

**THE OCCURRENCE OF PICLORAM (TORDON) AND
2,4-D IN GROUNDWATER IN THE DENBIGH SAND
HILLS, McHENRY COUNTY, NORTH DAKOTA**

by

Edward C. Murphy

and

Earl A. Greene

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ABSTRACT

Picloram (Tordon) and 2,4-D are commonly used in North Dakota to control leafy spurge. The Denbigh Sand Hills, of McHenry County, are heavily infested with leafy spurge and as a result there is widespread use of these herbicides in the area. The Denbigh Sand Hills are stabilized eolian dunes which formed as sand was transported by the wind from the shores and dried bottom of glacial Lake Souris. The United States Bureau of Land Management holds several tracts of land in this area and this study took place on four of these tracts. The near surface geology consists of poorly consolidated, fine to medium grained sand. The water table is generally within 15 feet of the surface in this area. Therefore, this area is highly susceptible to impacts from agricultural chemicals.

A total of 13 wells, ranging in depth from 5.5 to 31.75 feet, were drilled during this study. In addition, sediment cores were obtained from three additional test holes. Water levels were recorded on a monthly basis and nine separate rounds of water samples were taken. Precipitation was below average during the three year study and water levels in the monitoring wells declined an average of 3 feet during this

time period.

The highest concentrations of pesticides detected in the groundwater were 107 ppb of picloram and 1.78 ppb 2,4-D. The highest concentrations of pesticides detected in sediment samples was 160 ppb of picloram and 20 ppb of 2,4-D. The levels of pesticides detected in the groundwater are below the EPA Maximum Concentration Limits which take effect January, 1993.

Drought conditions during the study period likely resulted in a decrease in the frequency and amount of groundwater recharge in this area. It is therefore likely that the concentrations detected are much less than what would have been encountered during a time of normal precipitation.

There are other areas of the state that are equally vulnerable to impacts of agricultural chemicals; these areas should also be studied. The answers to the questions posed by agricultural chemical impacts will require long-term studies of groundwater and surface water.

AUTHOR'S NOTE

Earl A. Greene was a hydrologist with the U.S. Bureau of Land Management in Dickinson, North Dakota when this project began. He is now a ground water hydrologist

in the Water Resources Division of the United States Geological Survey in Rapid City, South Dakota.

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This study began as a cooperative project between the North Dakota Geological Survey and the United States Bureau of Land Management (BLM). The BLM paid for the chemical analyses of groundwater and sediment samples from 1987 through 1989. The North Dakota State Department of Health and Consolidated Laboratories assisted with the project by paying for the groundwater and sediment analysis in 1990.

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INTRODUCTION

In recent years, concern for the quality of our drinking water has increased as we became more aware of our impact upon both surface water and groundwater. In agricultural states such as North Dakota, this concern has focused on the potential impacts agricultural chemicals have on drinking water supplies. Agricultural chemicals have been detected in the groundwater and surface water in many states. Information from the United States Environmental Protection Agency in the late 1980s indicates that 74 pesticides had been detected in the groundwater in 38 states (NDS DH, 1989).

Leafy spurge (*Euphorbia esula*) is a very hardy and prolific weed that has spread throughout much of North Dakota. Herbicides have been widely used in an attempt to eradicate and control this weed. One area of heavy leafy spurge infestation is the Denbigh Sand Hills of McHenry County (figure 1). Farmers and ranchers in this area generally spot apply a mixture of picloram (Tordon; 4-amino-3,5,6,-trichloropicolinic acid) and 2,4-D ((2,4-dichlorophenoxy) acetic acid) to control the spread of this weed. Herbicides are usually applied in the early summer.

Purpose

The BLM owns several tracts of land in the Denbigh Sand Hills of McHenry County. Through an agreement with the lessees, the BLM provides the herbicides and the lessees apply it. The BLM was concerned that these herbicides might be reaching the shallow groundwater in this area. The purpose of this study was to monitor the fluctuations of the water table, analyze the shallow groundwater beneath selected BLM tracts for the herbicides picloram and 2,4-D, and recommend, if appropriate, means of preventing these pesticides from reaching the water table if they were detected.

Field and Laboratory Methods

The North Dakota Geological Survey's Mobile Drill B-50 was used to install 13 monitoring wells on four tracts of federal land in the Denbigh Sand Hills in McHenry County (figure 1) (appendices A and B). Monitoring wells were installed from May 5-7, 1987. Five monitor-

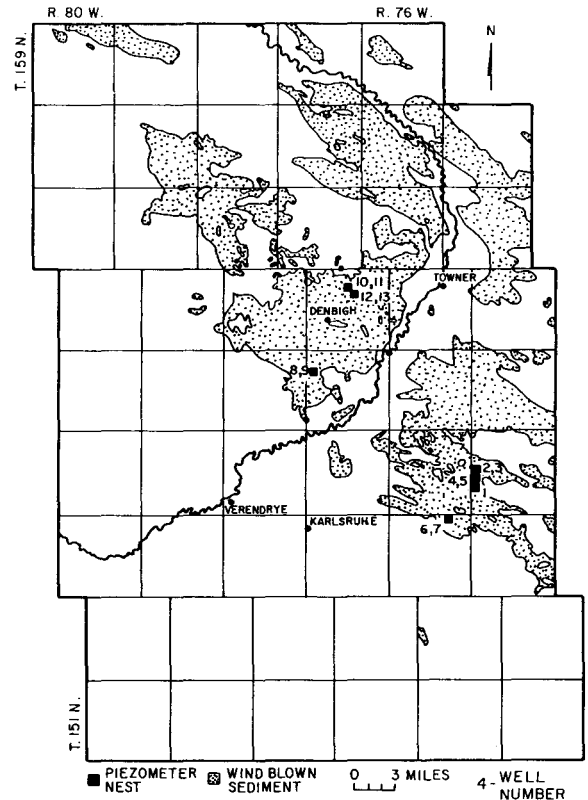


Figure 1. Location map of the Denbigh Sand Hills, McHenry County.

ing wells are located on the Anderson tract (154-75-19), two on the LeMar tract (153-76-2), two on the Best tract (155-77-7), and four on the Larson tract (156-77-10). The monitoring wells were nested in pairs with the shallow well screened at the water table and the deeper well screened 10 to 15 feet below this horizon. The depth of the water table ranged from 4 to 20 feet at the seven study sites. The nested wells were drilled within a 10 foot radius of each other. Monitoring well 1 was the only well not nested. The wells range in depth from 6 to 33 feet with an average depth of 20 feet (appendix B).

The monitoring wells consist of 2 inch schedule 40 PVC riser and 10 slot PVC screen. Stainless steel screws were used to connect the pipe; no solvents or cements were used in these wells. The well tops consisted of threaded PVC caps. The wells were vented from underneath the

cap by filing one side of the threads to enable air to enter the well yet minimize the chances of pesticide drift entering the well. Five gallon buckets were placed over the well tops to further reduce the impacts of pesticide drift. Due to the unstable nature of the sand in the borehole, the wells were generally installed inside the hollow stem flights. Because the hole usually collapsed at the water table, the screen interval was generally filled with a natural sand pack. Five feet of bentonite chips (medium) were placed in the borehole above the top of the screen. If there were no confining layers above this interval, the borehole was backfilled with cuttings to within five feet of the surface and two additional feet of bentonite chips, followed by two to three feet of cement, were placed in the borehole to the surface. If a confining layer was present above the screen interval, the borehole was filled with bentonite chips beginning one foot below the confining layer to one foot above the layer. The hole was then backfilled with cuttings to within five feet of the surface where a two foot bentonite and three foot cement plug were added. The auger flights were rinsed thoroughly with water after each drill hole was completed and allowed to dry before drilling commenced on the next hole.

Three test holes (90-1, 90-2, and 90-3) were continuously cored on April 3 and 4, 1990 (appendix A). These test holes were drilled adjacent to monitoring wells on the Anderson and Best tracts (154-75-19 and 155-77-7). Sediment cores were also obtained from selected intervals in the monitoring well test holes. Sediment samples were taken from these cores for pesticide analysis.

A continuous recording precipitation station was placed adjacent to an additional well containing the Stevens recorder to enable a comparison of precipitation to fluctuations of the water table and therefore enable a general determination of rates and times of recharge relative to precipitation in the area. The Stevens recorder and precipitation station were located in the Anderson tract (154-75-19). Unfortunately, both machines malfunctioned and we were unable to salvage data from either of these two pieces of equipment. Water levels were obtained from each monitoring well on a monthly basis using an electric tape. The portion of the tape which came

in contact with groundwater was rinsed with deionized water between wells. To further reduce the chances of contaminating the wells, the tape was not allowed to come in contact with either soil or vegetation at the sites.

The North Dakota State Department of Health and Consolidated Laboratories analyzed the 1987 water samples for major ions, picloram, and 2,4-D. The Health Department followed the U.S. Environmental Protection Agency's Safe Drinking Water procedure 515.1 for chlorophenoxy pesticide analysis in water (Krosse, 1992). The Health Department also performed pesticide analysis on sediment samples in 1988. Minnesota Valley Testing Laboratories (MVTL) in New Ulm, Minnesota analyzed both water samples and sediment samples for picloram and 2,4-D from 1988 through 1990. MVTL also followed EPA's SDW 515.1 for water analysis, their procedure for sediment analysis is presented in appendix C.

A total of 101 samples, 68 water and 33 sediment, were analyzed for herbicide content by these two laboratories (table 1). At least five well volumes were removed from the monitoring well before the water sample was obtained. The wells were bailed with a teflon bailer or, in a few cases, a Brainerd Killman handpump. Care was taken to prevent the teflon coated bailer wire from contacting either the water in the wells or vegetation and soil at the sites. When such contact occurred, the bailer wire was rinsed with deionized water. Between wells, the bailer was thoroughly rinsed with deionized water. When the pump was used, it was dismantled and rinsed with deionized water before reuse. The 1990 samples were obtained using disposable teflon bailers, one bailer to each well. Rubber gloves were worn during sampling and were thoroughly cleaned between each well. Water samples were stored in brown glass jars with teflon or tin foil lined lids. Samples were stored on ice and transported to the laboratory within one day of sampling. In a few instances, water samples were obtained from the hollow stem of the auger flights during drilling. In this case, the procedure followed was to raise the flights one foot above the base of the hole and several volumes of water were then removed from the borehole prior to sampling.

Table 1. Detection limits for herbicide analysis.

<u>Date</u>	<u>Picloram</u>	<u>2,4-D</u>
North Dakota State Health Department		
7/2/87	0.3 ug/l	0.3 ug/l
9/19/88	0.05 ug/g*	
Minnesota Valley Testing Laboratory		
6/1/88	0.3 ppb	0.1 ppb
9/7/88	1.0 ppb	0.05 ppb
6/18/89	1.0 ppb	1.0 ppb
7/6/89	1.0 ppb	1.0 ppb
8/29/89	0.05 ppb	0.05 ppb
9/20/89	0.05 ppb	0.05 ppb
5/1/90	1.0 ppb	0.1 ppb
5/1/90	0.01 ppm*	0.01 ppm*
6/25/90	1.0 ppb	0.10ppb

* soil analysis

Lessees were supposed to record the time and amount of herbicide applied within the vicinity of the monitoring wells. However, we were unable to coordinate this portion of the project and could not independently verify that the lessee had applied the pesticide according to label restrictions. Therefore, a mixture of Tordon (picloram) and 2,4-D was applied by a certified applicator during June, 1989, following label restrictions, to measured areas around four of the seven monitoring well nest sites. The pesticide was applied by hand using two gallon spray containers. Areas around trees and shrubs were not sprayed to prevent damage from the herbicides. Five gallon plastic containers were placed over the wells during herbicide application to prevent any spray from getting into the wells or on the plastic threads where it could be introduced into the well by the bailer or water-level tape.

Climate

The climate for North Dakota is continental, subhumid (Ruffner, 1985). The average annual precipitation in this portion of McHenry County is 16 inches with an average annual snowfall of 35 inches. The average length of the growing season is 120 days (Goodman and Eidem, 1976).

PREVIOUS WORK

A national computer search of picloram and 2,4-D articles was run through Dialog Information Services, Inc. in September, 1987 and through GEOREF and other systems in September, 1992 (Mayer, 1992). The search was run using various key words and yielded over 260 references to these herbicides. The vast majority of these articles were based on studies that focused on the movement or breakdown of picloram and 2,4-D in the soil horizon and did not include groundwater monitoring (e.g., Hunter and Strobbe, 1972; MacDonald et al., 1976; Selim et al., 1976; Elzeftway et al., 1976; Wilson and Cheng, 1976; Knight and Lewis, 1981; McCall and Agin, 1985; and Bovey and Richardson, 1991). There also has been a large number of studies on the occurrence and movement of pesticides in surface water (e.g., Evans and Duseja, 1973; White et al., 1976; Bovey et al., 1978; and Mayeux et al., 1984; and Chen and Alexander, 1989). One study in Montana (Watson et al., 1989) ran a study of picloram very similar in size and scope to this study. Watson et al. (1989) sprayed picloram in two different settings and monitored one site for 15 months and the other for 3 months. They determined that one year after one of the sites was sprayed, 13% of the picloram was still present.

At least nine projects have tested for pesticides in either the groundwater or surface water in North Dakota. Four of these studies

involved the sampling and pesticide analysis of existing municipal, private, and livestock wells (Glatt, 1985; Glatt, 1986; Lym and Messersmith, 1987; and Abel, 1992). Glatt (1985 and 1986) detected trace amounts of picloram in a few private wells (maximum concentration was 3.56 ppb) and in some municipal systems (maximum concentration was 1.46 ppb). Lym and Messersmith (1987) detected picloram in 32 (6%) of the 527 water samples they tested. The highest concentrations of picloram detected in groundwater was 12.8 ppb and 5 ppb in surface water (Lym and Messersmith, 1987).

The United States Bureau of Reclamation has installed over 100 monitoring wells near Oakes, North Dakota to obtain baseline information for this area prior to any changes occurring from the proposed Garrison Diversion Irrigation Project. Montgomery, et al. (1988) used these wells to test for nitrates and for the herbicides atrazine, alachlor, metolachlor, and simazine. Alachlor was the only herbicide detected. The Bureau of Reclamation wells were screened near the base of the unconfined aquifer and therefore did not allow for a determination of the water quality throughout the entire aquifer system.

The North Dakota State Water Commission began two studies of agricultural chemicals in 1988. One project monitored the groundwater in the Englevale Aquifer in western Ransom County. No detectable concentrations of 20 selected pesticides were found in the groundwater. The second project involves the monitoring of a confined glacial outwash aquifer near Carrington, North Dakota. The Carrington report is due out in 1993 (Schuh, 1992). The Water Commission recently began a study of the impact of pesticides on shallow groundwater at Camp Grafton (Schuh, 1992).

In 1989, the Energy and Environmental Research Center at the University of North Dakota began a long-term study of agricultural chemicals in groundwater. To date, monitoring wells have been installed near Manvel, Thompson, Center, Anamoose, and Inkster (Beaver, 1992).

In addition to the studies determining the impacts of pesticide application, the groundwater adjacent to six landfills in North Dakota was

recently analyzed for 17 common pesticides to determine if discarded pesticides were leaching into the groundwater at these sites (Murphy, 1992). None of the selected pesticides were detected in the groundwater or surface water at these landfills.

GEOLOGY

All but a small portion of McHenry County is covered by Pleistocene deposits. These deposits range in thickness from 10 to 424 feet (the latter within the New Rockford channel) (Randich, 1981). The glacial deposits (excluding the channel fill deposits) are, on average, between 50 and 75 feet thick in McHenry County (Randich, 1981a). The Bullion Creek Formation (Paleocene) outcrops near the base of some of the coulees leading from the Souris River Valley in the southwest corner of the county and the Cannonball Formation (Paleocene) is exposed in an outcrop near the town of Verendrye (Clayton, 1980).

The surface of central and northeastern McHenry County is dominated by eolian dunes (Bluemle, 1982). The study area is located within these dunes, which are known locally as the Denbigh Sand Hills (figure 1). The dunes reach heights of 65 feet or more, but are generally 10 to 20 feet high. The source for these silt and sand deposits were the upper reaches of density-current fans that formed in glacial Lake Souris (Bluemle, 1982). A veneer of eolian deposits are present throughout much of this area even when the dunes are not present. Approximately three-quarters of the glacial Lake Souris deposits are mantled by these eolian deposits (Bluemle, 1982).

HYDROGEOLOGY

Approximately 20 percent of McHenry County is underlain by shallow Pleistocene aquifers (figure 2). The New Rockford, Lake Souris, Souris Valley, Voltaire, and Denbigh Aquifers are among the most extensive aquifers in the county. The New Rockford Aquifer is generally under confined conditions and has a mean thickness of 90 feet. The Lake Souris, Souris Valley, Voltaire, and Denbigh Aquifers are generally unconfined and have mean thicknesses between 20 and 40 feet (Randich, 1981a).

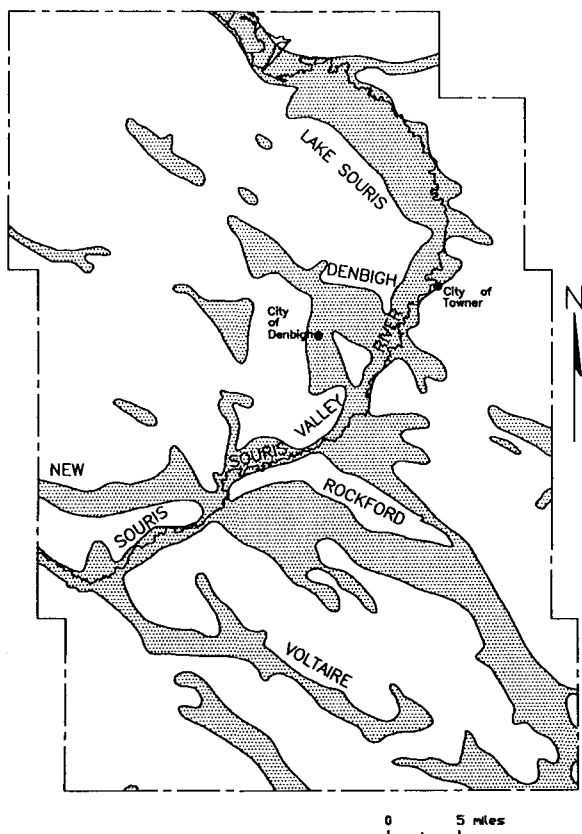


Figure 2. The major Pleistocene aquifers in McHenry County (modified from NDSWC State Aquifer Map).

Three of the seven study sites are located over, or adjacent to, known aquifers. Monitoring wells 6 and 7 are located adjacent to the New Rockford Aquifer and well nests 10-11 and 12-13 are situated above the Denbigh Aquifer. The groundwater table is generally within 20 feet of the surface throughout much of central McHenry County. The general direction of groundwater flow in these aquifers is to the southeast, although the direction of flow can be quite variable even within the same aquifer.

Groundwater Chemistry

The quality of the shallow groundwater monitored during this study was very good. The shallow groundwater in these sand hills is generally a calcium bicarbonate type and is generally very hard although one of the thirteen samples

was soft (table 2). The median value of chloride concentration of the shallow groundwater was less than 2 mg/l. The median value of total dissolved solids (TDS) was 202 mg/l (table 2). Nitrate was detected in only one sample, at 0.8 mg/l, far below the maximum permissible concentration limit of 10 mg/l (appendix D).

STUDY SITES

Monitoring Well 1

Monitoring well 1 is located in the sesesw section 19 (T154N R75W). The well was installed near the center of a shallow depression that is bordered to the east by trees (figure 3). The wooded area and the shallow depression are heavily infested with leafy spurge. Two test holes were drilled at this site, monitoring well 1 (13 feet) and test hole 90-2 (32 feet). The site is underlain by at least 32 feet of very fine to medium grained sand (appendix A). The water table fluctuated between 8 and 11 feet below the ground surface during the study. As a result, the water table fell below the base of this monitoring well during the latter part of 1988 and 1989 and the first six months of 1990 (figure 4).

The history of pesticide application at this site prior to 1987, as with the other sites, is not known. This site was not sprayed with herbicide during 1987 and 1988. Therefore, 1.4 gallons of a 6% mixture of picloram and 2,4-D (9 gallons water to 1 quart picloram and 1 quart 2,4-D) were applied to an area 44 feet by 31 feet (1,364 square feet) on June 5, 1989. The sprayed area was centered around the monitoring wells because there was not sufficient information available to determine the direction of shallow groundwater flow.

The groundwater in this well was sampled five times during this project (table 3). The well was sampled three times prior to the area being sprayed on June 5, 1989. Only one of the five water samples from this well contained picloram or 2,4-D above the detection limits. The June 1, 1988 water sample contained 0.13 ppb 2,4-D (table 3). Although this site had not been sprayed in 1987 or 1988 it had likely been sprayed in previous years and this, or spray drift from another area, might account for this reading.

Table 2. Chemical analyses of groundwater samples from the monitoring wells.

<u>Parameter</u>	<u>Minimum</u>	<u>Maximum</u>	<u>Median</u>
TDS	61	411	202
Hardness	48	427	188
Bicarbonate	60	494	246
Sulfate	5	47	9.5
Chloride	0.6	2.4	1.4
Calcium	13.4	141	53.8
Magnesium	3.5	44.7	12.9
Sodium	0.9	11.8	4.1
% Sodium	0.9	16.9	5.4
Fluoride	0.1	0.4	0.1

all values in mg/l



Figure 3. Photograph of the monitoring well 1 site. View is to the north. Stakes represent the limit of herbicide application (the southwest stake is missing).

This well went dry a month after the area was sprayed. Therefore, sediment cores were obtained adjacent to the well to determine if we could trace the movement of herbicides in the unsaturated zone (test hole 90-2). Detectable concentrations of picloram were detected at 1 and 3.25 feet and 2,4-D was detected at 8.25 and 17 feet (figure 5) (appendix F). The concentrations were low, generally at or slightly above the de-

tectable limits. Picloram concentrations decreased with depth; picloram was not detectable in samples below 3 feet (figure 5). 2,4-D was detected in sediment samples at 8.25 and 17 feet. The difference in detection of these two herbicides in the sediment may reflect the difference in subsurface mobility between the two organic compounds. A water sample, obtained through the hollow stem of the auger at a depth of 32 feet

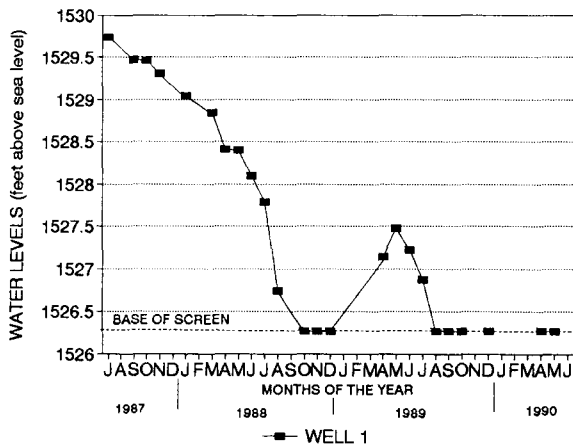


Figure 4. Hydrograph of groundwater levels at monitoring well 1 for the period July, 1987 - June, 1990.

in hole 90-2, did not contain detectable amounts of these two herbicides.

Monitoring Wells 2 and 3

Monitoring wells 2 and 3 are located in the senenw section 19 (T154N R75W). This nest was located in the center of a small depression that lies on the east flank of a dune ridge (figure 6). The site is bounded on the west by trees and shrubs. Although herbicides had likely been applied to this area prior to the study, no pesticides were applied to this site from 1987-1991.

The site is underlain by 11 feet of fine to medium grained sand that overlies at least 2 feet of shale (appendix A). The water table at this site declined from 3.8 to 6.8 feet below the surface during this study. As a result of the decline, well 3 was dry throughout the latter part of 1988 and 1989 (figure 7). Three rounds of groundwater samples were obtained for organic analysis from these wells (table 4). No picloram was found in the groundwater above the detection limits, but detectable amounts of 2,4-D were present in the groundwater sampled from both wells on June 1, 1988 and September 7, 1988 (table 4). The concentrations in both wells decreased by one half during this time period. These small concentrations may have been present in the July 2, 1987 sample and not discovered because they were close to the detectable limit. Or, this herbicide may have migrated with groundwater from an area where it was previously applied or had been flushed down to the water table by recharge during the spring of 1988.

Access to the site was difficult. As a result, these wells were not monitored as closely as the others.

Monitoring Wells 4 and 5

Monitoring wells 4 and 5 are located in swnesw of section 19 (T154N R75W). The wells are located near the center of a large flat area situated between two northwest trending dune ridges (figure 8). The site is bounded on the

Table 3. Organic analyses of groundwater in monitoring well 1.

<u>Date</u>	<u>Picloram</u>	<u>2,4-D</u>
7/2/87	<0.3	<0.3
6/1/88	<0.3	0.13
9/7/88	<1.0	*
6/5/89	-----	
6/18/89	<1.0	<1.0
7/6/89	<1.0	<1.0
8/29/89	*	*
9/20/89	*	*
5/1/90	*	*
6/20/90	*	*

* well was dry

values in ppb

---- date area around well was sprayed

north by trees and to the south by a dune ridge. The area is heavily infested with leafy spurge.

This site is underlain by at least 47 feet of fine to medium grained sand. A one half foot thick clay lens was encountered beneath the site at a depth of 40 feet (appendix A). The water table at the site declined from 7 to 11.75 feet below the surface during the course of the study. As a result of the decline, well 4 contained little water during 1989 and was dry during 1990 (figure 9).

The prior history of pesticide application at this site is not known. This area was not sprayed with herbicide during 1987 and 1988. However, detectable levels of 2,4-D were found in the groundwater in both wells during June and September of 1988 (table 5). The area was sprayed with a 9.5 gallon mixture of picloram and 2,4-D (one quart picloram and one quart 2,4-D to 9 gallons water to a 10,000 ft² area (1/4 acre) on June 5, 1989. The 100 foot by 100 foot spray area was centered around the monitoring wells. Detectable levels of 2,4-D were found in the groundwater 3.5 months after the herbicide mixture was applied. The highest concentration found in groundwater at this site came from a water sample taken at the base of a 40 foot drillhole on May 1, 1990, one year after the herbicide had been applied (0.54 ppb 2,4-D) (table 5).

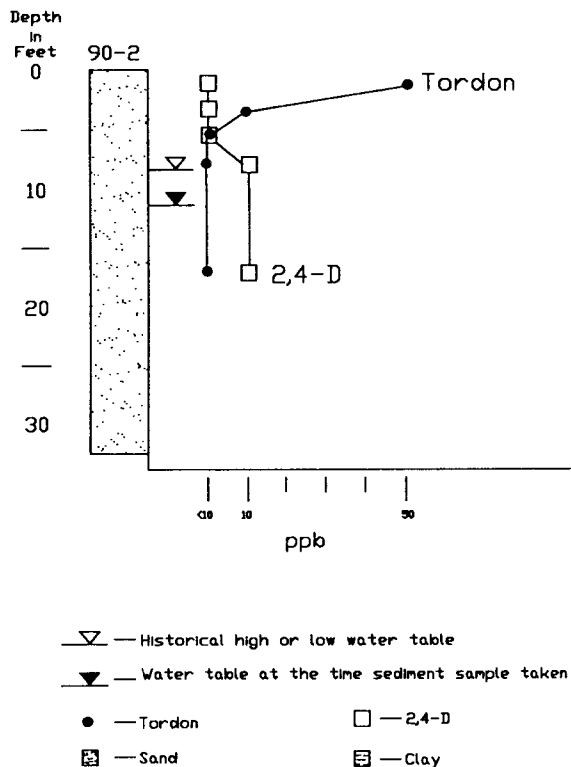


Figure 5. Concentration profiles of picloram and 2,4-D concentrations in sediment adjacent to monitoring well no. 1 (hole no. 90-2).

Table 4. Picloram and 2,4-D analyses of groundwater from monitoring wells 2 and 3.

<u>Date</u>	<u>Well #</u>	<u>Picloram</u>	<u>2,4-D</u>
7/2/87	2	<0.3	<0.3
	3	<0.3	<0.3
6/1/88	2	<0.3	0.4
	3	<0.3	0.18
9/7/88	2	<1.0	0.2
	3	<1.0	0.09

values in ppb

Table E. Organic analyses of groundwater samples from wells 4 and 5

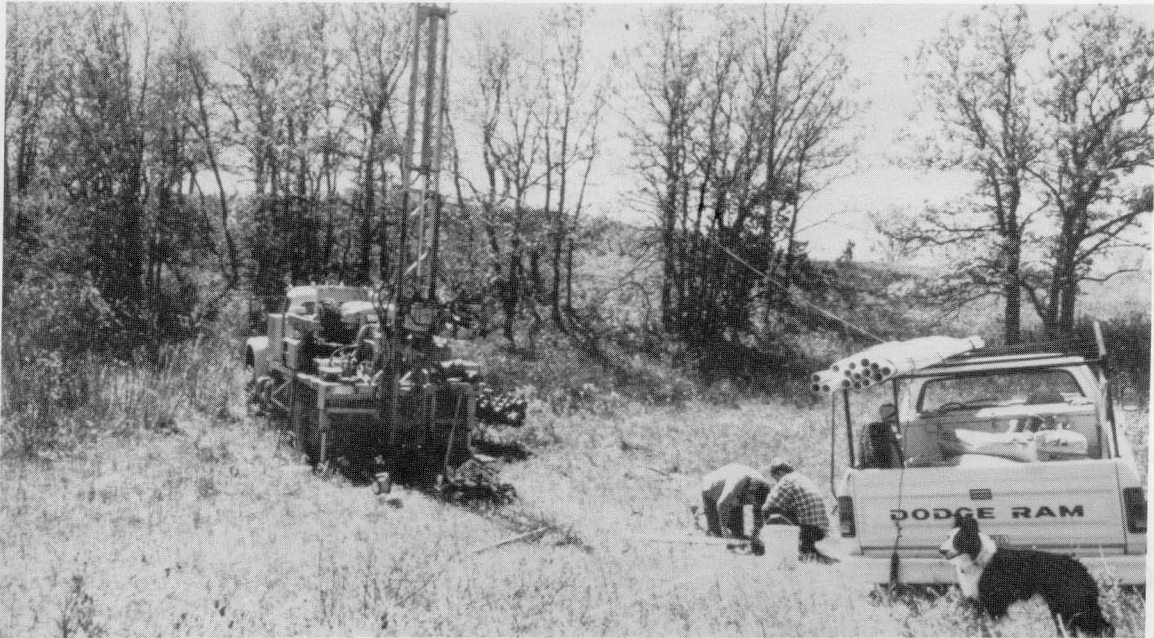


Figure 6. Installing monitoring well 2 at the well 2 and 3 nest. View is to the southwest.

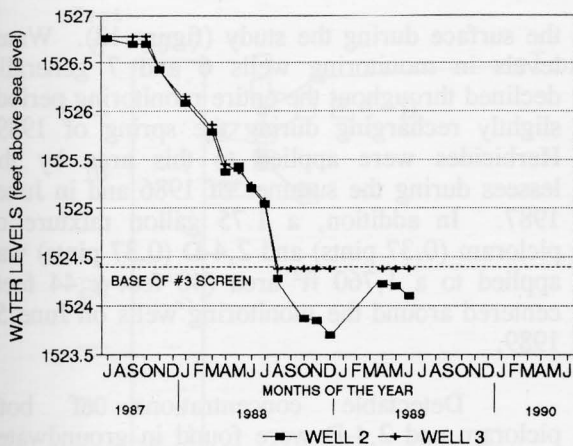


Figure 7. Hydrograph of groundwater levels at monitoring wells 2 and 3 for the period July, 1987 - June, 1990.

Sediment cores were obtained from a test hole augered adjacent to the monitoring wells on May 1, 1990. Detectable concentrations of

picloram were found in sediment within 0.5 and 1.5 feet of the surface and at a depth of 11.75 feet; the latter sample corresponds to the water table the day the sample was taken (figure 10) (appendix F). Detectable concentrations of 2,4-D were found at 3.75 feet and in sediment samples at the water table (11.75 feet) (figure 10). These results indicate that some of the organic compounds had been flushed to the water table and that concentrations of picloram and 2,4-D were still present in the soil profile.

Monitoring Wells 6 and 7

Monitoring wells 6 and 7 are located in the swnesw section 7 (T153N R76W). The site is located at the base of a north trending dune. The site is bounded on the west by trees and shrubs (figure 11).

The site is underlain by at least 33 feet of sand. A one-foot-thick clay lens is present at a depth of 17 feet. The sand below this lens is coarser grained than that above and contains occasional pebbles (appendix A). The water table declined from a depth of 20 feet to 24 feet below



Figure 8. Photograph of the monitoring well 4 and 5 nest. View is to the west-northwest. The monitoring wells are covered with 5 gallon plastic buckets.

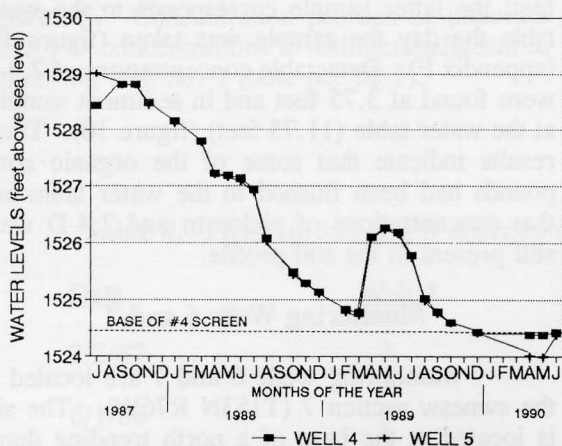


Figure 9. Hydrograph of groundwater levels at monitoring wells 4 and 5 for the period July, 1987 - June, 1990.

the surface during the study (figure 12). Water levels in monitoring wells 6 and 7 generally declined throughout the entire monitoring period, slightly recharging during the spring of 1989. Herbicides were applied to this area by the lessees during the summer of 1986 and in June, 1987. In addition, a 1.75 gallon mixture of picloram (0.37 pints) and 2,4-D (0.37 pints) was applied to a 1,760 ft² area (40 feet x 44 feet) centered around the monitoring wells on June 5, 1989.

Detectable concentrations of both picloram and 2,4-D were found in groundwater samples from both wells 6 and 7 in July, 1987 (table 6). These concentrations likely were the result of the lessees application of herbicide in this area in 1986 and potentially from the June, 1987 application. Detectable concentrations of 2,4-D were present in the groundwater samples from both wells in September, 1988, one year after the area was sprayed. The largest concentration of 2,4-D recorded at this site was found in well 6 on June 18, 1989, two weeks after appli-

Table 5. Organic analyses of groundwater samples from wells 4 and 5.

<u>Date</u>	<u>Well No.</u>	<u>Picloram</u>	<u>2,4-D</u>
7/2/87	4	<0.3	<0.3
	5	<0.3	<0.3
6/1/88	4	<0.3	0.19
	5	<0.3	0.17
9/7/88	4	<1.0	0.15
	5	<1.0	0.15
6/5/89		-----	
6/18/89	4	<1.0	<1.0
	5	<1.0	<1.0
7/6/89	4	<1.0	<1.0
	5	<1.0	<1.0
8/29/89	4	<0.05	<0.05
	5	<0.05	<0.05
9/20/89	4	<0.05	0.13
	5	<0.05	<0.05
5/1/90	5	<1.0	0.1
	5*	<1.0	0.54
6/25/90	5	<1.0	<0.10

values in ppb

5* groundwater sample taken from inside hollow stem auger flights at depth of 40 feet.

---- date pesticides were sprayed at site

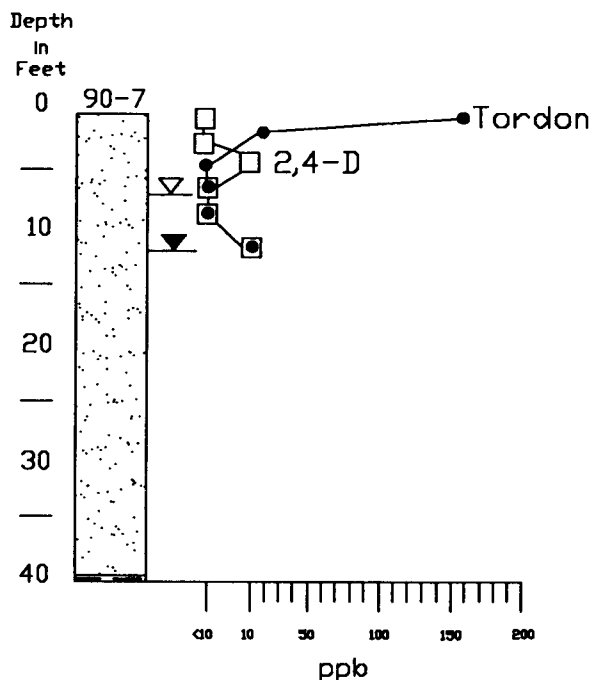


Figure 10. Concentration profiles of picloram and 2,4-D concentrations in sediment at wells 4 and 5.

cation of herbicide to the area (table 6). Of particular interest at this site is that well 6, the deeper of the two wells, consistently contained the higher concentrations of these two pesticides throughout the study. Since both of these pesticides are rather soluble in water, this occurrence is likely the result of normal transport of the pesticides along groundwater flow lines in an area with a stronger vertical than horizontal gradient.

Monitoring Wells 8 and 9

Monitoring wells 8 and 9 are located in the newsw section 7 (T155N R77W). The wells are situated on the south slope of an east trending dune. The site is bounded on the west by a grove of trees and on the east by a small ravine (figure 13). The site is underlain by at least 32 feet of fine to coarse grained sand. A one foot thick clay layer separates this unit from the underlying coarse grained sand and gravel (appendix A).

The site had been treated with a picloram and 2,4-D mixture by the lessee in 1986 and 1987. A number of shrubs had been killed by the herbicides and it was noted that leafy spurge was



Figure 11. Augering testhole for monitoring well 6. View is to the southeast.

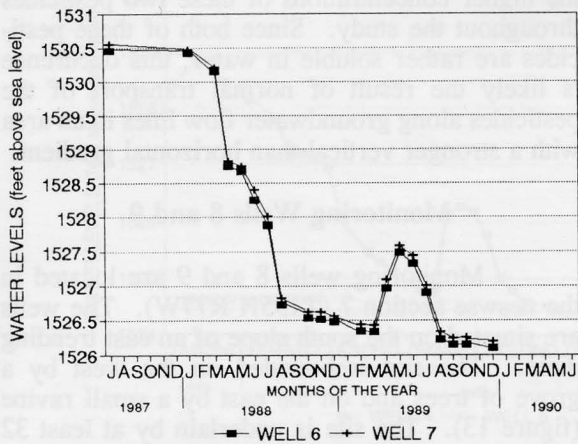


Figure 12. Hydrograph of groundwater levels at monitoring wells 6 and 7 during the period of July, 1987 to June, 1990.

one of the first plants to revegetate the area. There are some indications that the 1987 application may have been in excess of the recommended rate. On June 6, 1989, a 2.1 gallon mixture of picloram (0.45 pints) and 2,4-D (0.45 pints) was applied to a 2100 ft² area (35 feet x 60 feet) with the wells in the southeast quadrant of the rectangle.

At the beginning of this study, the water table was at a depth of 9.75 feet; near the end of the study it had declined to 14 feet. A two- to three-inch plug of bentonite at the top of the screen caused well 9 to be inoperable during the first 8 months of the study (figure 14). The water table dropped below the base of this well for the latter part of 1988, the winter and fall of 1988, and the winter and spring of 1990. The water table recovered at this site during the spring and early summer of 1989 and was recovering when the last reading was taken in June, 1990 (figure 14).

Table 6. Organic analyses of groundwater samples from wells 6 and 7.

<u>Date</u>	<u>Well No.</u>	<u>Picloram</u>	<u>2,4-D</u>
6/86			
6/87			
7/2/87	6	0.55	2.19
	7	< 0.3	0.66
6/1/88	6	< 0.3	< 0.1
	7	< 0.3	< 0.1
9/7/88	6	< 1.0	0.15
	7	< 1.0	0.15
6/5/89			
6/18/89	6	< 1.0	1.78
	7	< 1.0	< 1.0
7/6/89	6	< 1.0	< 1.0
	7	< 1.0	< 1.0
8/29/89	6	0.07	0.11
	7	< 0.05	< 0.05
9/20/89	6	< 0.05	< 0.05
	7	< 0.05	< 0.05

values are in ppb unless

--- dates pesticides applied at this site



Figure 13. Earl Greene pumping groundwater from monitoring well 9. Note the dead shrubs surrounding the wells. View is to the southwest.

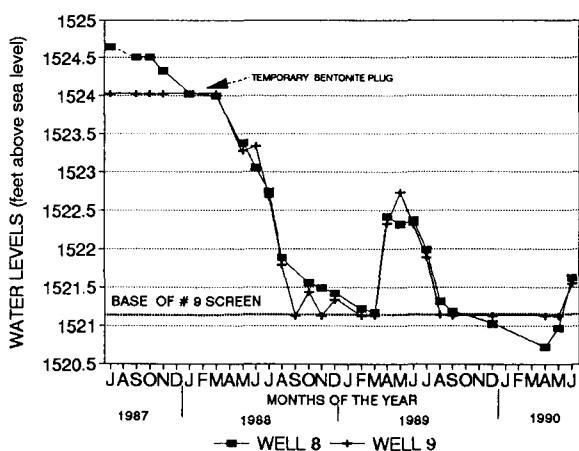


Figure 14. Hydrograph of groundwater levels at monitoring wells 8 and 9 during the period of July, 1987 to June, 1990.

Detectable concentrations of both picloram and 2,4-D were found in both wells 8 and 9 during this study (table 7). Elevated levels of picloram were detected in well 9 in June and September, 1988. An elevated concentration of picloram (18.4 ppb) was also detected in the groundwater in well 9 one month after the June 5, 1989 application of the picloram/2,4-D mixture to the area (table 7). We were not able to document the picloram concentrations at the water table over the next year because well 9 was dry when we took our four last samples.

Two sets of sediment core were taken at the site. The first set of core was obtained when testhole 8 was drilled in 1987. The second set of sediment core was obtained from a testhole drilled at this site in 1990. Selected intervals of both sets of sediment core were analyzed for picloram and the 1990 samples were also analyzed for 2,4-D (figure 15). Both picloram and 2,4-D were detected in the sediment samples from this site. In the 1987 core, picloram was detected below the water table at depths of 11 (0.08 ppb) and 12 feet (0.41 ppb). In the 1990 core, picloram was detected in sediment just below the surface (1.25 feet, 70 ppb) and at the

Table 7. Organic analyses of groundwater samples from wells 8 and 9.

<u>Date</u>	<u>Well No.</u>	<u>Picloram</u>	<u>2,4-D</u>
1986			
1987			
7/2/87	8	<0.3	0.59
6/1/88	8	<0.3	0.14
	9	91.3	0.29
9/7/88	8	<1.0	0.34
	9	107.0	*
6/6/89			
6/18/89	8	<1.0	<1.0
	9	<1.0	<1.0
7/6/89	8	<1.0	<1.0
	9	18.4	<1.0
8/29/89	8	<0.05	<0.05
9/20/89	8	<0.05	<0.05
5/1/90	8	<1.0	0.31
6/20/90	8	<1.0	<0.1

values are in ppb.

* sufficient sample was not available to do both analyses.

water table (13.75 feet, 10 ppb) and 2,4-D was detected both above the water table (8.75 feet, 20 ppb) and at the water table (13.75 feet, 10 ppb) (figure 15). The highest concentration of picloram occurred in a 1987 sand sample overlying a one-foot-thick clay lens at a depth of 12 feet. This suggests that the clay lens acts as a semi-permeable boundary and picloram that has been flushed to the water table migrates laterally along this horizon. Sand samples below this clay bed, taken in 1987, contained detectable concentrations of both picloram and 2,4-D, suggesting that either the clay lens is not laterally extensive or that groundwater does flow vertically through this layer.

Monitoring Wells 10, 11, 12, and 13

Monitoring wells 10 and 11 are located on a knoll in the nwsww section 10 (T156N-R77W). Monitoring wells 12 and 13 are located in a topographic low and are bounded on the north and east by trees and shrubs in the nesww section 10 (T156N-R77W) (figure 16). Both monitoring well nests are located in a BLM tract that has never allowed herbicide application. Wells 10 and 11 are located 300 feet, and wells 12 and 13 are located 700 feet, south of the north tract boundary (this is the closest tract boundary to these wells). The areas outside of the BLM tract have been sprayed repeatedly for leafy spurge.

Both sites are underlain by at least 28 feet of fine to medium grained sand (appendix A). A medium to coarse grained lens of sand occurs at a depth of 10 to 13 feet at the well 10 and 11 nest site. The water table was at a depth of 8.6 feet at wells 10 and 11 when this study began. The water table declined steadily throughout the fall of 1987 and all of 1988 before recharging during the spring of 1989 (figure 17). The water table declined from 5.8 feet to 8.3 feet below the surface during this same time period in monitoring wells 12 and 13 before also recharging during the spring of 1989 (figure 18).

Picloram was not detected in groundwater from any of these four wells. However, detectable concentrations of 2,4-D were present in groundwater samples taken in June and September, 1988 (table 8). These concentrations are low and were close to the detectable analytical limits

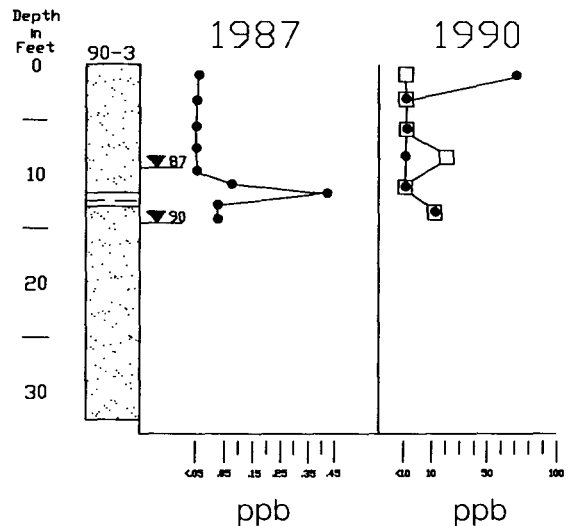


Figure 15. Concentration profiles of picloram and 2,4-D in sediment samples from monitoring well nests 8 and 9.

used in 1987. Therefore, these small concentrations may have been present in the groundwater prior to their detection in 1988. Since a minimum of 300 feet separates these wells from areas that receive herbicide application, the source of the 2,4-D in the groundwater at these sites would be either from aerosol drift into the area, groundwater transport from areas that receive herbicides, or a combination of both. In all cases of 2,4-D detection at these two sites, the highest concentration occurred in the deepest of the two wells (table 8).

HYDRAULIC CONDUCTIVITY

Due to low water levels, in-situ hydraulic conductivity tests (slug tests) were performed on only four of the thirteen monitoring wells. These wells were screened in fine to medium grained sand. The data was analyzed using methods developed by Hvorslev (1951). The hydraulic conductivities of the near-surface sand deposits ranged from 1.7×10^{-4} ft/s to 4.3×10^{-3} ft/s (5.2×10^{-3} cm/s to 1.3×10^{-1} cm/s) (table 9). These values fall within the normal range of hydraulic conductivities for silty to clean sand (Freeze and Cherry, 1979). The sand adjacent to the screen in monitoring well 8 was coarse grained and contained 10-20% gravel as compared to the



Figure 16. Dave Lechner stands at the north boundary of the BLM tract containing monitoring wells 10-13. Note the heavy infestation of leafy spurge in this area. The location of monitoring wells 10 and 11 is depicted with an (x), wells 12 and 13 by an (O). View is to the southeast.

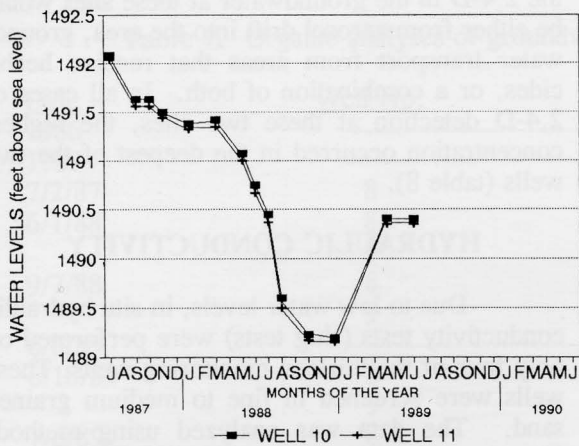


Figure 17. Hydrograph of groundwater levels at monitoring wells 10 and 11 for the period from July, 1987 to June, 1989.

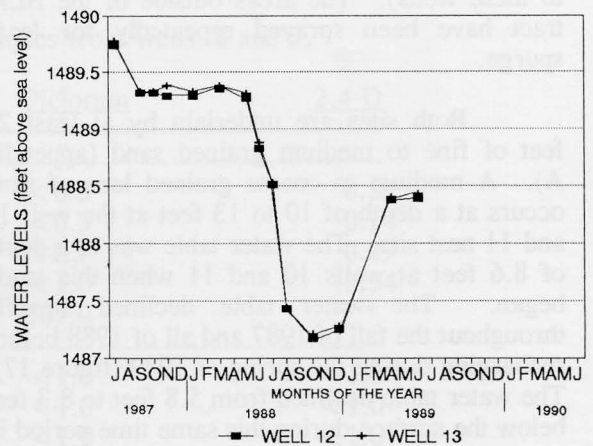


Figure 18. Hydrograph of groundwater levels at monitoring wells 12 and 13 from July, 1987 to June, 1989.

Table 8. Organic analyses of water samples from monitoring wells 10, 11, 12, and 13.

<u>Date</u>	<u>Well no.</u>	<u>Picloram</u>	<u>2,4-D</u>
7/2/87	10	<0.3	<0.3
	11	<0.3	<0.3
	12	<0.3	<0.3
	13	<0.3	<0.3
6/1/88	10	<0.3	0.36
	11	<0.3	0.2
	12	<0.3	<0.1
	13	<0.3	<0.1
9/7/88	10	<1.0	0.43
	11	<1.0	0.12
	12	<1.0	0.16
	13	<1.0	0.26

values are in ppb.

fine to medium grained sand adjacent to the screens in wells 10, 12, and 13 (appendix A). The increase in the hydraulic conductivity of the sediment adjacent to the well screen in well 8 is attributable to this increase in grain size (table 9). Horizontal gradients were determined between nests 10 & 11 and 12 & 13 and used to calculate the average linear velocities of groundwater in these units using the formula:

$$v = \frac{Ki}{n}$$

where v is the average linear velocity (ft/s), K is the hydraulic conductivity (ft/s), i is the hydraulic gradient (ft/ft), and n is the porosity (dimensionless) (Freeze and Cherry, 1979). The average linear velocities of groundwater in the near-surface sand unit varied from 65 to 943 feet/year (table 9).

PRECIPITATION

The mean annual precipitation for the

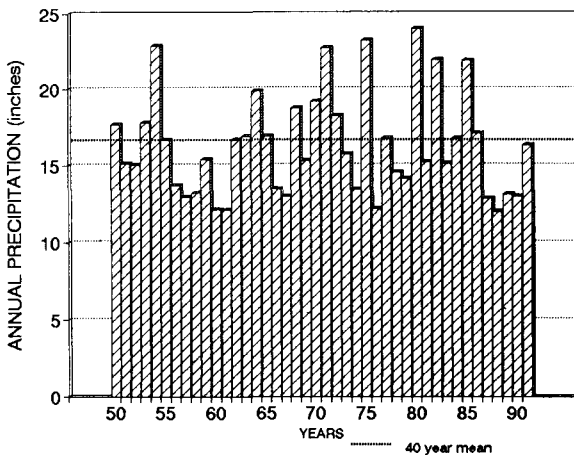


Figure 19. Annual precipitation for the Towner, North Dakota recording station from 1950 to 1991. Source: National Oceanic and Space Administration.

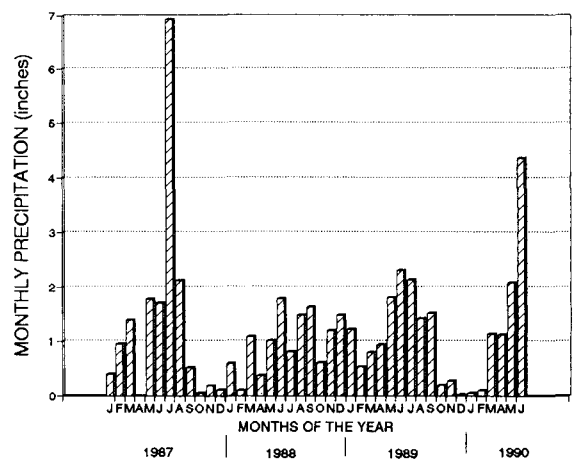


Figure 20. Monthly precipitation for the Towner, North Dakota recording station from July, 1987 to June, 1990. Source: National Oceanic and Space Administration.

Table 9. Hydraulic conductivities of sediment adjacent to monitoring well screens and the average linear velocities of groundwater in these units.

<u>Well</u>	<u>Gradient</u>	<u>Porosity</u>	<u>K</u>	<u>v</u>
8	NA	0.25	4.3×10^{-3} ft/s	-----
10	0.003	0.25	2.5×10^{-3} ft/s	943 ft/yr
12	0.003	0.25	1.7×10^{-4} ft/s	65 ft/yr
13	0.003	0.25	2.5×10^{-3} ft/s	943 ft/yr

K = hydraulic conductivity

v = average linear velocity

NA = horizontal gradient could not be determined

community of Towner from 1950 to 1991 was 16.43 inches. The annual precipitation for the Towner recording station during the three-year study averaged 12.76 inches, 3.67 inches below the 40 year-mean (figure 19). July, 1987 and June, 1990 received unusually high amounts of precipitation (figure 20). Most importantly, below average precipitation occurred during March and April, 1988 and 1989, when most groundwater recharge takes place (Rehm, et al., 1982).

CONCLUSIONS

1. The Denbigh Sand Hills consist of at least 30 feet of fine- to medium-grained sand. The water table is generally within 5 to 15 feet of the surface and was at an average depth of 9 feet at the seven monitoring sites. The shallow aquifers in this area are generally unconfined. The shallow groundwater is generally of very good quality with an average total dissolved solids (TDS) concentration of 200 mg/l.

2. Because of the drought during the study period, recharge to the water table was decreased. Water levels in the monitoring wells decreased an average of 3 feet over the course of this study.

3. Concentrations of Picloram in the Denbigh Sand Hills ranged from 0.07 to 107 ppb in groundwater and 10 to 160 ppb in the sediment. Concentrations of 2,4-D ranged from .09 to 2.19 ppb in groundwater and up to 20 ppb in the sediment. The Maximum Concentration Limit (MCL) for Picloram is 500 ppb and 70 ppb for 2,4-D in drinking water. These new limits

set by the U.S. Environmental Protection Agency take effect January 1, 1993 (Krosse, 1992). Therefore, the concentrations of the herbicides detected in groundwater during this study did not exceed the new MCL.

4. It is difficult to determine the exact source of the pesticides detected in the groundwater at these sites because areas surrounding most of these well nests had been sprayed at one time or another for a number of years preceding this study. The presence of detectable 2,4-D in the no-spray BLM tract (wells 10-13) suggests that the source for the pesticide was either drift from other areas (300 to 700 feet away), from migration in groundwater from these spray areas, or a combination of both.

5. The shallow groundwater in the Denbigh Sand Hills is extremely vulnerable to agricultural chemical application due to the permeability of the near surface sediments and the high water table.

RECOMMENDATIONS

This project was undertaken with a very small budget that precluded us from adequately instrumenting each of the four federal tracts. The decision was made at the start of the project to spread out the instrumentation to enable some data to be collected from each tract. Results of the study indicate that more information may have been gained by concentrating the monitoring wells in one, or at the most, two sites.

We recommend that future pesticide studies determine the direction of groundwater

flow and place additional wells downgradient from the spray area to determine migration of these organic chemicals within the saturated zone.

Also, because of budget restraints, we could not afford to completely seal the borehole with neat cement and to place a locking metal cover over the top of the monitoring wells. Ideally, this should be done to minimize any concern that improper well construction may have provided additional opportunities for the chemicals in question to migrate to the water table. Although we were not able to do this, the unconfined conditions and the homogeneity of the shallow sand deposits makes it unlikely that the herbicides would have preferentially migrated in the disturbed borehole. We set our screens below confining layers (thin clay beds) in only 3 of our 13 wells (appendix B).

Although we do not feel it adversely impacted the study, we recommend any future studies completely fill the borehole, above the screen interval, with a bentonite plug and neat cement and place a locking well cover over each well. This will minimize any speculation about well-completion techniques and their impact on the results of the study.

We found it difficult to coordinate the times that the lessees sprayed and the amounts that they applied to these test areas. When asked about the amount applied to an area, one lessee replied "I really soaked the plants down".

For this reason, we highly recommend that any future studies that monitor the impact of spot application of pesticides more closely coordinate with the applicators to insure that the label restrictions on application rates are followed closely, or do as we did and apply it yourself.

Seven major sand dune areas occur in North Dakota (figure 21). The geologic and the hydrogeologic conditions at these sites are similar to those found in the Denbigh Sand Hills, i.e., sand, a shallow water table, unconfined aquifers, etc. Therefore, it is anticipated that these areas are also susceptible to impact from activities such as agricultural chemical application.

We recommend these areas be targeted by future studies of the impacts of agricultural chemical application to determine the extent of any such impact.

This three-year study (July, 1987 to June, 1990) took place during a prolonged drought. As a result, less frequent recharge to the shallow groundwater occurred than during a year with normal precipitation. The exception to this may have been the large amount of precipitation that fell during July, 1987. The concentrations of picloram and 2,4-D found in the groundwater during this study are likely to be less than would have been detected during a time of normal or above-normal precipitation. The decrease in precipitation enabled the herbicides to stay on the plant or near the surface rather than be flushed into the subsurface with precipitation. Picloram breaks down in ultraviolet light, but 2,4-D undergoes only minor loss from photodecomposition (WSSA, 1983). According to the Weed Science Society of America (WSSA), both herbicides undergo microbial breakdown in warm, moist soils. The climate of North Dakota (relatively dry and cool) may slow biodecay and therefore enable these herbicides to persist in the subsurface longer here than they would in a warmer, moisture climate (Watson et al., 1989).

More detailed investigations during years of normal or above normal precipitation are needed to adequately determine the fate of these herbicides in the subsurface. Periodic coring of sprayed areas will enable the herbicides to be traced through the unsaturated zone.

A number of studies on the environmental impacts of agricultural chemicals have been undertaken in North Dakota over the last eight years. The results of the studies currently underway will help us to better understand the movement of agricultural chemicals in the subsurface. In some environmentally sensitive areas of the state we may want to control leafy spurge with nonchemical methods. The control of leafy spurge by insects and farm livestock such as sheep and goats may hold much promise. In the meantime, educational programs, which alert farmers and ranchers to the potential environmental impacts of misapplication of farm chemicals, along with the North Dakota Weed Control

Association maps that identify areas vulnerable to agricultural chemical application, are important

tools in reducing the impacts of agricultural chemicals on groundwater and surface water.

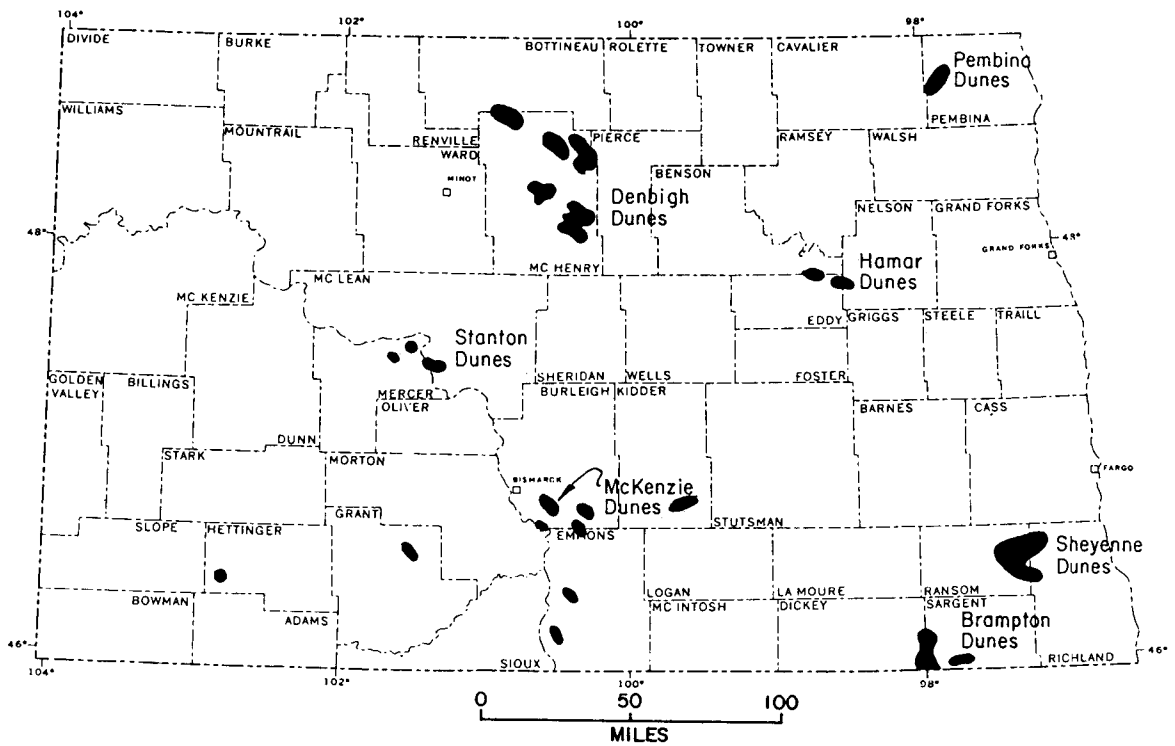


Figure 21. Major sand dunes of North Dakota (from Bluemle, 1991). The shallow groundwater beneath these areas may be susceptible to impact from agricultural chemicals.

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APPENDICES

APPENDIX A
Lithologic descriptions of test holes

SAND	Gray/green, medium to fine grained, quartz, lignite and rock fragments, subangular grains.	13-29
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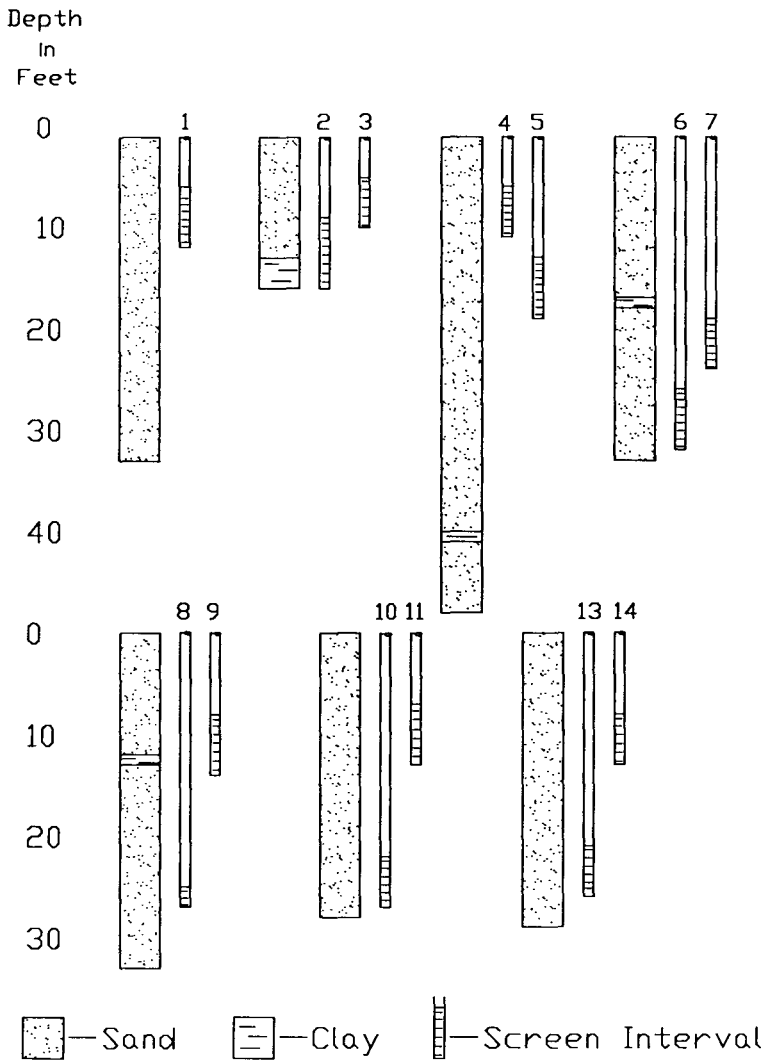
#12 and #13
T156N R77W, neswsw 10

Depth drilled (ft): 28	Surface elev. (ft): 1495
Screen interval (ft): 12 = 21-26, 13 = 8.25-13.25	

<u>Lithology</u>	<u>Description</u>	<u>Depth</u>
TOPSOIL		0-1
SAND	Light brown, fine to medium grained, quartz.	1-8
SAND	Medium brown, fine to medium grained.	8-10
SAND	Medium gray, fine to medium grained.	10-28

APPENDIX B
Well Completion Data

<u>Well No.</u>	<u>Screen Interval (ft)</u>	<u>Lithology</u>
1	5.5 - 10.5	sand
2	8 - 13	sand & shale
3	3.5 - 5.5	sand
4	6 - 11	sand
5	13 - 18	sand
6	26.75 - 31.75	sand
7	19.5 - 24.5	sand
8	25 - 27	sand & gravel
9	8 - 14	sand & clay
10	22 - 27	sand
11	7.75 - 12.75	sand
12	21 - 26	sand
13	8.25 - 13.25	sand



APPENDIX C
Laboratory Procedure for Sediment Analysis

1.0 SCOPE

This procedure describes the method for extraction and quantification of 2,4-D, Silvex (2,4,5-TP), Banvel (dicamba), and Tordon (picloram) in soil.

2.0 PRINCIPLE

Chlorinated phenoxy acids are extracted from a basic, then acidified, sample solution with chloroform. The extracted acids are methylated and analyzed by gas chromatography using electron capture detection.

3.0 GLASSWARE

Centrifuge bottles, plastic, 200 ml
Graduated cylinders
Boiling flasks, 250 ml
Separatory funnels, 250 ml
Beakers
Concentrator tubes
Volumetric pipettes
20 ml scintillation vials
Glass stoppers
7 ml saver vials
Shimadzu GC vials, with caps and septa

4.0 EQUIPMENT

Scale, accurate to 0.1 mg
Wrist action shaker
Rotary evaporator
Centrifuge
Boiling stones
Stand with small 3-finger clamps
Methylation apparatus (see diagram)
Tube heater
Filter paper, 2V and 226
Micro-spatula
Snyder columns, small
Stand with small three-finger clamps

5.0 CHEMICALS AND SOLUTIONS

Chloroform, Residue Grade
Acetonitrile, Nanograde
RODI Water > 15 MOhm
Concentrated sulfuric acid. ACS Grade
2,2,4-trimethyl pentane Pesticide Residue Grade
Diethyl ether, anhydrous, not preserved with ethanol or peroxides (in the tin can) Nanograde
Methanol, Residue Grade
Carbitol (Diethylene glycol monoethyl ether), 99+ %
Heptane, HPLC Grade
Acetic acid, ACS Grade
Sodium hydroxide, ACS Grade

Sodium chloride, ACS Grade
Diazald, 99%
Nitrogen, zero grade

35% H₂O/acetonitrile (Measure 1400 ml water and 2600 ml acetonitrile into glass jug. Mix on stir plate)

3% NaOH solution (Dissolve 3.0 g NaOH pellets in water and dilute to 100 ml. CAUTION--Exothermic Reaction)

10% H₂SO₄ (Pipet 100 ml concentrated H₂SO₄ into a 1 L volumetric flask half-full of water. Dilute to volume. CAUTION--Exothermic Reaction)

1% acetic acid (Pipet 10 ml concentrated acetic acid into 1 L volumetric flask half-full of water. Dilute to volume)

60% NaOH solution (dissolve 60.0 g NaOH pellets in water and dilute to 100 ml. CAUTION--Exothermic Reaction)

6.0 ANALYTICAL PROCEDURE

- 6.1 Weigh a 25.0 g portion of ground soil into plastic centrifuge bottle. (With every set of 10 samples, a duplicate, blank, and spike must be run).
- 6.2 Spike
2,4-D, Silvex, and Banvel: 1 ml of 1.0 ppm acid std into 25.0 g blank soil
Tordon: 2 ml of 1.0 ppm acid into 25.0 g blk soil
- 6.3 Add 150 ml of 35% H₂O/acetonitrile. Shake on wrist-action shaker for 30 min. Centrifuge 10 min at 2500 rpm.
- 6.4 Pour through 226 filter paper fitted inside 2V paper into graduated cylinder. Pipet 100 ml aliquot into a 500 ml boiling flask.
- 6.5 Rotovap (water bath 50° C) until water droplets start coming off (usually 25-30 ml sample left in boiling flask).
- 6.6 Add 1 gm NaCl to aqueous residue in boiling flask and transfer contents to 250 ml separatory funnel.
- 6.7 Add 25 ml 3% NaOH solution to separatory funnel and swirl to mix.
- 6.8 Add 40 ml chloroform to separatory funnel and shake 1 min. Allow layers to separate. Drain chloroform (lower) layer into waste beaker and discard in chlorinated solvent waste.
- 6.9 Repeat Step 6.8, but with 25 ml chloroform. Discard chloroform layer.
- 6.10 Acidify contents in separatory funnel with 25 ml 10% H₂SO₄ and swirl to mix.
- 6.11 Add 50 ml chloroform. Shake 1 min. Allow layers to separate and collect chloroform (lower) layer in 250 ml boiling flask.
- 6.12 Repeat Step 6.11 twice, collecting chloroform layer each time in boiling flask.

- 6.13 Add 0.5 ml 2,2,4-trimethyl pentane to 250 ml boiling flask. Rotovap contents to dryness.
- 6.14 Add 5 ml anhydrous diethyl ether to dried boiling flask and pipet contents into concentrator tube. Add 2 boiling chips and 0.5 ml methanol.

METHYLATION

- 6.15 Methylate each sample as defined in the MVTL method "Bubbler Methylation Reaction Vessel".
- 6.16 After each sample and standard has been methylated, attach small two-ball Snyder columns to concentrator tubes and insert them in the tube heater. Concentrate to less than 1 ml. (Heater set at about 8.) Remove from heater and allow to cool.
- 6.17 Remove Snyder columns. Add 5 ml 1% acetic acid and 5 ml heptane to each tube, rinsing Snyder column joints with the heptane. Stopper and shake vigorously 30 sec.
- 6.18 Allow phases to separate for about 15 min. Pipet portion of the top (heptane) layer into a Shimadzu GC vial. Store the rest of this layer in a 7 ml saver vial.

7.0 STANDARDS

- 7.1 2,4-D Silvex, and Banvel: From methylated 10.0 ppm standard, prepare 0.01, 0.05, 0.1, 0.50, and 1.0 ppm standards in heptane.
- 7.2 Tordon: From methylated 5.00 ppm standard, prepare .2, .5, 1.0, and 2.0 standards in heptane.

8.0 CONDITIONS

Instrument: Shimadzu 14-A

Detector: ECD

Column: Methyl silicon, 25 meter, .5 micron film thickness

Temperatures:

Injection port: 225° C

Detector: 275° C

Oven Program: 145° C for 10 min (For Tordon, 20 min). Ramp at 30° C/min. to 250° C, hold for 5 minutes.

Gases: Carrier Hydrogen
Make-up Nitrogen (Ultra High Purity)
Compressed air operates the auto-sampler

Run time: 2,4-D, Silvex, Banvel: 10.0 minutes
Tordon: 20.0 minutes

Data Acquisition: Maxima System

Injection volume: 4.0 microliters

APPENDIX D
Water Levels

WATER LEVELS

WELL NO.	1	2	3	4	5	6	7	8	9	10	11	12	13
ELEV.	1537	1530	1530	1535	1535	1550	1550	1535	1535	1500	1500	1495	1495
RE ELEV.	1537.42	1530.5	1530.58	1535.58	1535.75	1550.75	1550.5	1535.67	1535.83	1500.75	1500.92	1495.63	1495.58
JULY,87	1529.74	1526.75	1526.77	1528.42	1529.01	1530.46	1530.55	1524.64	1524.03	1492.09	1492.04	1489.74	1489.78
AUG.,87													
SEPT,87	1529.47	1526.69	1526.77	1528.81	1528.8	1524.51	1524.03	1491.64	1491.56	1489.32	1489.33		
OCT,87	1529.46	1526.69	1526.77	1528.81	1528.8	1524.51	1524.03	1491.64	1491.56	1489.32	1489.33		
NOV,87	1529.31	1526.43	1526.44	1528.48	1528.42	1524.33	1524.03	1491.5	1491.44	1489.29	1489.38		
DEC,87													
JAN,88	1529.04	1526.08	1526.15	1528.14	1528.1	1530.42	1530.47	1524.03	1524.03	1491.38	1491.32	1489.29	1489.33
FEB,88													
MAR,88	1528.84	1525.78	1525.86	1527.79	1527.76	1530.15	1530.21	1524	1524.03	1491.42	1491.35	1489.35	1489.38
APR,88	1528.41	1525.37	1525.45	1527.21	1527.19	1528.75	1528.83						
MAY,88	1528.4	1525.43	1525.38	1527.18	1527.15	1528.67	1528.75	1523.38	1523.28	1491.07	1491	1489.27	1489.31
JUNE,88	1528.1	1525.2	1525.23	1527.13	1527.07	1528.25	1528.4	1523.06	1523.34	1490.75	1490.67	1488.83	1488.88
JULY,88	1527.79	1525.04	1525.07	1526.94	1526.88	1527.89	1528.01	1522.74	1522.67	1490.45	1490.37	1488.51	1488.53
AUG,88	1526.74	1524.28	1524.38	1526.07	1526.02	1526.73	1526.83	1521.89	1521.79	1489.6	1489.5	1487.43	1487.44
SEPT,88	1524.38	1521.13											
OCT,88	1526.27	1523.87	1524.38	1525.48	1525.43	1526.54	1526.63	1521.56	1521.44	1489.23	1489.17	1487.17	1487.21
NOV,88	1526.27	1523.85	1524.38	1525.28	1525.27	1526.52	1526.63	1521.49	1521.13				
DEC,88	1526.27	1523.7	1524.38	1525.13	1525.1	1526.48	1526.57	1521.42	1521.33	1489.2	1489.15	1487.25	1487.28
JAN,89													
FEB,89	1524.83	1524.77	1526.35	1526.45	1521.22	1521.13							
MAR,89	1524.77	1524.72	1526.34	1526.44	1521.17	1521.13							
APR,89	1527.14	1524.22	1524.38	1526.1	1526.09	1526.97	1527.1	1522.42	1522.33	1490.41	1490.35	1488.38	1488.4
MAY,89	1527.48	1524.2	1524.38	1526.26	1526.23	1527.49	1527.59	1522.32	1522.73				
JUNE,89	1527.22	1524.1	1524.38	1526.18	1526.15	1527.33	1527.44	1522.37	1522.31	1490.4	1490.35	1488.39	1488.43
JULY,89	1526.87	1525.77	1525.73	1526.91	1527.01	1521.99	1521.89						
AUG,89	1526.27	1525.02	1524.97	1526.23	1526.34	1521.32	1521.14						
SEPT,89	1526.27	1524.78	1524.75	1526.15	1526.24	1521.19	1521.13						
OCT,89	1526.27	1524.6	1524.59	1526.15	1526.25								
NOV,89													
DEC,89	1526.27	1524.43	1524.4	1526.1	1526.2	1521.02	1521.13						
JAN,90													
FEB,90													
MAR,90													
APR,90	1526.27	1524.38	1524.01	1520.72	1521.13								
MAY,90	1526.27	1524.38	1524	1520.97	1521.13								
JUNE,90	1524.43	1524.37	1521.63	1521.55									

APPENDIX E
INORGANIC CHEMISTRY

MCHENRY COUNTY

Well No.	1	2	3	4	5	6
Date	7/2/87	7/2/87	7/2/87	7/2/87	7/2/87	7/2/87
pH	7.6	8.0	7.3	7.6	7.7	7.9
Conductivity (umhos/cm)	162.0	360.0	405.0	117.0	348.0	240.0
Total Dissolved Solids (C)	91.	189.	221.	61.	182.	128.
Total Hardness (as CaCO3)	89.	161.	216.	48.	169.	120.
Chloride (Cl)	2.4	1.9	1.4	2.0	1.1	0.6
Total Alkalinity (CaCO3)	80.	188.	217.	49.	176.	117.
Bicarbonate (HCO3)	98.	230.	265.	60.	215.	143.
Carbonate (CO3)	0.	0.	0.	0.	0.	0.
Nitrate (as N)	0.0	0.0	0.0	0.0	0.0	0.0
Fluoride (F)	0.1	0.4	0.3	0.2	0.2	0.1
Percent Sodium (%)	4.0	8.4	5.4	16.9	5.5	6.3
Field Temperature (c)	14.	15.	21.	17.	13.	17.
Turbidity (NTV)	3.00	21.0	2.00	26.0	3.00	<1
Sodium Adsorption Ratio	0.08	0.23	0.17	0.28	0.15	0.15
Field Conductivity (umhos/cm)	120.0	270.0	310.0	80.00	220.0	160.0
Calcium (Ca)	28.9	53.4	61.9	13.4	52.1	34.0
Iron (Fe)	0.612	4.41	2.76	3.25	0.000	0.378
Magnesium (Mg)	4.0	6.8	15.0	3.5	9.4	8.5
Manganese (Mn)	0.025	1.01	0.347	0.229	0.026	0.221
Potassium (K)	0.700	1.00	1.80	0.800	0.500	0.500
Sodium (Na)	1.7	6.8	5.7	4.5	4.5	3.7
Sulfur as Sulfate (SO4)	5.	6.	5.	7.	9.	10.
Total Hardness (as CaCO3) (grains/gallon)	5.18	9.43	12.6	2.80	9.87	7.01

Well No.	7	8	9	10	11	12
Date	7/2/87	7/2/87	7/2/87	7/2/87	7/2/87	7/2/87
pH	7.9	7.8	7.5	7.5	7.3	7.5
Conductivity	346.0	419.0	500.0	742.0	619.0	732.
Total Dissolved Solids (C)	184.	215.	297.	411.	311.	381.
Total Hardness (as CaCO3)	166.	207.	310.	427.	249.	320.
Chloride (Cl)	1.3	1.5	0.8	0.9	2.2	1.9
Total Alkalinity (CaCO3)	165.	215.	266.	405.	328.	364.
Bicarbonate (HCO3)	202.	262.	325.	494.	401.	444.
Carbonate (CO3)	0.	0.	0.	0.	0.	0.
Nitrate (as N)	0.8	0.0	0.0	0.0	0.0	0.
Fluoride (F)	0.1	0.1	0.1	0.2	0.1	0.3
Percent Sodium	3.2	0.9	1.2	1.1	9.3	6.9
Field Temperature	14.	12.	10.	10.	10.	11.
Turbidity	2.00	<1	<1	<1	<1	<1
Sodium Adsorption Ratio	0.08	0.03	0.04	0.04	0.33	0.27
Field Conductivity	230.0	275.0	320.0	480.0	370.0	470.
Calcium (Ca)	48.7	57.8	97.7	141.	67.9	54.3
Iron (Fe)	0.485	0.000	9.68	3.24	0.000	0.0
Magnesium (Mg)	10.8	15.2	16.0	18.3	19.2	44.7
Manganese (Mn)	0.030	0.221	0.428	1.53	0.015	0.055
Potassium (K)	1.20	0.400	1.80	1.20	2.10	3.3
Sodium (Na)	2.5	0.9	1.8	2.1	11.8	11.
Sulfur as Sulfate (SO4)	17.	10.	19.	5.	10.	47.
Total Hardness (as CaCO3)	9.71	12.1	18.1	24.9	14.5	18.7

* Values in Mg/l unless otherwise noted

APPENDIX F
Sediment Analyses

SEDIMENT ANALYSES

Well No. 1 (90-2)

<u>Depth (ft)</u>	<u>Tordon</u>	<u>2,4-D</u>
1	50	< 10
3.25	10	< 10
5.75	< 10	< 10
8.25	< 10	10
17	< 10	10

Well No. 4 (90-7)

<u>Depth (ft)</u>	<u>Tordon</u>	<u>2,4-D</u>
0.5	160	< 10
1.5	20	< 10
3.75	< 10	10
6.25	< 10	< 10
8.75	< 10	< 10
11.25	10	10

Well No. 8 (1987)

<u>Depth (ft)</u>	<u>Tordon</u>
2	< .05
4	< .05
6	< .05
8	< .05
10	< .05
11	.08
12	.41
13	< .1
14	< .1

Well No. 8 (90-3)

<u>Depth (ft)</u>	<u>Tordon</u>	<u>2,4-D</u>
1.25	70	< 10
3.75	< 10	< 10
6.25	< 10	< 10
8.75	< 10	20
11.75	< 10	< 10
13.75	10	10

* All values in ppb unless otherwise noted.
Sediment samples obtained in 1990 unless otherwise noted.