATIONS OF SOLID-PHASE EXTRACTION IN DEVELOPING IMMUNOASSAY METHODS FOR HERBICIDES AND THEIR METABOLITES: AN EXAMPLE FOR ALACHLOR AND ALACHLOR-ETHANESULFONIC ACID**

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**D.S. Aga and E.M. Thurman, U.S. Geological Survey, Lawrence, Kansas**

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The resolving property of solid-phase extraction (SPE) and the sensitivity of enzyme-linked immunosorbent assay (ELISA) were combined to produce a highly selective and ultra-sensitive analytical technique for the analysis of ultra-trace levels of the herbicide alachlor and its metabolite, alachlor-ethane sulfonic acid (ESA). The high cross reactivity of the anti-alachlor antibody towards ESA was used as a positive feature, rather than a drawback, for developing a method for both the parent compound and the metabolite. Alachlor and ESA were separated using SPE by sequential elution with ethyl acetate followed by methanol. The ethyl acetate effectively elutes the alachlor while leaving the ESA adsorbed in the C<sub>18</sub> resin. The succeeding elution with the more polar solvent methanol removes more than 95% of the ESA from the resin. The extracts were evaporated to dryness and re-dissolved in water/methanol (80/20) for analysis by ELISA. The method has a detection limit of 0.01 µg/L for alachlor and 0.05 µg/L for alachlor-ESA, with a precision of ± 10%. Results obtained from the analysis of surface- and ground-water samples were confirmed by high-performance liquid chromatography with photodiode array detection and gas chromatography/mass spectrometry, and results agreed to within ± 10%.





# **USE OF GEOGRAPHIC INFORMATION SYSTEM PROCEDURE TO ESTIMATE ATRAZINE IMPACT**

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**John S. Hickman, Ray E. McDonald, H.L. Seyler, and Michel D. Ransom, Kansas State University, Manhattan, Kansas**

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Kansas is the first State in the Nation to form a Pesticide Management Area to address elevated pesticide concentrations in surface waters. A Pesticide Management Area was formed for atrazine in the Delaware River watershed in northeast Kansas. Atrazine management practices, conservation practices, and riparian management are considered as pollution-control practices to reduce atrazine runoff. A geographical information system procedure is being used to evaluate data for atrazine impact analysis in the Delaware River watershed. Important data layers include soils, land cover, and hydrology.

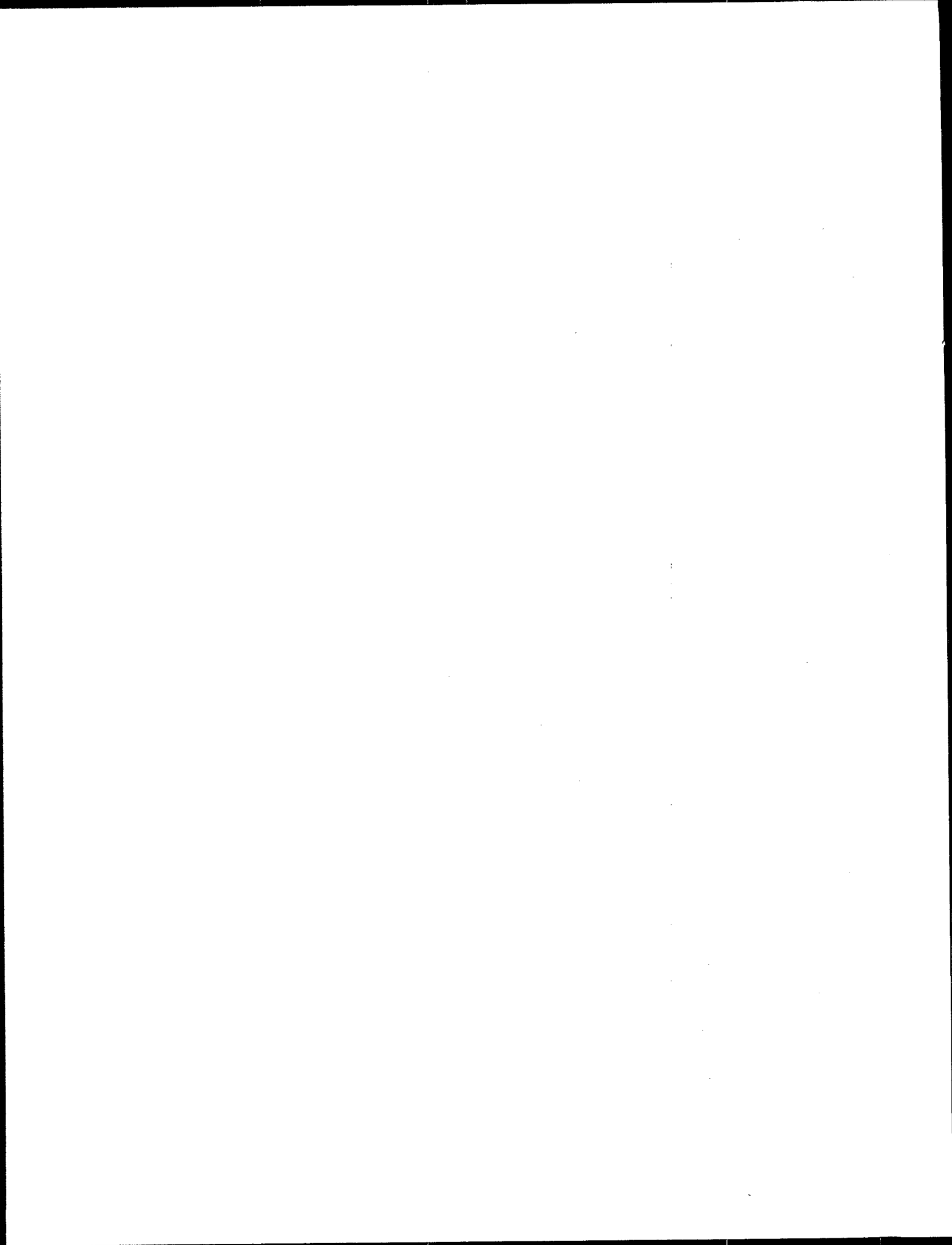
The study area consists of three subwatersheds within the Delaware River watershed (Grasshopper Creek, Coal Creek, and Cedar Creek). Three digitized data layers and accompanying data bases (soils, land cover, and hydrology) were combined using ARC/INFO. The soils data layer is being digitized at the Kansas State University GISSAL (GIS Spatial Analysis Laboratory) at a 1:24,000 scale. Soil digitization is part of a separate project to complete digitization of soils in Kansas. Atrazine loss potential was estimated using hydrologic groups, with hydrologic group D soils having the most severe solution-loss potential and hydrologic group A soils the least. Hydrologic group has proven to be a good indicator of pesticide solution-loss potential. Highly erodible land status was also determined for each soil mapping unit. It should be noted that mapping highly erodible land status by soil mapping units is not representative since actual status is determined on a field basis.

The land-cover data layer was digitized at the Kansas Applied Remote Sensing laboratory at the University of Kansas. Land cover was determined from 30-meter LANDSAT images taken in 1988. Five classes of land-cover data were considered: cropland, grassland, woodland, water, and other. The hydrology data layer was traced from 7.5-minute U.S. Geological Survey quadrangles. Information was scanned and imported into ARC/INFO. Twenty and four (24)-meter buffers were created around hydrology features.

The geographic information system procedure proved valuable in estimating potential impact of atrazine loss to surface water. There were some discrepancies between the soil, hydrology, and land-cover data, especially relative to water features. Also, the digital land-cover data contained some polygons that had too many arcs for PC ARC/INFO version 34d. This information had to be read and clipped using a workstation version of ARC/INFO.

Digitized soil information enabled rapid display of atrazine loss potential. Addition of digitized land-cover information identified cropland, the land cover most likely to receive applications of atrazine. Soil erodibility status provided information on practices that can be used to reduce atrazine runoff. Highly erodible soils have conservation requirements needed to meet the conservation compliance provision of the 1985 Farm Bill. Such soils rely on structural and residue management practices to meet soil-erosion goals. Such practices also help reduce atrazine runoff losses. There was some non-highly erodible cropland identified with a severe atrazine runoff loss potential. Non-highly erodible soils have additional tillage and incorporation options to reduce atrazine runoff losses. Buffering hydrologic features in a GIS format provided information on atrazine loss potential in riparian areas. Ground truth has not been completed to determine whether 30-meter LANDSAT images accurately reflect land cover in the riparian area.

This project was funded in part from a grant from the National Agricultural Pesticide Impact Assessment Program (NAPIAP).



## ESTIMATING POLLUTANT SOIL RATINGS

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Estimating soil potential for pesticide loss is an important consideration in planning for nonpoint-source pollution control. Several screening procedures have been developed by the USDA to group soils into severe, moderate, or slight utensils for pesticide runoff and leaching. The objective of this study was to evaluate soil-screening procedures for solution, adsorbed, and leaching loss of pesticide using the GLEAMS model.

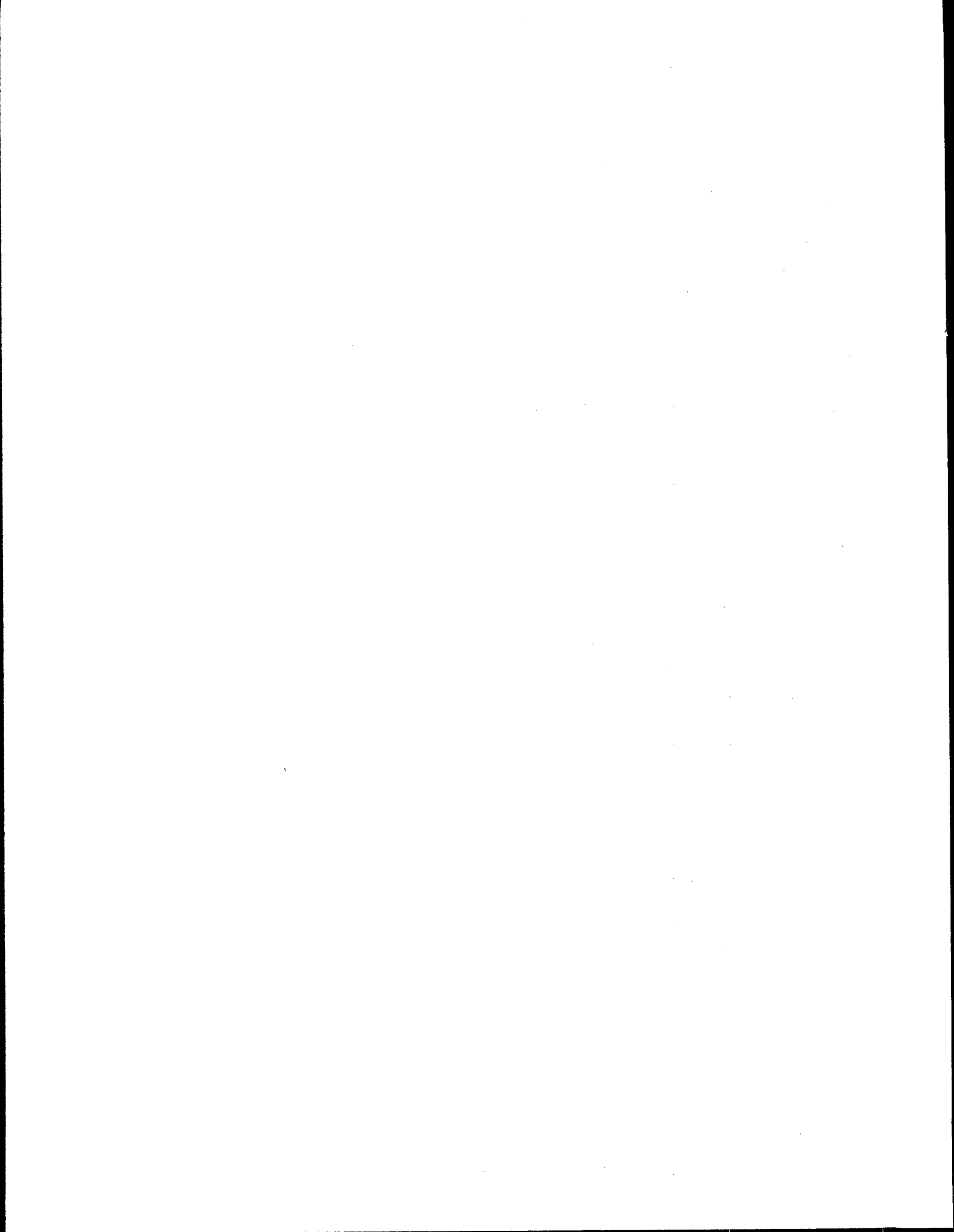
Pesticide loss was simulated for soil mapping units from five Kansas counties using the GLEAMS model (version 1.8.55). The counties represent vastly different geographic and climatic regions. Thirty-year simulations were completed for continuous grain sorghum under dryland and irrigated conditions. The pesticides atrazine, glyphosate, and aldicarb were simulated to represent solution, adsorbed, and leaching loss, respectively. Evaluation of screening procedures was completed by comparing to simulated pesticide loss values.

GLEAMS predicts runoff based on a curve-number approach, which is significantly affected by hydrologic soil group (HSG) but not by slope. An improved soil-screening procedure was developed that uses HSG as an initial variable to group soils. Slight-rated soils are HSG A, moderate-rated soils are HSG B, and severe-rated soils are HSG C and D. Differences in climate were considered by lowering HSG C soils (dryland only) one class if in a Ustic moisture regime. Further modifications for flooding were added to reflect soils in an occasional or frequent flooding class.

None of the existing screening procedures did a good job of grouping soils for adsorbed loss. These procedures did not account for important factors such as slope, slope length, soil erodibility, and climate. The improved soil-screening procedure uses the RKLS factor in Universe Soil Loss Equation to group soils for adsorbed loss. Values of RKLS of 20 and 40 were chosen to group soils into rating classes. All soils with a RKLS > 40 are considered highly erodible due to sheet and rill erosion for the conservation compliance provision of the 1985 Farm Bill and are rated severe for pesticide absorbed loss. Soils with an RKLS factor between 20 and 40 are rated moderate, while those below 20 are rated slight. As in solution-loss ratings, further modifications for flooding were considered.

Existing pesticide-leaching screening procedures use HSG, surface-horizon depth, and surface organic-matter content to initially categorize soils for leaching loss. Further modifications are made for climate, slope, water table, depth to highly permeable material, and bedrock. The GLEAMS model did not predict lower amounts of percolation or leaching on highly sloping soils. An improved soil-screening procedure was developed that did not consider slope and only considered apparent water tables not perched water tables. Type of water table and permeability of bedrock are important variables and need careful evaluation in the soil data base.

This project was funded in part from grants received from the U.S. Environmental Protection Agency, the Kansas Department of Health and Environment, and the State Conservation Commission.



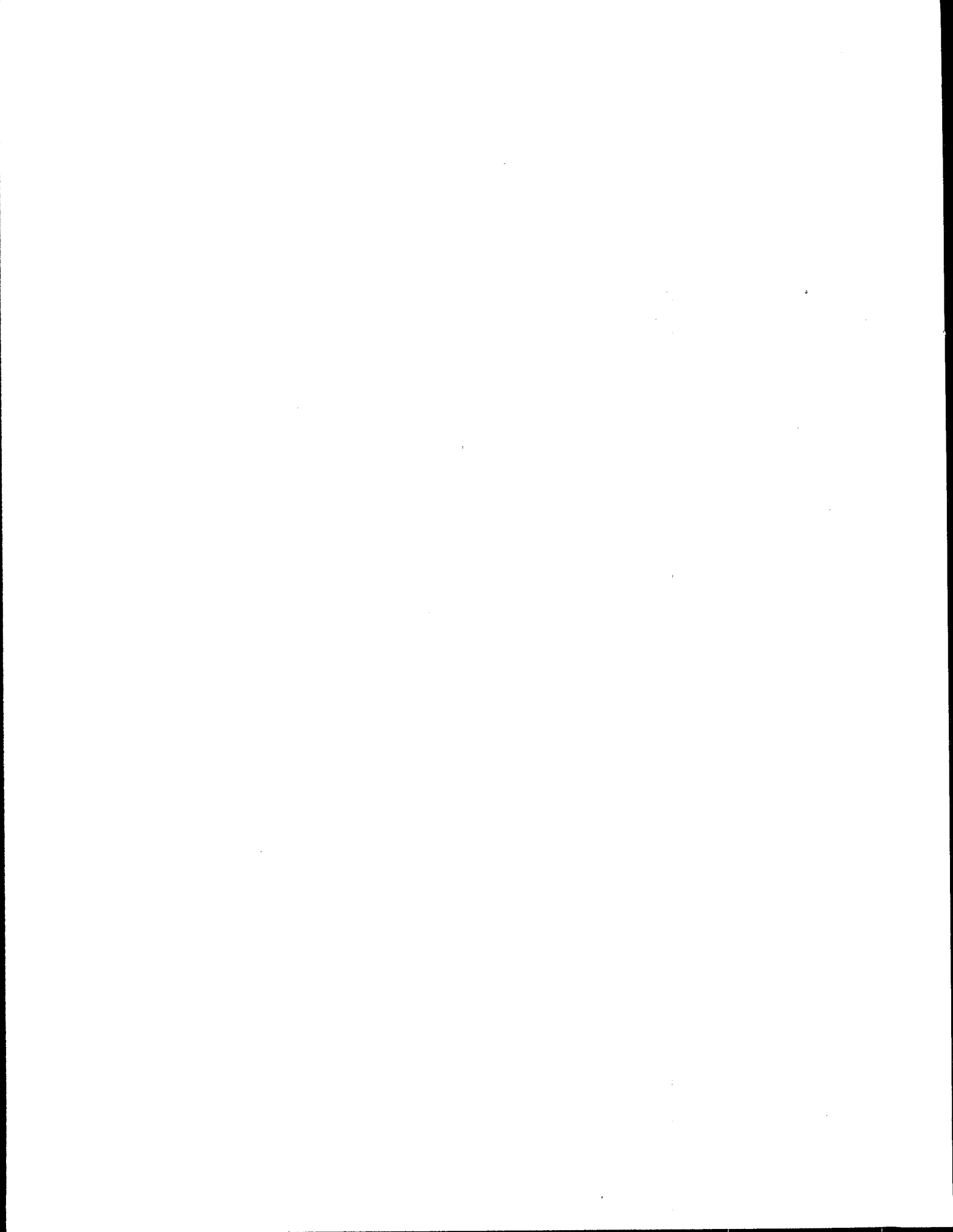
# **RECONNAISSANCE DATA FOR HERBICIDES AND THEIR METABOLITES IN SURFACE WATER OF THE MIDWESTERN UNITED STATES: IMMUNOASSAY AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

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**Elisabeth A. Scribner, E. Michael Thurman, and Donald A. Goolsby, U.S. Geological  
Survey, Lawrence, Kansas, and Lakewood, Colorado**

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Chemical data were collected during 1989-90 for an assessment of preemergent herbicides and their metabolites from 147 rivers and streams located in 10 states in the midwestern United States. All water samples were collected using depth-integrating techniques at three to five locations across each stream. Sites were sampled three times in 1989--before application of herbicides, during the first runoff event after application of herbicides, and in the fall during a base-flow period when most of the streamflow was derived from ground water. Fifty sites were resampled with a stratified random procedure for both pre- and post-application in 1990 to verify the 1989 results. Samples were analyzed by enzyme-linked immunosorbent assay (ELISA) and confirmed by gas chromatography/mass spectrometry (GC/MS). The results proved useful in studying herbicide transport, comparing the spatial distribution of the concentrations of 10 herbicides and 2 metabolites (deethylatrazine and deisopropylatrazine) in streams and rivers after their application on a regional scale, examination of the persistence of herbicides and their metabolites in surface water, and usefulness of atrazine metabolites as indicators of surface- and ground-water interaction.



## **ATRAZINE MANAGEMENT TO MEET WATER-QUALITY CRITERIA**

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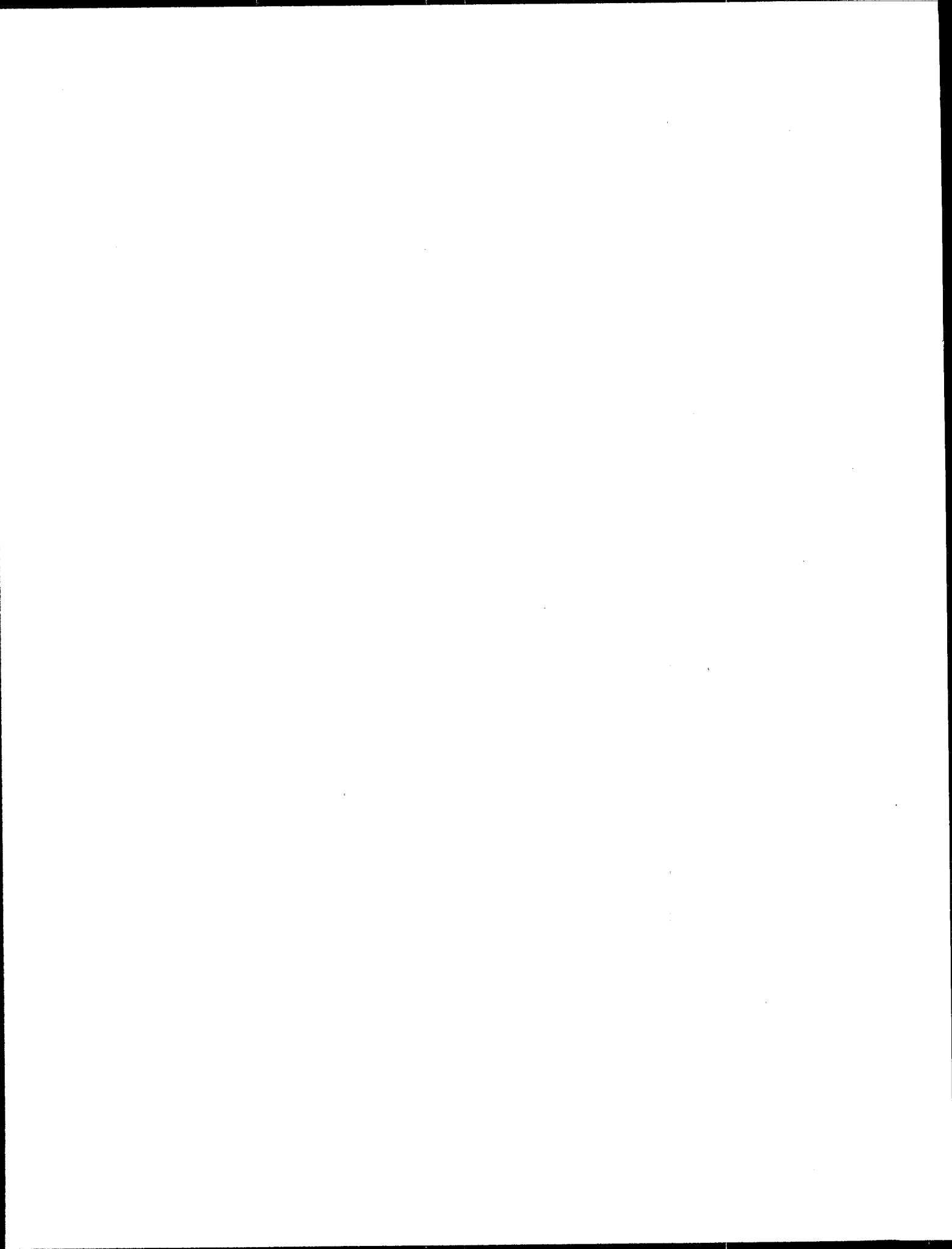
**David L. Regehr, Dallas E. Peterson, and John S. Hickman, Kansas State University, Manhattan, Kansas**

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Atrazine is the pesticide most frequently exceeding the Environmental Protection Agency's proposed Maximum Contaminant Level (MCL) in Kansas surface waters. Northeast Kansas, a region that depends heavily on surface waters for public water supplies, is the most severely impacted. Atrazine concentrations above the 3 ppm MCL are common in many streams during the summer months and may occur year around below major reservoirs.

Pesticides in surface-water runoff are partitioned into either the adsorbed (sediment) or solution (water) phase, depending on their solubility and partition coefficient. About 90% of atrazine lost in surface runoff is in the solution phase. Atrazine loss is highest in the first runoff event after application, with the first runoff having the highest atrazine concentrations. Most of the atrazine lost in runoff comes from the "mixing zone," the top half inch of soil.

Thirty years of northeast Kansas weather data were used to predict atrazine losses associated with different application practices. Atrazine applied in early April is less than half as susceptible to runoff loss as that applied in late May and June, due to differences in rainfall amounts and intensities. Soil incorporation of atrazine decreases runoff losses by about 65%, compared to surface application. Reducing atrazine rates through banding or foliar applications decreases runoff losses dramatically. These factors can be used to formulate atrazine-use programs with the aim of reducing atrazine concentrations in surface waters by 50%.

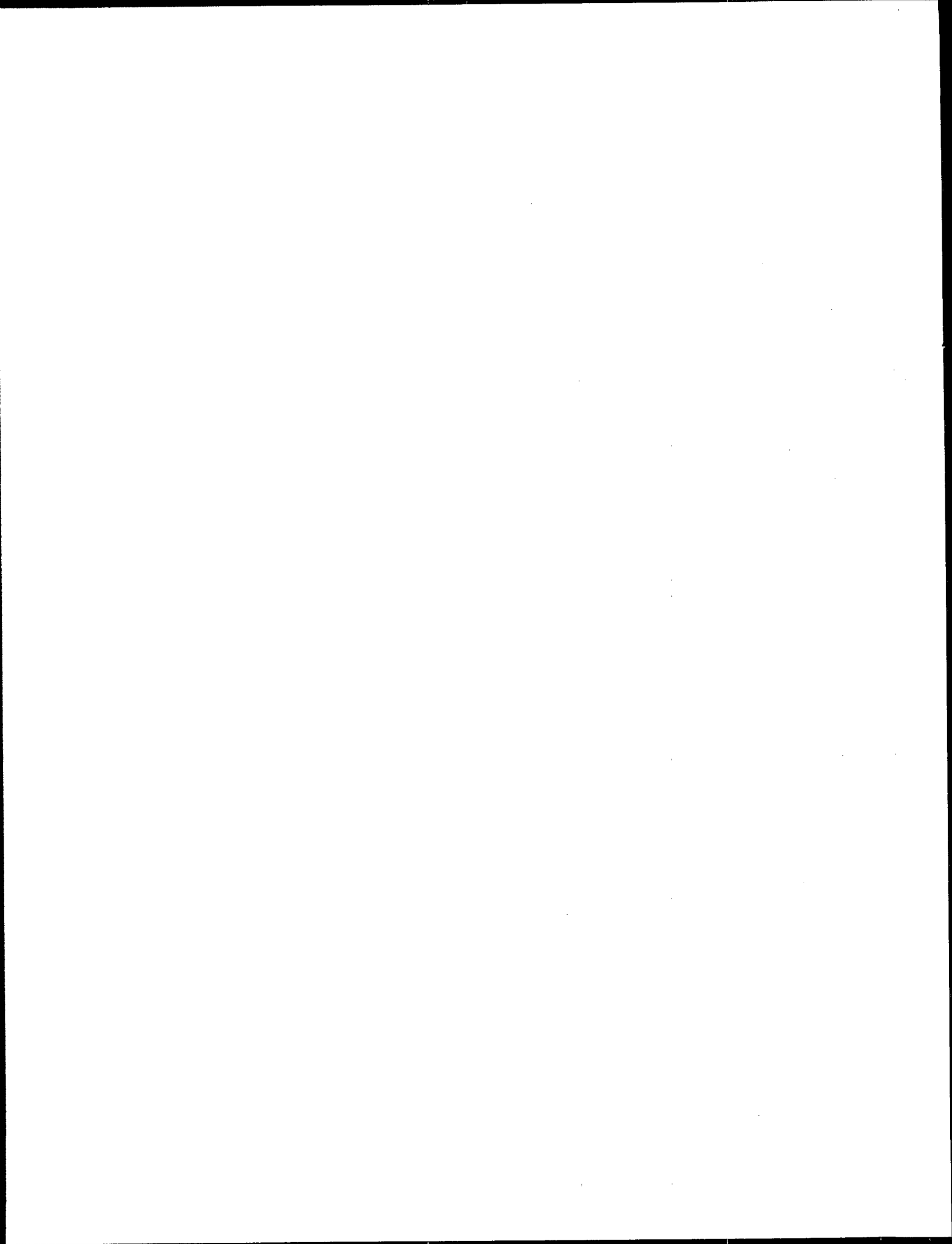




# EFFECTS OF PORE-SIZE DISTRIBUTION AND SATURATION CYCLES ON ATRAZINE AND BROMIDE TRANSPORT THROUGH SOIL

E.A. Smith, P.J. Shea, W.L. Powers, and D.R. Tupy, University of Nebraska-Lincoln, Lincoln, Nebraska

Recent research in Nebraska revealed a relationship between soil pore-size distribution (PSD), reflected in a PSD index, and atrazine transport through surface soil. Atrazine and bromide transport through a Crete silt loam from a corn producing area was related to PSD and bulk density. Undisturbed soil cores were collected to a depth of 7 cm from wheel traffic and non-wheel traffic locations and within rows in a conventionally tilled continuous corn field. Atrazine and bromide were applied at 4.9 kg a.i. ha<sup>-1</sup> (approximately twice the field rate) and 66 kg ha<sup>-1</sup>, respectively, to each core and allowed to equilibrate 72 h. Leachate was collected at increasing water potentials between 10 and 1,000 cm during multiple desaturation cycles. The Brooks and Corey equation was used to calculate PSD from relative soil-water content and matric tension. A significant positive association between total bromide eluted and PSD index and a significant negative association between total atrazine eluted and PSD index suggested more bromide transport and less atrazine transport in soils with a larger fraction of larger sized pores. Observations indicated that pore-size distribution may be a more sensitive indicator of atrazine transport than bulk density. Relatively equal amounts of bromide eluted in the first three desaturations, while decreasing amounts of atrazine eluted after each desaturation. First-order degradation can explain the atrazine reduction after desaturation two, while the reduction in atrazine eluted during the third desaturation may be due, in part, to other physical and chemical processes.



## **Selected Herbicides in Bottom Sediments and Water of Water-Supply Lakes in Iowa**

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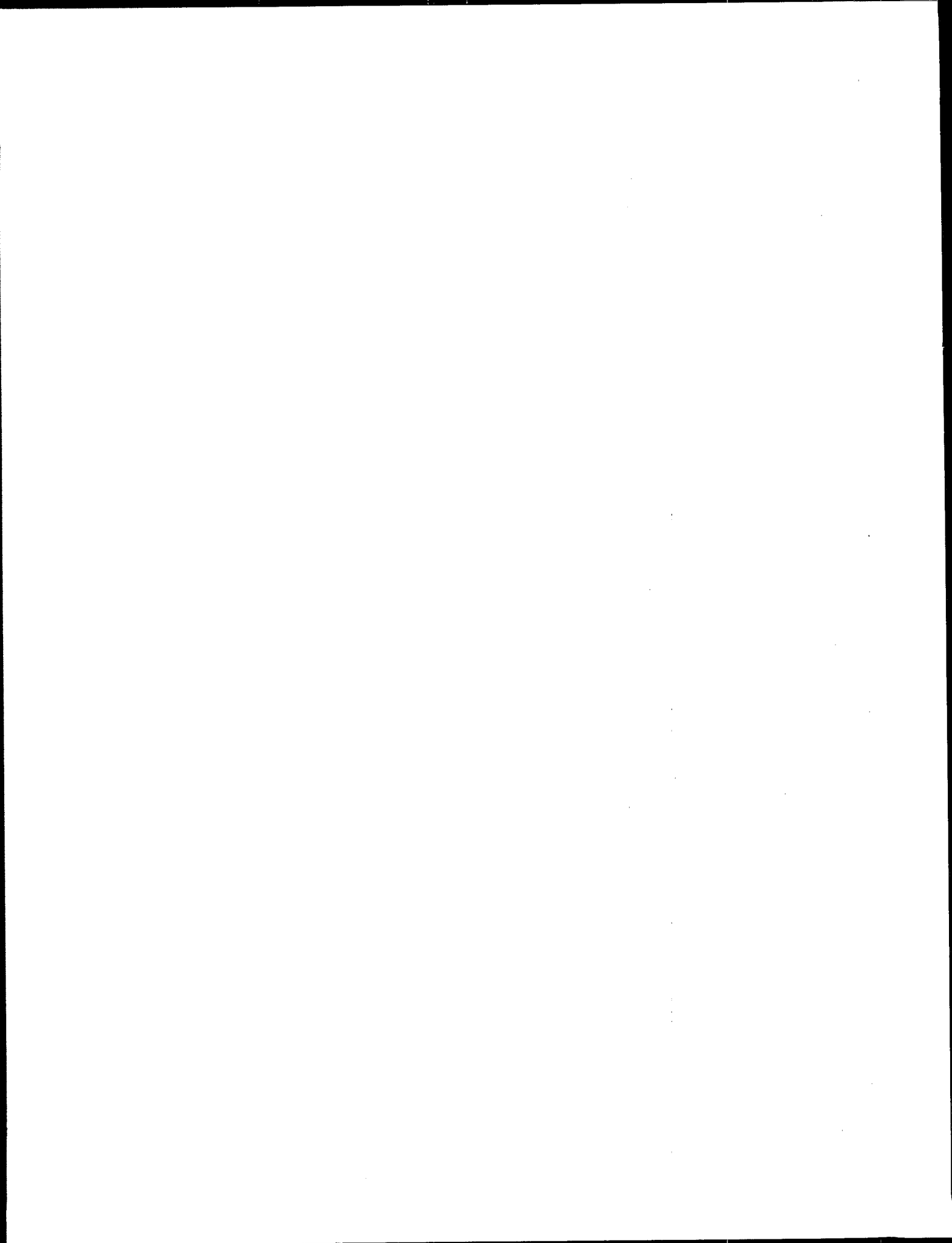
<sup>3</sup> Iowa Department of Natural Resources, Des Moines, Iowa

A cooperative study to investigate the occurrence of several common herbicides in 15 water-supply lakes in Iowa was conducted by the Iowa Department of Natural Resources, the University of Iowa Hygienic Laboratory, and the U.S. Geological Survey. The study was conducted in February and March 1993 when the lakes were ice covered to ensure minimal input of sediment from runoff and minimal sediment resuspension due to wave action. The lakes sampled ranged from 12 to about 5,700 acres in size, with drainage areas of about 500 to 15,000 acres. Land use within the watersheds is primarily row-crop agriculture. Samples were collected from 12 lakes in the southern Iowa and three natural lakes in northwestern Iowa and analyzed for alachlor, atrazine, butylate, cyanazine, metolachlor, metribuzin, and trifluralin. Bottom-sediment and water samples were collected at a site in shallow water near the primary inflow and at a site in the deepest part of the lake; on two lakes, samples were collected only from the inflow site.

Three of the seven herbicides were detected (detection limit varied from 3 to 5 µg/kg) in sediment samples. Atrazine was detected in the sediment samples from eight lakes, cyanazine in two lakes, and alachlor in two lakes. Atrazine was detected in 46% of all sediment samples, cyanazine in 14%, and alachlor in 14%. Metolachlor, metribuzin, butylate, and trifluralin were not detected. Atrazine concentrations ranged from less than the detection limit to 16 µg/kg; cyanazine concentrations ranged from less than the detection limit to 14 µg/kg; and alachlor concentrations ranged from less than the detection limit to 90 µg/kg. Atrazine concentrations in sediment samples from the deep sites were not significantly different ( $p>0.05$ ) at the 95% confidence level than in sediment samples from the shallow sites, even though atrazine was detected more frequently in sediment at the deep sites (62%) than at the shallow sites (33%).

Four of the seven herbicides were detected (detection limit 0.1 µg/L) in water samples. Atrazine was detected in the water samples from 14 lakes, cyanazine in 8 lakes, metolachlor in 3 lakes, and trifluralin in 1 lake. Atrazine was detected in 89% of all water samples, cyanazine in 50%, metolachlor in 14%, and trifluralin in 4%. Alachlor, metribuzin, and butylate were not detected. The atrazine concentrations in water ranged from less than the detection limit to 2.3 µg/L; cyanazine concentrations ranged from less than the detection limit to 1.2 µg/L; and metolachlor concentrations ranged from less than the detection limit to 0.19 µg/L. Atrazine and cyanazine concentrations in the water were not significantly different ( $p>0.05$ ) between the shallow and deep sampling sites.

Atrazine concentrations in the bottom sediment were determined to have a weak but significant relation ( $r^2=0.37$ ;  $p=0.0005$ ) to the atrazine concentrations in the overlying water. This relation could not be tested for the remaining herbicides studied because of the lack of detectable concentrations in the sediment, water, or both.



# THE COMPREHENSIVE ENVIRONMENTAL ECONOMIC POLICY EVALUATION SYSTEM: AN APPLICATION TO ATRAZINE AND WATER QUALITY

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**Aziz Bouzaher, Center for Agricultural Rural Development, Ames, Iowa, and Andrew Manale, U.S. Environmental Protection Agency, Washington, D.C.**

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The Comprehensive Environmental Economic Evaluation System (CEEPES) is an analytical framework designed to generate trade-offs for regulating nonpoint source reduction. Its current configuration is set up to evaluate herbicide policies centered on the use of atrazine and 15 other chemicals in the midwestern region of the United States (Corn Belt, Lake States, Northern Plains, Kansas).

CEEPES is a system of linked physical and economic models. The key components of the system are (i) a mathematical programming model of agricultural decision making used to simulate producer responses to alternative agricultural and environmental policies, (ii) physical process models used to simulate weed competition, herbicide weather impact, and herbicide fate and transport in multiple environmental media. The system is based on a novel approach of linking models and aggregating their outcomes using response function methodology (metamodeling).

CEEPES evaluation includes (i) assessment of producers' substitution responses and their market consequences, (ii) simulation of fate and transport processes which lead to herbicide concentrations in environmental media, (iii) valuation of human risks and other damages caused by those concentrations, and (iv) comparison of quantitative measures of the policies.

The economic indicators generated by CEEPES, for each policy option, at the producing area (PA), state, and USDA region levels, include producer net return, cost of production, crop mix, tillage practices, conservation practices, relations, weed control strategies, herbicide use, fertilizer use, erosion, and commodity program participation.

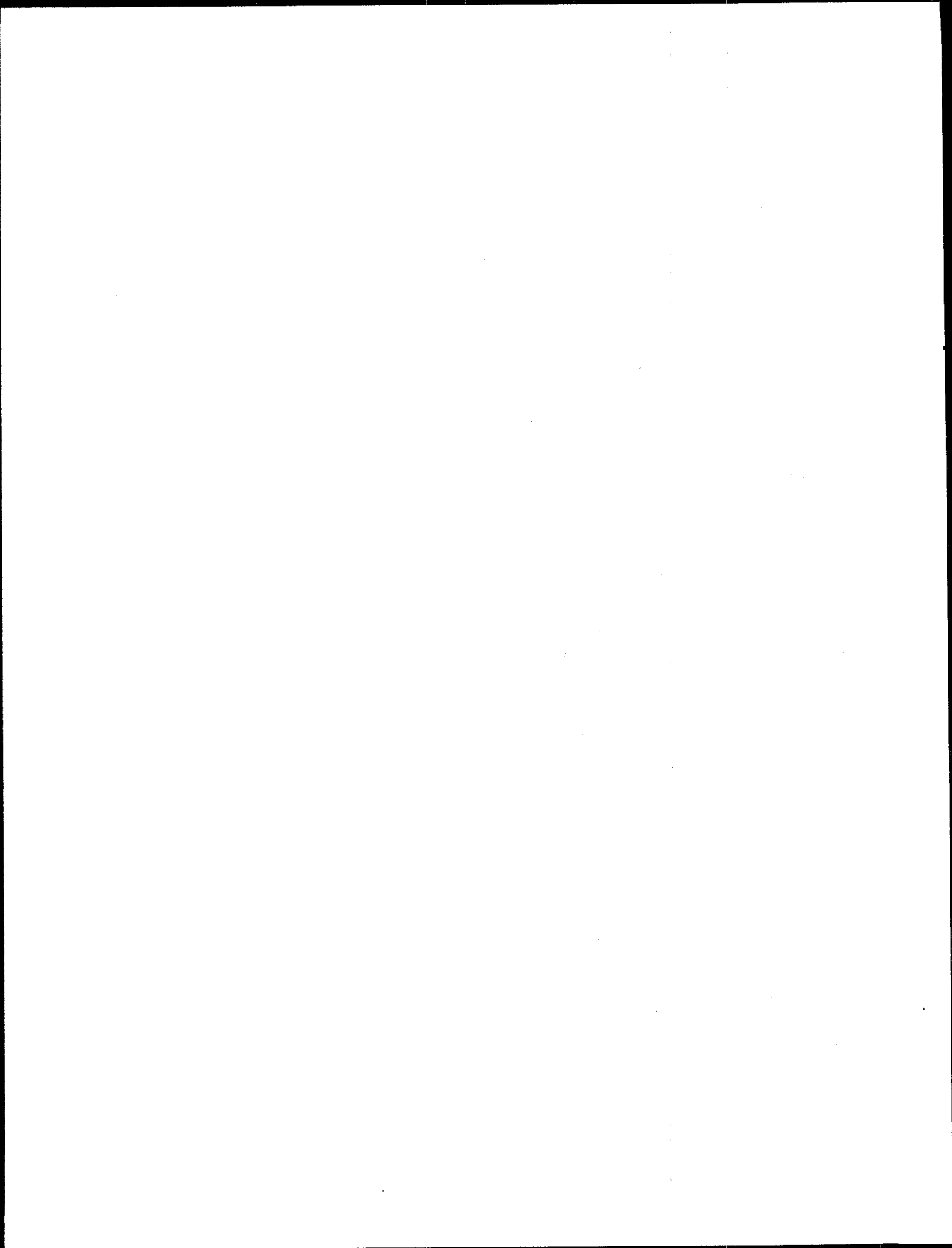
The environmental indicators generated by CEEPES, for each policy option, by crop, tillage system, soil series, county, P.A. state, and region, include groundwater concentrations at (1.2 meters, 7.0 meters, and 15 meters), surface water concentrations, air concentrations, and both surface water and groundwater exposures (relative risk).

Atrazine is the most widely used herbicide for corn and sorghum, and one of the most commonly encountered in surface and ground water. In addition to water quality problems, atrazine poses hazards through air transport, food residue, and the exposure of applicators, and wildlife. If atrazine use is restricted, substitute herbicides will come into wider use, imposing different environmental stress, cost or efficiency penalties, and shifts in production and resource use patterns.

The preliminary results generated are for an atrazine ban and a triazine ban and for an atrazine post-application (timing restriction). We estimate that overall the benefits of an atrazine ban are questionable since this option results in decreased producer and consumer surplus, increased risk from other herbicides, and increased erosion. In addition, restricting application rates of atrazine to 1.5 pounds of active ingredients would not produce significant environmental benefits. A triazine ban (atrazine, cimazine, and cyanazine) results in larger decreases in net return, increased soil erosion, and increased risk from other herbicides, in particular the sulfonylureas (under specific model assumptions).

One of the most important aspects of CEEPES is a detailed characterization of weed control technology which, in addition to standards of control measures like bans, rate restrictions, and timing restrictions, can lend itself to the evaluation of incentive-based options such as best management practices, and tax on chemical inputs.

Finally, we note that CEEPES framework has also been used in assessing the carbon sequestration impacts of row crop agriculture and is being extended to produce nutrient loadings from agricultural activity, including confined livestock operations.



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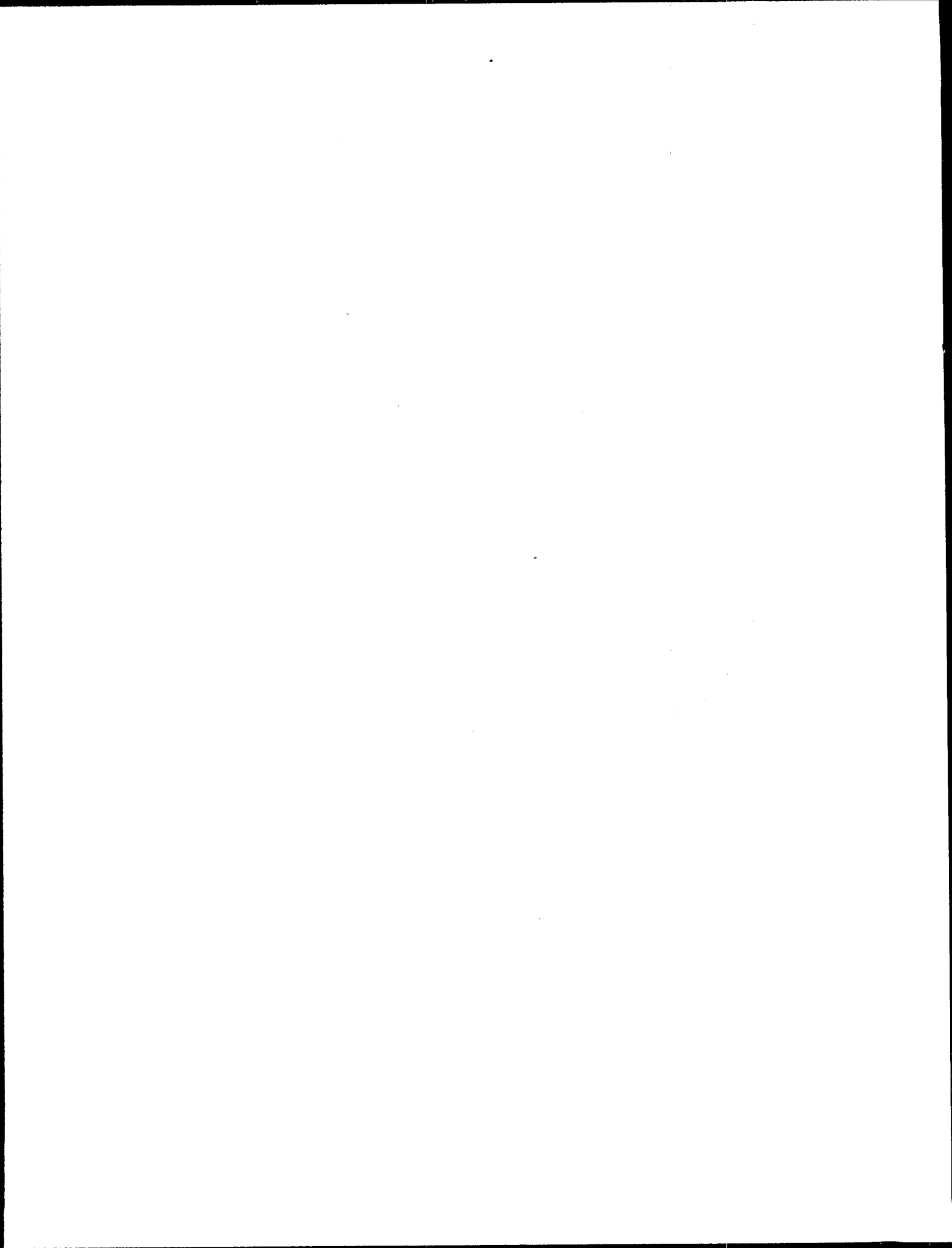
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