# Preliminary Results of Pesticide Investigation

# Augusta, Arkansas

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by Tim Kresse and Ed Van Schaik
Arkansas Department of Pollution Control & Ecology
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## Acknowledgments

## Author's Note

One of the primary reasons for conducting the present study was the fact that bentazon exceeded the health advisory limit (HAL) of 20 $\mu$g/L established by the U.S. Environmental Protection Agency (EPA). The Arkansas Agricultural Chemical Ground Water Management Plan (SMP) specifies that the Arkansas Department of Pollution Control & Ecology will respond to incidents involving agricultural chemicals that are found in ground water at the maximum contaminant level and/or HAL. There were indications from discussions among the SMP Committee, primarily on the part of BASF Corporation, that the EPA was reviewing the most current bentazon toxicity data and was prepared to change the 20 $\mu$g/L HAL to 200 $\mu$g/L. This change in status was enacted at the time of the final draft of this document in October, 1996 and the present HAL for bentazon is 200 $\mu$g/L. However, it should be noted that the following text refers to the previous HAL of 20 $\mu$g/L.

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# Abstract

A site-specific investigation was conducted in Woodruff County where the pesticide bentazon was detected in a domestic well at levels exceeding the Safe Drinking Water Act health advisory limit (HAL) of 20 $\mu$g/L. Concentrations ranging between 40 and 69 $\mu$g/L were detected in three samples taken between May and June, 1994. Concentrations exceeding the HAL for bentazon were also noted at two other sites in the State. The exceedance of the HAL for bentazon at three separate sites demonstrated the need for investigating the potential of bentazon contamination by established management practices.

The investigation included a review of the site history and pesticide usage; the advancement of five soil borings including the retrieval of continuous soil cores; and the installation of four monitoring wells. Analysis of the soil samples demonstrated a lack of detectable concentrations in either vadose zone or saturated soils. Water analyses revealed lower concentrations east and west of the suspected source area and concentrations below detection in a well 800 feet down-gradient and south of the source area. Elevated concentrations upgradient from the domestic well and the suspected source area suggest the possibility of two separate source areas of contamination. Releases apparently were associated with overfilling of pesticide application tanks and possible pesticide drum leaks and spillage.

Water samples from the upgradient monitoring well (MW4) and a monitoring well to the west of the domestic well (MW3) also had detections of the pesticide, dinoseb. The presence of dinoseb supports the hypothesis of two separate contaminant source areas and also the assertion by the property owner that bentazon had not been used at the site for 10 - 12 years, as dinoseb has been banned for use as an ingredient in pesticides since 1986.

The persistence of these pesticides over time warrant the need for further site-specific investigations at other contaminated sites across the State. Only through the knowledge gained by identifying the pathways and sources of pesticide contamination, can our State make critical decisions concerning the use and management of pesticides.

# Introduction

The monitoring of pesticides in ground-water in Arkansas has accelerated at a rapid pace within the last four years. Prior to 1992, pesticide analyses of ground water samples was performed mainly by the Arkansas Department of Pollution Control & Ecology (ADPC&E) as part of their ongoing, ambient ground-water monitoring program and through short-term investigations on the part of the University of Arkansas (Lavy et al., 1985; Cavalier et al., 1987; Cavalier et al., 1989; and Lavy et al., 1989).

In response to various factors, primarily the various EPA programs targeting pesticides in ground water (EPA, 1986a; 1986b; 1987; 1990; 1992a) and the mandates for states to develop State Management Plans for pesticide use (EPA, 1992b; 1992c), Arkansas began to increase the level of pesticide monitoring in ground water.

Monitoring work by the Arkansas Water Resources Center in cooperation with the Arkansas State Plant Board (ASPB) identified a well-water sample from a site near Augusta, Arkansas in Woodruff County that contained bentazon at concentrations exceeding the HAL. The ASPB has authority for banning the use of any pesticide which is demonstrated to cause environmental impacts through normal management and application practices. Because bentazon had been detected during the same approximate period at another site at a level exceeding the 20 $\mu$g/L HAL, the ASPB expressed the need for determining the source of the ground water contamination. The Arkansas Agricultural Chemical Ground-Water Management Plan (SMP) lists the ADPC&E as the responsible agency for addressing contamination of private wells and the Arkansas Department of Health as the responsible agency for municipal wells. Because the level of contamination required a response on the part of the ADPC&E, it was decided a site-specific investigation would be initiated at the Augusta site, with other sites to follow as funding mechanisms were identified. Following a series of meetings of the SMP committee, the Ground Water Protection and Management Committee, and meetings between the ADPC&E and the Plant Board, funds were allocated through the ASPB to initiate the Augusta pesticide investigation.


**Methodology**

A total of five borings and four monitoring wells were completed at the site on May 2-3, 1996. The borings were advanced using 8-inch augers attached to a truck-mounted rotary drill rig. A 5-foot, split-spoon sampler was advanced slightly ahead of the rotating augers in order to retrieve relatively undisturbed soil cores. The soil cores were extracted from the samplers and placed on plastic, where the soil was logged and selected portions were placed in containers for chemical analysis. Soil samples were typically taken at 5-7 foot intervals, beginning at approximately one foot, for a total of 27 samples. The soil samples were delivered by ASPB personnel to the ASPB laboratory for bentazon analyses by Association of Official Analytical Chemist method 60-1070, with extraction according to the FDA Pesticide Analytical Method 222.13.

The four monitoring wells were completed by installing threaded PVC slotted screen (10 foot section) and riser directly into the hollow-stem auger, which served to keep the hole open, and by pouring the sand pack and bentonite pellets around the PVC pipe as the auger was extracted. After allowing the pellets to expand and seal the sand pack, the hole was completed to surface with a 7% bentonite, neat-cement mixture. The wellhead was protected against vandalism and tampering by use of a locking, steel well protector. The wells were initially developed by use of bailers and, at a later date, by use of dedicated pumps.

Dedicated bladder pumps were installed in each well to prevent possible cross-contamination during sampling events. The bladder pumps were operated using a mobile compressor and pneumatic controller system. The wells were purged until temperature, pH, and conductance readings stabilized. Ground-water samples were placed on ice and delivered under chain-of-custody to the ADPC&E laboratory. The ground water samples were analyzed for selected pesticides including bentazon and general water-quality parameters including $NH_3$-N, Cl, $NO_2$ + $NO_3$-N, ortho-phosphate, total P, $SO_4$, TKN, TOC and TDS.

## Site Characteristics

### Geology and Soils

The site is located approximately 3 miles northeast of Augusta (Figure 1) in section 16, township 8 north, range 3 west. The site is underlain completely by alluvial sediments of Quaternary age. The Quaternary alluvium generally consists of a lower unit comprised of sand and gravel, grading into an upper unit comprised of silt and clay (Boswell et al, 1968). The alluvium in this area of the state is approximately 90 feet thick and rests upon Tertiary-age sands and clays, which comprise the Wilcox Formation (Broom and Lyford, 1981).

The soil mapping unit at the site is classified as Dubbs silt loam. Dubbs Series soils basically consist of brown to dark grayish-brown, well drained to moderately well drained, permeable soils along channels of major rivers. The Dubbs silt loam generally has a surface layer (4-7 inches) of brown, friable silt loam and a subsoil (18-45 inches) of brown silty clay loam. The underlying material is a brown to dark-brown fine sandy loam or silt loam (Maxwell et al., 1968). Continuous soil cores extracted from four borings at the site tended to match the descriptions for the Dubbs silt loam. The cores showed the occurrence of a fine sand at approximately 13-14 feet in depth. The sand was limonitic with varying amounts of carbonaceous material and traces of mica. Although a slight increase in grain size was noted, the sand was basically a very fine to fine sand from 14 feet to total depth (approximately 30 feet). The material overlying the sand was dominantly a silt to silt loam, with an increasing clay content (silty clay loam) occurring between 3-7 feet.

Immediately west of the house and domestic well, the soil is classified as Amagon silt loam. The Amagon mainly differs from the Dubbs in the increasing clay content within the subsoil, which can cause problems due to wetness. The change from the Dubbs to Amagon soil at the site was noted through the occurrence of iron/manganese nodules in the 1/8 to 1/4 inch size range at the surface of the land. Area farmers refer to these soils as "Buckshot" soils because of likeness of the nodules to buckshot.

### Subsurface Hydrology

The saturated portion of the alluvial sediments is referred to as the Mississippi River Valley alluvial aquifer and provides most all of the water used for irrigation in Woodruff County. Depth to water at the site in the monitoring wells averaged approximately 20 feet below the surface. This water level is similar to depths taken from driller logs in the immediate area, which listed depths ranging from 11 to 30 feet below the surface with an average depth of 17 feet. Westerfield (1977) listed information for 26 wells in Woodruff County including water levels, which ranged from 4 to 47 feet and averaged 21 feet below the ground surface. The monitoring wells were surveyed to within 0.01 inch and this information together with the water level was used to calculate water table elevations and produce potentiometric surface maps. Figure 2 is a potentiometric surface map produced from water elevations measured in May, 1996.
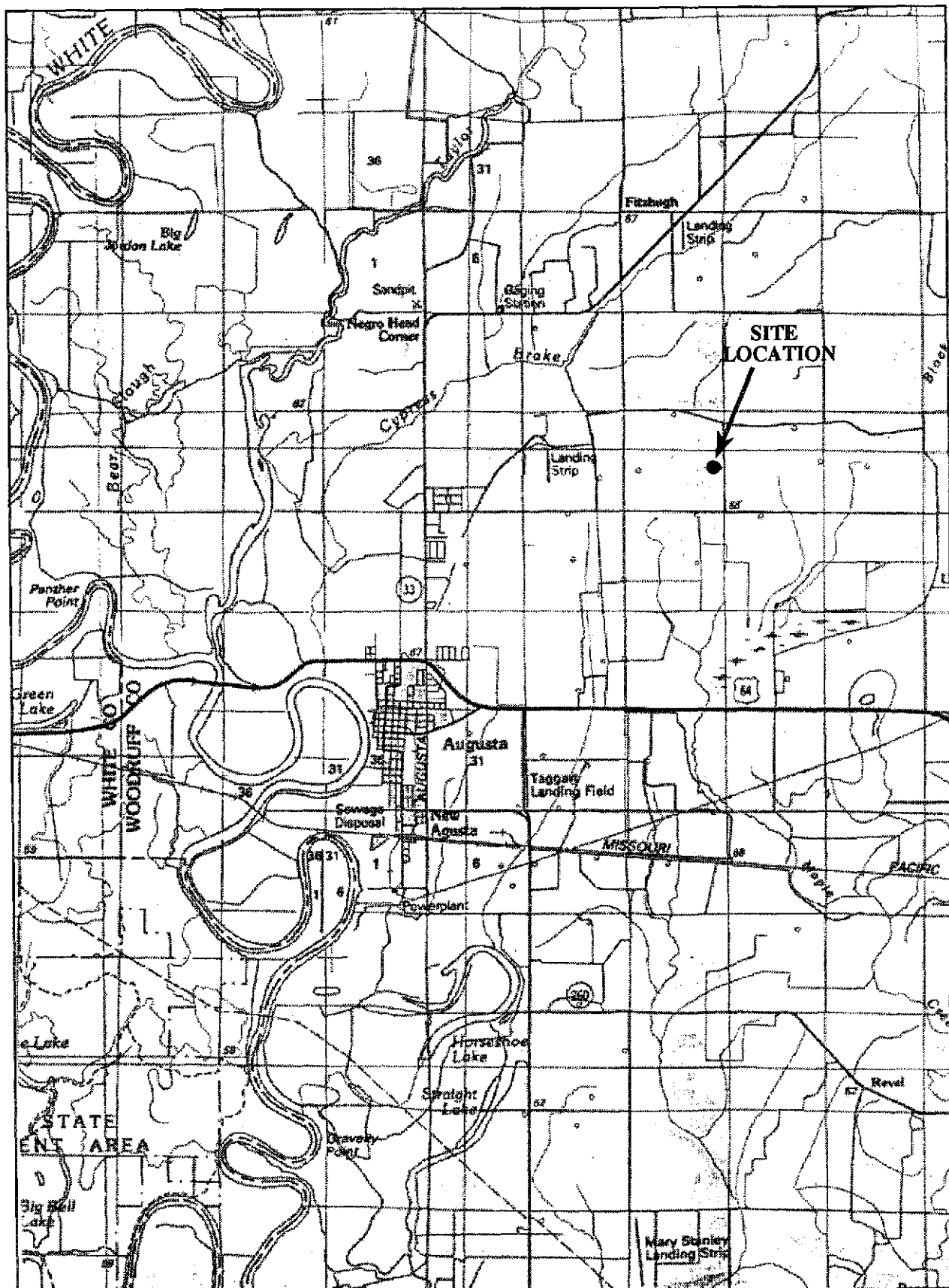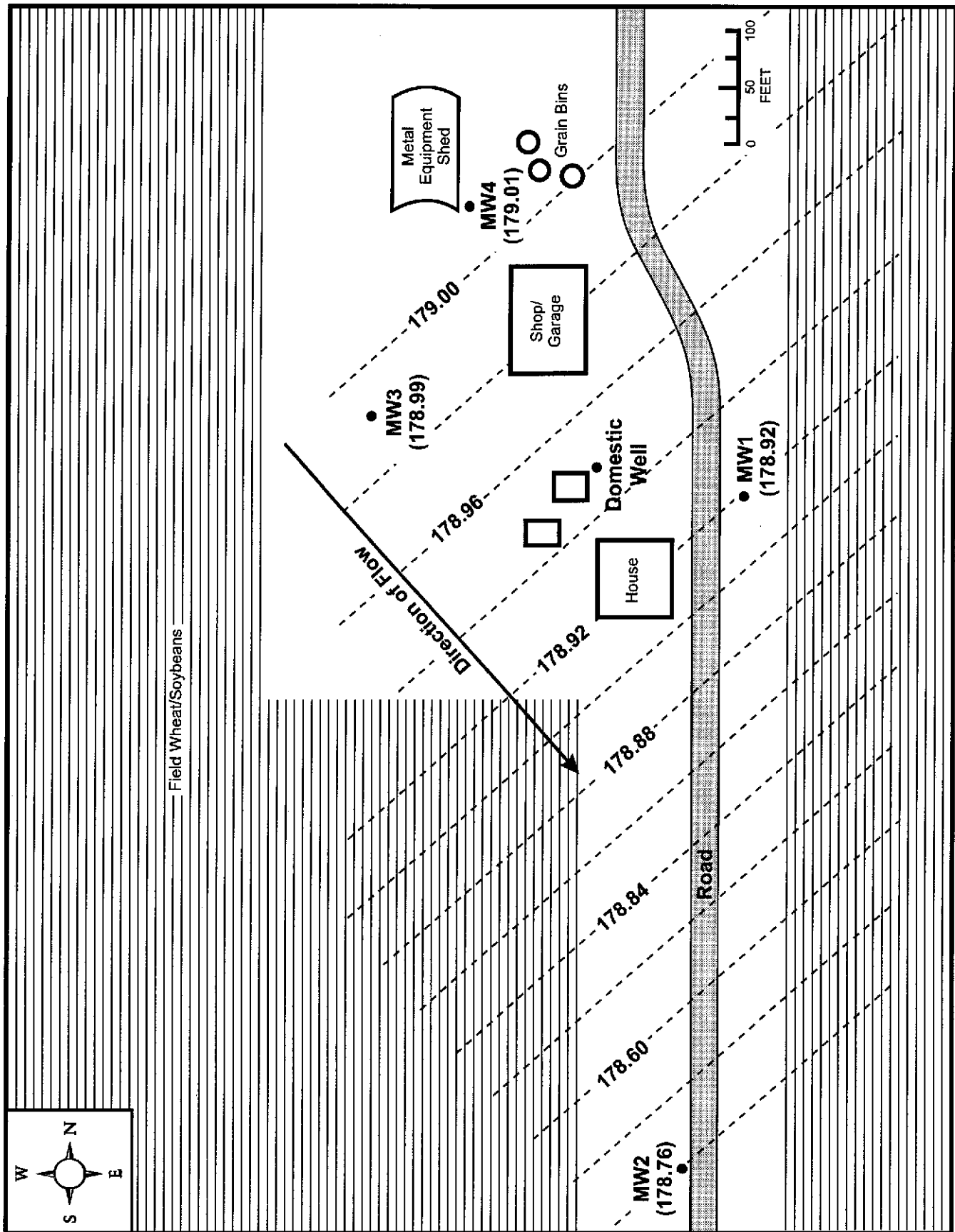
**Figure 1.** Location of study site.

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**Figure 2. Potentiometric surface map developed from monitoring well elevations.**

The study site is bounded on the west by the White River and on the east by the Cache River. These rivers act as a source of discharge for the ground water within the alluvial aquifer. Westerfield and Gonthier (1993) provide a potentiometric surface map for the alluvial aquifer in eastern Arkansas using water elevations measured in 1989. The map depicts a ground-water divide within the vicinity of the study site with southwest flow directions west of the divide toward the White River and southeasterly flow toward the Cache River on the east side of the divide. This same configuration is also noted in an earlier potentiometric map produced from water elevations measured during the spring of 1973 (Broom and Lyford, 1981).

Because of the scale of the maps and the central location of the site in relation to the two rivers, it was difficult to predict the local flow direction and receiving stream. However, the potentiometric surface map produced from onsite measurements indicate that ground water flows to the southeast beneath the site. The steeper gradients in the southern portion of the site may reflect the influence of the irrigation wells which are to the south of MW1. However, it should be noted that the contours are in increments of 0.02 feet, which is close to the margin of error for both the electronic measuring devise and the accuracy of the surveying equipment, and this situation may produce the subtle differences in water table elevations and the resulting potentiometric map.

Information gained from the monitoring wells together with published values for the thickness of the aquifer (in the vicinity of the study area) and transmissivity values (Broom and Lyford, 1981) was used to calculate a ground-water velocity of 0.26 feet/day beneath the site. This value is in close agreement with other published values for ground-water velocities within the alluvial aquifer in eastern Arkansas (Counts, 1957; Mahon and Ludwig, 1990; Broom and Lyford, 1981).


**Ground Water Quality**

A list of general water quality parameters is presented in Table 1, which provides the minimum, maximum and mean concentrations for selected parameters. Ground water quality is very good in the vicinity of the study area. Values for TDS ranged from 105 to 195 mg/L (mean of 147 mg/L) and chloride concentrations ranged from 1.2 to 5.1 mg/L (mean of 1.7 mg/L). These values are somewhat lower than TDS and chloride concentrations for Woodruff County as cited in Westerfield (1977), who listed TDS concentrations ranging from 162 to 363 mg/L with a mean of 237 mg/L and chloride concentrations ranging from 3.8 to 14.0 mg/L with a mean of 6.8 mg/L. It is interesting to note that to the west of the White River in White County, which has a similar geological setting, ground water within the alluvial aquifer is of a poorer quality and chloride concentrations are reported as high as 1,870 mg/L with an average chloride concentration of 169 mg/L (Counts, 1957).

Table 1. Statistical analyses of selected parameters for ground water samples from site wells.

| | Al µg/L | Fe µg/L | Mn µg/L | Zn µg/L | Ca mg/L | K mg/L | Na mg/L | Mg mg/L | NH$_3$-N mg/L | NO$_3$-N mg/L | SO$_4$ mg/L | Cl mg/L | TDS mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| min. | 146 | 2,450 | 272 | 32 | 5.3 | 0.5 | 5.6 | 0.006K[1] | 0.05K | 0.16 | 8.3 | 1.21 | 105 |
| max. | 6,665 | 11,600 | 672 | 62 | 24.0 | 1.3 | 19.6 | 6.7 | 0.05K | 10.04 | 36.7 | 5.17 | 195 |
| mean | 2,688 | 4,426 | 506 | 43 | 12.1 | 1.0 | 10.0 | 1.9 | 0.05K | 2.89 | 15.6 | 1.67 | 147 |

[1] actual value is known to be less than listed value

Table 2. Data for detected pesticides in domestic and monitoring wells (1st row of numbers is from 6/18/96 sampling event; the second row is data from 7/1/96 sampling event.

| | MW 1 | MW2 | MW3 | MW4 | Domestic Well |
|---|---|---|---|---|---|
| Bentazon µg/L | 0.922<br>0.881 | 0.015K[1]<br>0.021K | 6.409<br>1.277 | NS[2]<br>21.364 | 25.12<br>2.267 [3] |
| Dinoseb µg/L | 0.074K<br>0.065K | 0.070K<br>0.070K | 1.806<br>1.734 | NS<br>30.678 | 0.060K<br>0.047K |

[1] actual value is known to be less than listed value
[2] no sample - sample was destroyed
[3] well was purged for approximately 30 minutes prior to sampling

Concentrations for iron, manganese and aluminum exceeded the secondary maximum contaminant levels (SMCL), which are unenforceable federal guidelines regarding taste, odor, color and other non-aesthetic effects of drinking water (EPA, 1996). The SMCL for iron, manganese and aluminum are 0.3, 0.05, and 0.05 mg/L, respectively. Although the metals analyzed for this study represent total rather than dissolved concentrations, both the iron and manganese compare very closely with the range of dissolved metal concentrations listed in Westerfield (1977). High iron concentrations are typical in the alluvial aquifer and generally limit its use for municipal, industrial and domestic supply purposes unless it is treated (Broom and Lyford, 1981).

Table 2 lists the pesticide detections for the domestic well and the four monitoring wells. Bentazon, in addition to being present in the domestic well, was found in three of the monitoring wells. Bentazon was not present in the downgradient well, MW2. Concentrations decreased sharply to the east and west of the domestic well in wells MW3 and MW1. This situation would suggest a source of pesticide contamination near to the domestic well and/or upgradient of the domestic well. Conversations with the resident, who has managed the present site since 1987, revealed that there were indications of spillage and overfilling associated with pesticide mixing in the form of colored stains on the ground between the house and shop (Figure 2) at the time he moved into the house. Spills in this area could account for the high levels of bentazon in the domestic well and the decreased concentrations away from the well.

In addition to the detections of bentazon, dinoseb was detected in two of the monitoring wells; wells MW3 and MW4. The detection of dinoseb in the upgradient and westernmost monitoring wells suggests the possibility of an additional source of pesticide contamination in the vicinity of MW4, or that only one source of contamination exists for all wells and is in the vicinity of MW4 and the migration of dinoseb was retarded relative to bentazon. Although the chemical characteristics of each of the pesticides (see following section) could account for the relative retardation of dinoseb, the detection of dinoseb in MW3 and the higher concentration of bentazon in the domestic well would more strongly indicate that two or more sources of contamination exist at the site.


## Results of Pesticide Investigation

Physical and Chemical Properties

Results of all the analyses to date at the site demonstrate the existence of two pesticides in the ground water at the site, bentazon and dinoseb. Both bentazon and dinoseb are selective contact herbicides and are both metabolized by resistant plants into various plant metabolites. These pesticides differ to some degree in their physical and chemical characteristics and, therefore, differ in both their fate in the surface and subsurface environment and their transport within the hydrologic system. Information on dinoseb, especially in regard to fate and transport studies including field dissipation, metabolism and half-life under various soil conditions, was difficult to obtain as dinoseb has been banned for use as a pesticide since 1986 (EPA, 1990).

Bentazon is sold as a herbicide in the sodium salt form, referred to as sodium bentazon. Although the water solubility of the parent acid is 500 mg/l, the sodium salt form is infinitely soluble; in deionized water, 2.3 kg of sodium bentazon will dissolve in one liter of water. The high solubility of bentazon in conjunction with a low $K_{OC}$ of 34 and a resistance to hydrolysis indicates a high mobility and high potential for contaminating ground water. However, bentazon degrades rapidly in the upper soil layer and in surface waters due to both photodegradation and microbial breakdown. Field dissipation half-life values are typically less than two weeks under aerobic soil conditions with normal use (USDA, 1996; BASF, 1996) and were less than one month with an application of 3lb/acre (BASF, 1996).

Dinoseb is a phenolic herbicide (dinitrophenol) with a moderate solubility (50 mg/L) in its phenolic form and an increased solubility in the salt form (2,200 mg/L); dinoseb salts are formed upon mixing with inorganic and organic bases (Hartley, 1990). The dominant carrier for dinoseb is water with the dinoseb in a oil/water emulsion or an oil solution. As such, the solubility in water under normal conditions would be assumed to approach the lower solubility for the parent phenolic form.

Dinoseb is a highly to extremely toxic compound and exposure can occur through direct contact, ingestion, and inhalation. Spray operators have been known to have died from dermal exposure. One fatality involved a farm worker who was killed using a backpack sprayer that leaked dinoseb onto his body and penetrated his skin (USDA, 1996). Dinoseb appears to be more persistent in the environment than bentazon. Values vary among sources but $K_{OC}$ ranges between approximately 200-500 ml/g. The authors calculated a $K_{OC}$ of 330 ml/g from a $K_{OW}$ value of 2138 (Saarikoski et al., 1986) using the formula:

$$\text{Log } K_{OC} = 0.69 \text{ Log } K_{OW} + 0.22 \text{ (Piwoni and Keely, 1990)}$$

In conjunction with the higher $K_{OC}$ and a ten-fold decrease in the parent solubility, one would predict a higher rate of retardation for the migration of dinoseb in the subsurface environment relative to that of bentazon.

Fate and Transport

In order to gain an understanding of the movement of pesticides in the subsurface environment, it is useful to estimate the partitioning between the soil and solution phase within the saturated zone and to estimate the retardation of the pesticide plume in relation to the ground water flow. When calculating the partition coefficient ($K_d$), it is important to note that sorption is highly dependent on site-specific soil conditions including pH, organic content, and ground water flow rates.

BASF (1996) calculated $K_d$ and $K_{OC}$ values for bentazon using soils from different states, which varied in their type, soil moisture, organic carbon and organic matter, cation exchange capacity, and other characteristics. Values of $K_d$ were determined using the batch equilibrium method and calculations were performed using the Freundlich equation, $C_s = K_d \times C_w^{1/n}$ ; $K_{oc}$ was then calculated using the resulting $K_d$ according to the formula, $K_{OC} = K_d \times 100/\%$ Organic Carbon. The resulting values of $K_{OC}$ and $K_d$ ranged from 13.2 - 175.6 and 0.176 - 3.056, respectively.

It should be noted that the highest $K_d$ and $K_{oc}$ value was calculated from a soil with a low pH (4.3) and the range of each parameter was smaller in soils with pH values between approximately 5 to 7.5 (see Figure 3). The slow kinetics of the sorption process can be strongly affected by high velocities associated with highly conductive aquifer systems and, as such, sorption may be overestimated in aquifer systems with relatively high flow rates (Piwoni and Keely, 1990). However, where more than one pesticide exists, calculated estimates of both sorption and retardation rates assist in understanding the relative movement and concentration of one pesticide to another, and can also be helpful in understanding the phase distribution and mobility in cases where only one pesticide is detected.

The following calculations were performed to estimate the pesticide distribution between the solid and the aqueous phase; methodologies were adapted from Piwoni and Keely (1990).

Field measurements:
Average ground water concentration near source area = 50 $\mu$g/L bentazon; 30 $\mu$g/L dinoseb
Soil organic carbon (Rutledge, 1996; U of A, 1992) = 0.2 percent or $f_{oc}$ = 0.002
Soil density (Rutledge, 1996; U of A, 1992) = 1.6 g/cc (1.6 kg/L)
$K_{oc}$ = 34 for bentazon; 330 for dinoseb
Porosity = 33%

Where $K_d = K_{oc}(f_{oc})$, then
$$K_d \text{ (bentazon)} = 34(0.002) = 0.068$$
From the definition of $K_d$,
$$K_d = \text{Sorbed (mg/kg)/Solution (mg/L)}$$
Then,
$$\text{Sorbed} = 0.068(0.050\text{mg/L})$$
$$= 0.0034 \text{ mg/kg}$$

Given a soil density of 1.6 kg/L and a porosity of 33%, 3 liters of aquifer material would contain 1 liter of water and 4.8 kg of soil. Under equilibrium conditions, the amount of bentazon in the solid phase would be 4.8(0.0034) or 0.0163 mg, and the amount in the solution phase would be 0.05 mg. As such, approximately 75% of the bentazon would occupy the solution phase and 25% would be in the solid phase. In regard to the sorption of dinoseb, the following relationship would apply:

$$K_d = K_{oc}(f_{oc})$$
$$= 330(0.002)$$
$$= 0.66$$
and,
$$\text{Sorbed} = 0.66(0.030) = 0.020 \text{ mg/kg}$$

Under equilibrium conditions, the amount of dinoseb in the solid phase of 3 liters of aquifer material would be 4.8(0.020) or 0.096 mg. As such, approximately 76% of the dinoseb would be sorbed to the aquifer material and 24% would be in the ground water.

Although there are numerous variables affecting the sorption and phase distribution of both pesticides, the above calculations certainly provide qualitative information on the relative transport characteristics of each of the pesticides found at the site. Bentazon, as expected from the high solubilities for the salt form of bentazon, is much more mobile in the environment than dinoseb; whose transport would be greatly retarded relative to bentazon based solely on sorption as the retarding mechanism.

Because the solubility of both bentazon and dinoseb vary based on their chemical form and the pH of the subsurface environment, a more useful relationship to explore is the dissociation constant of the chemical and the pH of both the onsite soils and ground water. To demonstrate the effect of soil pH on the mobility of a given pesticide, $K_d$ values were compared to soil pH, using information from the sorption studies provided by BASF. Figure 3 demonstrates that the $K_d$ increases from values less than 0.5 ml/g to a value of greater than 3 ml/g at a pH of 4.3. Although there are only five data points, the relationship demonstrates the effect of the low pH on the mobility, or lack thereof, of bentazon. The disassociation constants ($pK_a$) for bentazon and dinoseb are 3.3 and 4.6, respectively. For bentazon, the pKa value indicates that at a pH of 3.3, half of the bentazon would be in the un-ionized form and half would exist as the more mobile ionized form. The same relationship would be extended to dinoseb at a pH of 4.6.

The concept of dissociation underscores the importance in understanding the pH of the soil and ground water at a particular site and the resulting effect on the mobility of any pesticide. For instance, if the soil at a given site has a uniform pH value of 4.3, then there would theoretically be 10 times as much bentazon (approximately 90%) in the soluble ionized form as exists in the less soluble parent acid form. At a pH of 5.3, the relationship would be 100:1 and virtually all of the bentazon would be in the ionized form. Because both pesticides are weak acids, one can better understand the effect of a low pH environment on the mobility of each pesticide. Although soil pH was not quantified at the site, the pH of the ground water ranged from 5.7 to 6.5 standard units. In theory, at the lower pH practically all of the bentazon (`99%) would be in the more-soluble, ionized form and most of the dinoseb (`90%) would be in the soluble form.

The information provided in the above paragraphs implies that bentazon is highly mobile within the subsurface at the study site. Assuming the pesticide plume(s) moves with the ground water, and using a velocity of 0.26 feet per day, then the plume should have moved a distance of approximately 950 feet in ten years. If the conservative assumption is made that retardation of the plume is occurring under equilibrium conditions, then the velocity of the contaminant plume is as follows (Fetter, 1988):

$$\overline{v}_c = \overline{v} / (1 + P_b) K_d$$

Using this formula to calculate retardation of the plume due to sorption, the velocity of the contaminant plume is 0.20 feet per day and the plume would move 730 feet in ten years instead of the 950 feet projected for movement of the plume with ground water flow rates.
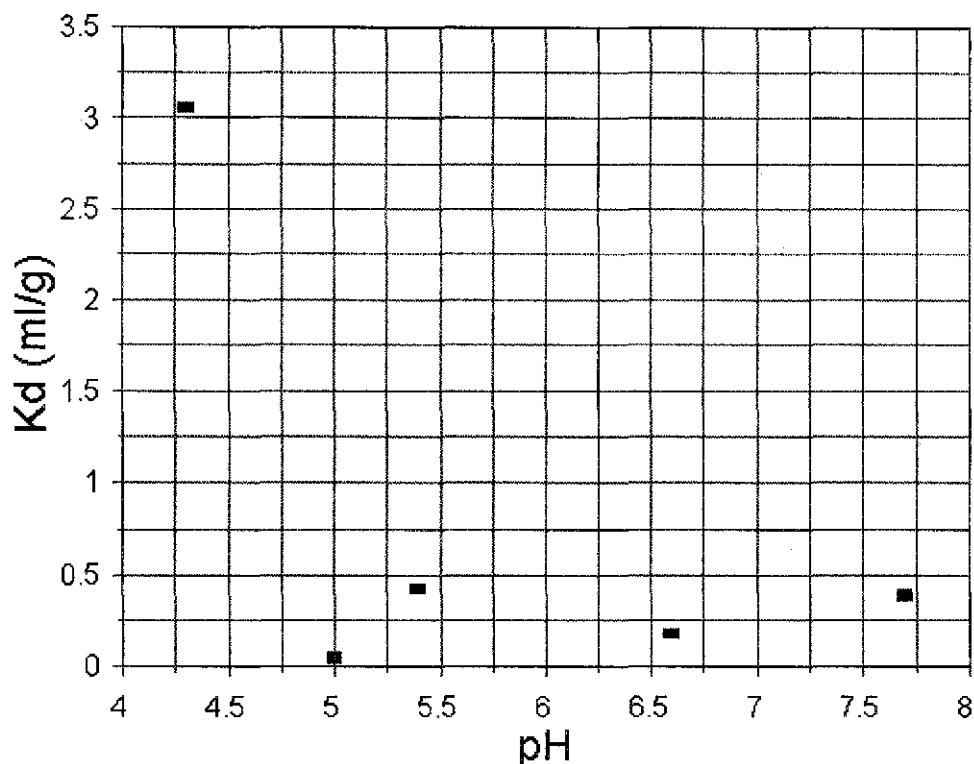
3.5

3

2.5

Kd (ml/g)

2

1.5

1

0.5

0

4    4.5    5    5.5    6    6.5    7    7.5    8

pH

**Figure 3.  pH versus $K_d$ for various soil types (data from BASF, 1996)**

Even if one uses the rate of contaminant movement for the retarded plume, the plume should have dissipated to a greater degree than is evident at the site.  The bentazon concentration in water from the domestic well has remained consistently high (25 - 69$\mu$g/L) although the plume is not evident 800 feet downgradient of the source area and is less than 1 $\mu$g/L at MW1, which is approximately 150 feet from the domestic well.  The well was pumped for approximately 30 minutes during the 7/1/96 sampling episode, resulting in a substantially decreased concentration of 2.3 $\mu$g/L.  The substantial decrease in concentration with continued pumping indicates that a residual source of pesticide contamination exists near the well and diffuses into the ground water at a rate which is less than the velocity that is created from pumping of the well.  This situation reflects the behavior of a highly sorptive, hydrophobic pesticide; although each of the pesticides are moderately to highly soluble and have low sorption coefficients.  Instead, it appears that the spills might have occurred over an extended period of time, which allowed the contaminants time to diffuse into low- permeability, stagnant zones.  Migration out of these zones would also occur under diffuse rates of flow.

The continual detection and persistence of hydrophilic pesticides has been documented in several studies as reviewed by Barbash and Resek (1996). These pesticides included DBCP, atrazine, metolachlor, dicamba, and simazine with solubilities ranging from 28 to 6500 mg/L. Sudicky et al. (1985) demonstrated this phenomena in the laboratory using a non-reactive tracer (sodium chloride) and noted observed tailing effects as a result of the diffusive exchange of tracer between strata of varying hydraulic conductivity in a layered system. Given the information on the chemical properties of the pesticides under investigation in this study, it appears that molecular diffusion into the more impermeable regions of the vadose zone as the pesticides traverse along the macropore regions is accounting for the persistence of both bentazon and dinoseb at the site.

**Identification of Contaminant Sources**

Site History

Preliminary interviews with the site owner prior to the investigation revealed that pesticides were not mixed near the domestic well, and bentazon had never been used at the site by the present owner. The land to the west of the road depicted in Figure 2, including the house and the domestic well, was owned by another party prior to 1987. However, interviews with the farm manager, who has farmed in the area for over 25 years and managed the land east of the road during most of that time, revealed that the previous owner had mixed pesticides next to the domestic well. This well served as the source of water used for pesticide mixing and cleaning of the truck and various other equipment. The farm manager, who moved into the house at the time the present site was purchased, stated that there was a stained area between the well and the shop (Figure 2), which was the result of overflow associated with the mixing practice. He also stated that the area behind the shop and next to the shed (the location of MW4) was cluttered with empty pesticide drums and other debris.

Results of Soil Analyses

The initial investigation workplan included the extraction of soil cores during the drilling operation. Because the monitoring wells were located over 150 feet from the domestic well, an additional boring was advanced in an area approximately 20 feet from the well. Samples generally were taken every 5-7 feet during the boring phase, and a total of 27 soil samples were extracted for analyses by the ASPB Laboratory. Because little of the site history was known prior to the investigation, the intent of the soil sampling was to isolate the source of contamination. Contamination of the soil profile in areas removed from the domestic well would normally indicate the potential for contamination from general application. However, all soil samples were nondetect for bentazon at 2 $\mu$g/L, which was the only parameter selected for soil analyses.

In general, the amount of pesticide residue in the solid (soil) phase is at least an order of magnitude higher than the amount determined in the aqueous media (Barbash and Resek, 1996). Because of the persistence of the pesticide at the site and the variability of the ground water concentrations in the domestic well with continued pumping, it is strongly believed that a residual source exists in the soil profile. The lack of detection in the soil samples suggests either laboratory error or that the source area was missed during the soil sampling phase.

## Conclusions and Recommendations

Elevated concentrations of bentazon were documented and verified at a site near Augusta, Arkansas, between May, 1994 and July, 1996. The detection and continual persistence of bentazon presented an unusual situation because bentazon had not been used at the site for over 10 years. The installation of four monitoring wells at the site also revealed the presence of dinoseb, which was banned for use as a pesticide in 1986. Both dinoseb and bentazon have high solubilities in conjunction with low sorptive capacities. These characteristics create a high potential for ground water contamination due to leaching and migration into the saturated zone. However, the same characteristics suggest a contaminant transported under advection/dispersion flow conditions that would not be persistent at the site over an extended period of time.

Analyses of water samples from the onsite monitoring wells demonstrate decreased and non-detect pesticide concentrations away from the domestic well in all directions excluding the upgradient well. Elevated concentrations of bentazon and the occurrence of dinoseb in the upgradient well indicate the possibility of at least two separate source contaminant areas.

A detailed inspection of the chemical characteristics of both pesticides, including partition coefficients, phase distribution and retardation-related velocities, support assumptions of transport characteristics based on the solubilities of the pesticides. An explanation for the persistence of the pesticides would be the migration of the pesticides into deeper soil profiles, where degradation due to photolysis and microbial action are diminished, and diffusion into less permeable stagnant zones. The rate of diffusion out of less permeable zones is often related to the period of time a release has been occurring or the residence time for the contaminant source within the subsurface. It is plausible that several releases related to overfilling and/or drum leakage occurred over the time period that the pesticides were in use.

Analyses of soil samples extracted from continuous soil cores demonstrated the lack of detectable pesticide concentrations in the soil profile for the sampling locations. This information, together with decreased downgradient and sidegradient concentration, strongly suggests a point source(s) of contamination, rather than from leaching associated with general application of the pesticide (nonpoint source).

It is important that additional studies be performed at other well locations where elevated concentrations of pesticides have been detected; especially at sites where the detections appear in two consecutive seasons. Laboratory analyses should include the pesticides known to be used in a given area. Predictions of pesticide occurrence based on dissipation half-lives, sorption, solubility, and other criteria can be misleading due to other variables which may exert a stronger influence on contamination potential including timing of application (in relation to rain event), preferential flow along macropore pathways and high vadose zone permeabilities.

**Future Investigations**

Although the investigation appears to have been successful in isolating the contamination as a point source rather than a nonpoint source, many questions remain concerning the location of the residual source of contamination and the potential for more than one release area. Current plans are to advance additional borings in the suspected source areas at the Augusta site and to install one additional well upgradient of MW4 and possibly one additional well between the domestic well and MW2. Preferential soil profiles for sampling and analyses would include the zone of increasing clay content (3-7 feet) and the saturated silt loam immediately above the occurrence of the sand unit (10-13 feet). Potential funding sources include BASF, which assisted in various phases of the project, including furnishing data on soil sorption and dissipation studies.

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