PESTICIDES AND GROUNDWATER:

SURVEYS OF SELECTED MINNESOTA WELLS

Prepared for the

Legislative Commission on Minnesota Resources

Minnesota Department of Health
and
Minnesota Department of Agriculture

February 1988

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EXECUTIVE SUMMARY

Between July 1985 and June 1987, the Minnesota Departments of Health (MDH) and Agriculture (MDA) conducted cooperative surveys of water wells for selected pesticides. The surveys were funded by the Legislative Commission on Minnesota Resources and were intended to provide baseline information on the occurrence and extent of agricultural pesticide contamination in the State's groundwater and drinking water.

Pesticides were selected for survey consideration based on an evaluation of existing information related to use, toxicology and environmental transport and fate. Emphasis in the final selection was placed on those pesticides which were commonly used in the State and/or which appeared to be more likely to adversely impact groundwater and public health. Analytical methods were developed for the selected pesticides by the MDH and MDA laboratories. Only one of the selected pesticides, 2,4-D, had a Federal or State drinking water standard. In order to address the public health concerns presented by the detection of pesticides in drinking water, the MDH established recommended allowable limits (RALs) for the other pesticides considered in the survey.

In general, wells were selected for sampling in agricultural regions of the State and, within those regions, from areas where the local or regional soils and hydrogeologic conditions make the groundwater especially susceptible to pesticide contamination. Karst aquifers and shallow sand and gravel aquifers overlain by coarse-textured soils were viewed as particularly sensitive and most likely to show evidence of groundwater contamination by pesticides. Some wells were also selected outside of these sensitive areas to provide areal coverage of the State's agricultural regions and diverse cropping patterns.

The MDA sampled 100 observation, irrigation, and private drinking water wells and five drain tiles on a time-series or repetitive basis (typically, four samples per site). The MDH collected a single sample at each of 400 public drinking water wells. A second sample was collected from each well in which pesticides were detected in the initial sample.

The results of the surveys indicated that several pesticides were present in groundwater, especially in hydrogeologically sensitive areas of the State. One or more pesticides were detected in 165 (33 percent) of the 500 wells sampled. Pesticides were observed more frequently in observation and private drinking water wells than in public drinking water wells. This difference is most likely attributable to the shallower depths of many of the observation and private drinking water wells and to their closer proximity to fields receiving pesticide applications.

Fifteen pesticides, including thirteen herbicides, one insecticide and one wood preservative, were detected in the surveys. Atrazine, the most commonly detected pesticide in each survey, was found in 154 (31 percent) of the 500 wells sampled and in over 90 percent of the wells which tested positive for pesticides. Alachlor, the next most commonly occurring compound in each survey, was found in 17 wells. Each of the remaining thirteen pesticides was detected in seven or fewer wells.

Although the percentage of wells with detectable levels of pesticides was relatively high, the concentrations detected were usually low. Eighty-four percent of all pesticide occurrences were at concentrations less than 1.0 µg/l. Levels exceeding the RALs were observed in samples collected from ten wells, including four public drinking water wells and one private drinking water well.

At the low concentrations typically observed in these surveys, the public health concerns focus on potential chronic health effects. Chronic toxicity information for many pesticides is limited. Although this body of information has improved significantly in recent years, it is difficult to associate specific health effects with exposure to low levels of pesticides in drinking water.

Pesticides were detected in wells in 51 counties, but were most commonly found in wells completed in the karst formations in southeastern Minnesota, the shallow, outwash sand and gravel aquifers in central Minnesota and the shallow, alluvial sand and gravel aquifers in southwestern Minnesota. Few pesticide occurrences were observed in northwestern and south central Minnesota.

The widespread occurrence of pesticides, primarily atrazine, at low concentrations in certain areas indicates that groundwater contamination may result from normal pesticide use as well as from spills, leaks, back-siphonages and other point sources.

Significant vertical differences in pesticide and nitrate-nitrogen occurrence and concentration were observed in adjacent observation wells in certain central Minnesota sand and gravel aquifers. The nature of this vertical stratification varied from site to site.

While pesticides were observed more frequently in wells in certain areas of the State, the potential for contamination in a specific well is determined by a complex set of factors, including the contaminant source, chemical properties, local groundwater vulnerability, local agricultural practices and well construction. These factors vary considerably from area to area and from well to well.

Nitrates were analyzed to determine if there was a relationship between nitrate and pesticide occurrence and concentration in groundwater and to evaluate nitrate testing as a surrogate for pesticide testing. Nitrates were not found to be a reliable indicator of pesticide occurrence or a quantitative predictor of pesticide concentration.

The baseline information generated in these surveys has significantly expanded our knowledge of pesticide contamination in Minnesota groundwater and drinking water. Nevertheless, it is important to recognize the limitations of the surveys. A limited number of wells and pesticides were studied during a relatively short time frame under unusual precipitation conditions. As a result, these surveys do not provide a comprehensive statewide assessment of the extent of groundwater contamination by pesticides. Additional monitoring, research, regulatory and educational efforts will be needed to minimize the impact of pesticides on groundwater quality and public health.

INTRODUCTION

Agricultural lands in Minnesota account for over 30 million of the State's 53 million total acres. In 1986, Minnesota ranked fifth in the nation in crop acreage planted with 20.6 million acres under cultivation. A wide range of soil and climatic conditions result in diverse cropping patterns across the State. The most widely planted crops are corn, soybeans, wheat, barley, oats and alfalfa. Other crops of local or regional significance include sugar beets, sunflowers, potatoes, sweet corn, rye, peas, edible beans and flax.

Pesticides are used extensively in agricultural crop production. In a Minnesota Agricultural Statistics Service publication covering the 1984 crop year, Minnesota farmers were reported to have used pesticides on over 96 percent of their corn, soybean and sugar beet acreage, nearly 90 percent of their wheat and sunflower acreage and on 60 percent of their small grain acreage (Minnesota Agricultural Statistics Service, 1985). In total, an estimated 40-45 million pounds of active pesticidal ingredients were applied to approximately 16.5 million acres of Minnesota farmland during the 1984 crop year.

This extensive pesticide use has both benefits and risks. Pesticide use has allowed farmers to increase crop yields while decreasing the time and fuel spent on crop production. At the same time, there has been increasing evidence that certain pesticides are entering ground and surface waters, posing a potential threat to drinking water.

In response to concerns generated by the detection of pesticides in certain Iowa and Wisconsin groundwaters and by the limited pesticide monitoring data available for Minnesota groundwaters, the Minnesota Departments of Health (MDH) and Agriculture (MDA) initiated cooperative surveys of water wells for selected pesticides. The surveys were funded by the Legislative Commission on Minnesota Resources (LCMR) in July 1985 and were intended to provide baseline information on the occurrence and extent of agricultural pesticide contamination in the State's groundwater and drinking water.

All samples were collected between July 1985 and June 1987. The MDA sampled 100 observation, irrigation, and private drinking water wells and five drain tiles on a time-series or repetitive basis (typically, four samples per site). The MDH collected a single sample at each of 400 public drinking water wells. A second sample was collected from each well in which pesticides were detected in the initial sample. The surveys will be referred to in this report as the MDA survey and the MDH survey.

Additional funding was obtained from the United States Environmental Protection Agency (U.S. EPA) and used by MDH to conduct complementary monitoring of approximately 225 private drinking water wells. The methods and results of that survey are presented in a separate report (MDH, 1988).

COMMON METHODS AND BACKGROUND INFORMATION

Pesticide Selection

The pesticide selection process involved the evaluation of information and data related to use, toxicology and environmental transport and fate. Pesticide use information was obtained, primarily from the Minnesota Agricultural Statistics Service, for each of the major crops grown in the State. Information on toxicology and environmental transport and fate was obtained, in part, through consultation with the MDH's Section of Health Risk Assessment, the University of Minnesota and other State agencies. Work performed by the U.S. EPA (Cohen et al., 1984) and the states of Wisconsin (Goethel et al., 1983), California (Litwin et al., 1984; and Bowes, 1984) and Iowa (Hallberg et al., 1984) was also utilized. Limited information was available on the environmental transport, fate and toxicology of many of the compounds in current use.

After evaluation of existing information, the MDH and MDA jointly selected 45 pesticides for further consideration. Emphasis in the final selection was placed on those pesticides which were commonly used in the State and/or which appeared to be more likely to adversely impact groundwater and public health.

The MDH and MDA laboratories were requested to develop and verify analytical methods for the selected pesticides. The two laboratories coordinated efforts to ensure that similar analytical methods and reporting limits would be developed and used in the surveys. Some variation resulted from differences in laboratory equipment, procedures and personnel, but these variations did not significantly affect the findings of this report.

Due to time constraints and limitations in laboratory capability, analytical methods were developed and verified for only 30 of the 45 pesticides on the original list. Both laboratories developed analytical capabilities for chlorinated acid herbicide and base/neutral extractable compounds. In addition, the MDA laboratory developed analytical capabilities for aldicarb and performed these analyses for both departments. The pesticides, analytical methods and reporting limits are presented in Tables 1 and 2 for the MDA and MDH surveys, respectively. A brief description of each pesticide included in the surveys is presented in Appendix A. Narrative information on the analytical methods is provided in the methods section for each survey.

Recommended Drinking Water Limits

Federal and State drinking water standards have been established for six pesticides. Only one of these chemicals, 2,4-D, is commonly used in Minnesota and included in the surveys. In order to address the public health concerns presented by the detection of pesticides in drinking water, the MDH established recommended drinking water limits for the remaining pesticides in the survey (Table 2). These recommended allowable limits (RALs) were established utilizing health effects data available from the U.S. EPA and other sources. The MDH used standard methods, developed by the U.S. EPA, for: 1) determining whether a contaminant should be considered carcinogenic or noncarcinogenic; and 2) calculating an acceptable level for the contaminant in drinking water.

For noncarcinogens, an acceptable level was calculated based on a no-observed-adverse-effect-level (NOAEL) obtained from human and/or animal studies. Safety factors were applied to the NOAEL to account for various uncertainties, including extrapolation from animal studies to humans, gaps in the toxicologic profile, and the variable sensitivity of a heterogenous human population to a toxicant. This calculation yielded a reference dose level (RFD). Exposure levels that exceeded the RFD were considered unsafe.

The health risks associated with known or suspected carcinogens were evaluated based on the assumption that consuming drinking water containing any amount of a carcinogenic contaminant would increase the cancer risk of the consumer. Exposure levels (the concentration of the carcinogen in drinking water) were converted to risk levels using potency slopes obtained from the U.S. EPA or other reputable sources. This calculation was based on methods prescribed by U.S. EPA's Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986). Risk levels were then evaluated in relation to the acceptable risk of one cancer per 100,000 population per lifetime. Risks which exceeded this level were judged to be unacceptable.

Drinking water containing multiple pesticides, all at concentrations below their respective RALs, was evaluated based on additive effects or risks. Additivity assumes that the toxic effects of two or more chemicals are similar and that the total toxic effect is the sum of their individual effects. The exposure level for multiple contaminants was judged to be unacceptable if the sum of each contaminant's concentration (C) divided by its RAL exceeded one:

$$\frac{C_1}{RAL_1} + \frac{C_2}{RAL_2} + \cdots\cdots + \frac{C_n}{RAL_n} > 1$$

The RALs were developed as health advisories, not as enforceable standards, and are subject to change as better health effects information becomes available. The RALs were modified in January 1988 to reflect the U.S. EPA draft health advisories which were prepared for certain pesticides as part of the National Pesticide Survey.

Well Selection

In general, wells were selected in agricultural regions of the State and, within those regions, from areas where the local or regional soils and hydrogeologic conditions make the groundwater especially susceptible to pesticide contamination. Karst aquifers and shallow sand and gravel aquifers overlain by coarse-textured soils were viewed as particularly sensitive and most likely to show evidence of pesticide-related groundwater contamination.

The karst region in southeastern Minnesota is generally characterized by shallow depths to porous and permeable carbonate bedrock and, in some areas, by features such as sinkholes, caves and disappearing streams. These conditions can result in rapid transport of surface water containing dissolved or soilbound pesticides into the groundwater.

Shallow sand and gravel aquifers overlain by coarse-textured, low organic matter soils occur throughout the State and are particularly widespread in central Minnesota (Figure 1). These aquifers are comprised primarily of glacial outwash and alluvial deposits, but also include beach ridge deposits in northwestern Minnesota. The potential for pesticide movement to groundwater is increased in these areas because the soils typically allow rapid water infiltration and have a low capacity for adsorption of organic compounds. Irrigation, which is commonly practiced in many of these areas, may also contribute to the downward migration of pesticides.

Some wells were also selected outside these sensitive areas to provide areal coverage of the State's agricultural regions and diverse cropping patterns. Additional information on well selection is provided in the methods section for each survey.

Soil Moisture and Precipitation, Fall 1985-Spring 1987

Soil moisture and precipitation are important factors in the downward movement or leaching of soluble pesticides into groundwater. Although these factors were not directly considered in the surveys, the soil moisture and precipitation conditions existing immediately before and during the surveys may have had an important influence on the occurrence of pesticides in groundwater.

In 1985, Minnesota experienced the fifth consecutive year of wet fall soil conditions. A mathematical model based on precipitation information gathered at measuring stations across the State indicated that soil moisture conditions in significant portions of Minnesota were wet or very wet heading into the spring of 1986 (Figure 2). Since the map prepared by the State Climatological Office and the University of Minnesota's Department of Soil Science is based on medium- to fine-textured soils, the soil moisture conditions in areas of coarse-textured soils are underestimated.

Following the wet fall of 1985, precipitation in the hydrologic year ending September 1986 greatly exceeded normal amounts in large portions of the State (Figure 3). Some areas recorded three times the normal precipitation in April. September was generally regarded as one of the wettest on record. Central Minnesota received the greatest amount of above normal precipitation, with some areas receiving 20 inches or more above normal.

In sharp contrast, precipitation was greatly below normal amounts in most areas of the State during the remaining months of the surveys (October 1986-June 1987). Precipitation typically ranged from 4 to 10 inches below normal during this period (Figure 4).

METHODS: MDA PESTICIDE SURVEY

Site Selection

The purpose of the MDA pesticide survey was to evaluate the possibility of pesticide movement to groundwater in Minnesota. Accordingly, agricultural regions thought to be susceptible to movement of pesticides to groundwater were emphasized in site selection. In addition, some wells were selected in regions or conditions that were thought to be less susceptible in order to evaluate results from several hydrogeologic and agronomic conditions.

Susceptible regions were defined by soil and hydrogeologic characteristics that permitted rapid recharge and minimal filtration. Two general regions fit these criteria: 1) the unconfined, surficial sand and gravel aquifer regions; and 2) the karst region of southeastern Minnesota.

Unconfined, Surficial Aquifers. Unconfined, surficial aquifers are concentrated in central Minnesota where extensive areas of glacial outwash and sand plains exist. While most soils in these areas are coarse textured, a mixture of soil types in local areas is common. Alluvial valleys in southwestern Minnesota, where there are soil associations similar to those seen in central Minnesota, also present conditions that were thought to be susceptible to pesticide movement to groundwater.

The general criteria for well selection in unconfined aquifers were: 1) agricultural fields in immediate proximity to the wells; 2) water table less than 30 feet deep and preferably with the well screen located within 10 feet of the water table; 3) well location in the estimated downgradient direction of groundwater flow from agricultural fields; 4) distribution of locations with regard to crops, soils, climate and pesticide usage; 5) history of pesticides or nitrates in the well.

Karst. The karst region is located in southeastern Minnesota and is characterized by disappearing streams, springs, sinkholes and fractured limestone or dolomitic bedrock. Karst aquifers feature cracks and crevices in the bedrock that allow rapid water movement. Fractured bedrock is overlain by variable depths of loess-derived, silt-textured soils. Silt soils are typically well drained.

Wells were sampled in four southeastern areas with varying karst features. The nature of the karst aquifers prevented monitoring of specific fields without extensive hydrogeologic studies that were beyond the scope of this project. Regions or wells were selected for sampling in the southeast based on information obtained from the Minnesota Geologic Survey (MGS), Minnesota Pollution Control Agency (MPCA), local health sanitarians, and previous nitrate or pesticide analysis.

In addition to the shallow wells in the unconfined, surficial aquifers in susceptible regions and the wells in the karst, a limited number of other sites were also selected. Two irrigation wells screened beneath a confining layer were selected because of intense pesticide use near these wells. Five tile lines were sampled in southern and western Minnesota. Tile lines provide subsurface drainage for excess soil moisture in poorly drained, fine-textured soils and are common throughout southern and western Minnesota.

Well Type

The majority of wells selected in the unconfined, surficial aquifers were water table observation wells which were originally installed and monitored by the Department of Natural Resources (DNR) or the United States Geologic Survey (USGS). A few of the wells were specifically installed for water quality monitoring. The typical observation well had a 1.25- to 2-inch diameter steel casing with a 2- to 3-foot sand point screen. Three of the observation wells were polyvinyl chloride (PVC). The majority of the wells were installed several years prior to the study; however, two wells were installed as recently as 1985. A total of 65 observation wells were sampled in the study.

Thirty-one drinking water wells were utilized in areas where established observation wells were not available. Twenty drinking water wells were sampled in the southeast, two in the southwest, three in the northwest, and six in central Minnesota.

Four high capacity (500-1000 gpm) irrigation wells were sampled. These wells were located in highly susceptible areas with coarse-textured soils; two were located in close proximity to intensive pesticide use.

Sample Collection

Timing. Samples were obtained from most of the 100 wells in the spring, summer and fall of 1986 and a fourth sample was collected in the winter or spring of 1987. Although four samples were typically collected from each well, eight wells were only sampled three times due to well closures, dropped water tables or inaccessibility. Individual sampling intervals varied due to collection scheduling or laboratory analytical capacity.

Tile lines were only sampled in the spring of 1986. Three tile lines were sampled once and two were sampled twice. Tile lines at these sites did not run in the fall of 1986.

Sampling Protocol. Observation and drinking water wells were pumped to evacuate three volumes of standing water prior to sample collection. The MDA laboratory provided washed and capped one-liter amber bottles with Teflon-lined caps. The bottles were rinsed with sample water immediately before filling. One bottle was filled for each analytical extraction procedure. Sulfuric or orthophosphoric acid was added as a stabilizer for the chlorinated acid herbicide and N-methylcarbamate procedures, respectively. The nitrate-nitrogen samples were collected in 125-milliliter (ml) polypropylene bottles. All samples were placed in an insulated cooler, refrigerated with prefrozen cold packs or ice and transported to the laboratory. Samples were delivered to the laboratory within 48 hours of sampling.

Observation wells were evacuated and sampled with a peristaltic pump or, in a few instances where water tables were deeper than the lift capacity of the pump, with a bailer. Prior to each sampling, the pump's silicone tubing or the bailer was rinsed with triple-deionized water and acetone. The polypropylene tubing, dedicated to each well, was stored in a plastic bag between sampling events. Drinking water wells were sampled from the tap.

A few variations of the above procedure were necessary. Irrigation wells were sampled at a nozzle or a tap during field irrigation or after pumping an estimated three volumes of water. Tile lines were sampled at the outlet during the spring flowage in 1986. A few observation wells that were pumped dry during evacuation were allowed to recharge before sample collection. Nine samples were collected from four sites by University, DNR or county personnel following MDA sampling instructions. These samples were shipped by one-day delivery service to the laboratory in a refrigerated cooler.

Laboratory Analysis

All samples were analyzed by the MDA Laboratory Services Division except for 21 samples analyzed by the MDH Public Health Laboratories Division. Prior to the initiation of the field phase of the project, a method reporting limit was determined for each analyte in the base/neutral extractable and chlorinated acid herbicide procedures. Method reporting limits were established for the N-methylcarbamate and nitrate-nitrogen procedures based on daily signal-to-noise assessment and prior analyst experience.

Upon delivery to the laboratory, samples were refrigerated at 4°C until extraction. The maximum holding time prior to extraction was 10 days, though the majority were extracted in less than seven days. Analysis was completed within 30 days of extraction.

Base/neutral pesticides. This procedure identified and quantified some of the most widely used pesticides in Minnesota. All samples collected in the survey were analyzed with this procedure.

Sample preparation for gas chromatography analysis entailed the extraction of one liter of sample water with methylene chloride followed by concentration to a volume of 3 ml. Retention times and peak areas were compared with known standards after single-port injection into dual DB-1 columns mounted on a Varian 3400 gas chromatograph equipped with a Ni-63 electron capture (EC) detector and a nitrogen/phosphorus (NP) detector. Positive values were confirmed on either a Perkin Elmer Sigma 2 gas chromatograph equipped with a DB-17 column and EC and NP detectors or a Perkin Elmer Sigma 300 gas chromatograph equipped with a Supelcowax 10 column and EC and NP detectors.

Chlorinated acid herbicides. This procedure was run at least once on samples from all but a few wells. Samples collected from certain wells, such as those in the southeast or those with a chlorinated acid herbicide history, were routinely analyzed with this procedure.

Sample preparation for this procedure included field stabilization of the sample by acidification. In the laboratory, the sample was extracted with methylene chloride. The derivatives of the chlorinated acids, acid esters and salts were hydrolyzed with potassium hydroxide, extracted with methylene chloride and concentrated. The acids were converted to methylesters with methyl iodide and tetrabutylammonium hydroxide. Benzene was added and the sample was then concentrated for injection.

Gas chromatography analysis was conducted on a Tracor Model 560 with a Hewlett-Packard Model 3388A integrator. A Hall electroconductivity detector with a DB-1 megabore column was used for initial analysis and a Ni-63 EC detector with a OV-17 column used for confirmation.

N-methylcarbamate/pesticides. This procedure was used primarily on samples collected near areas of probable aldicarb use. Field stabilized samples were extracted with dichloromethane, evaporated to dryness and dissolved in a methanol and water solution. The solution was analyzed by HPLC/post column fluorometric detection with confirmation by gas liquid chromatography with NP detectors.

Nitrate-nitrogen. Nitrate-nitrogen analyses were conducted on all samples. A Perkin Elmer 552 spectrophotometer was used to measure absorbency following color development with chromatropic acid. The method reporting limit was 1 mg/l.

Quality Control. Standard quality assurance practices were observed. Glassware, reagents, and other potential sources of interference were evaluated and monitored. Method blanks, field blanks and blind duplicate samples accounted for approximately 20% of the total analyses. Spiked samples, for procedure validation, accounted for another 10% of the samples.

Spiked laboratory procedure validation samples were routinely analyzed during the survey. Average percent recoveries (and standard deviations) for three commonly detected pesticides were: atrazine, 91 (17); alachlor, 90 (21); and cyanazine, 67 (26). Spiking levels were 1 µg/l or less for the three pesticides.

RESULTS AND DISCUSSION: MDA PESTICIDE SURVEY

One or more pesticides were detected at least once in 51 of the 100 wells and in three of the five tile lines sampled. The highest proportion of detections occurred in the southeastern and central Minnesota regions (Figure 5).

Eight pesticides, including six herbicides, one insecticide and one wood preservative, were detected and confirmed in the MDA survey (Table 3). Atrazine, the most commonly detected pesticide, was found in 47 of the 51 wells in which a pesticide was detected. Atrazine accounted for 78 percent (112 of 144) of all pesticide detections. Alachlor, the second most commonly detected pesticide, was found in eight wells and accounted for six percent (9 of 144) of all pesticide detections. Metribuzin was found in four wells, while cyanazine and pentachlorophenol were each found in three wells. Aldicarb was detected in samples collected from two wells. Simazine and dicamba were each found in only one well.

Samples collected from 41 of the 51 wells in which a pesticide was detected contained only one pesticide. Ten wells had samples collected from them in which more than one pesticide was detected. Two of these wells had multiple pesticides in all four samples.

Concentrations of most of the pesticide detections were less then 1.0 μg/l. Median concentrations for the most commonly detected pesticides, atrazine and alachlor, were 0.38 and 0.37 μg/l, respectively. Thirteen wells contained pesticide concentrations greater than 1.0 μg/l.

Pesticide use information collected for fields adjacent to wells indicated that a variety of pesticides were applied near wells sampled in this survey. Although the information collected on pesticide use was not sufficient to allow examination of the nature of the relationship of nearby pesticide applications to groundwater contamination, many pesticides applied near wells were not detected in groundwater samples.

Nitrate-nitrogen concentrations averaged greater than 1 mg/l for 61 percent of the wells. Nitrate-nitrogen concentrations averaged over 10 mg/l in 23 percent of the wells sampled. The high frequency of occurrence and the high concentration of nitrate-nitrogen was not unexpected due to the proximity of the wells to agricultural fields and the selection of wells in susceptible regions.

Pesticides and nitrate were frequently present together in the wells sampled, although no concentration relationship was evident. Figure 6 illustrates the pesticide and nitrate-nitrogen concentrations observed from all samples that contained detectable concentrations of pesticide and nitrate-nitrogen. The absence of a definitive relationship is further supported by the detection of pesticides in 24 samples where nitrate-nitrogen was not detected. Also, nitrate-nitrogen was commonly detected in the absence of pesticides. However, wells with concentrations of nitrate-nitrogen greater than 10 mg/l were more likely to contain a detectable pesticide.

Some results from the MDA survey are presented below by geographical regions. While the survey data are organized by region, and the regional conditions influence the potential impacts on groundwater in the vicinity of the monitoring wells, the results are not intended to be representative of all groundwater or drinking water in each region. Rather, the results may be largely dependent on the immediate soils, hydrogeology or other site-specific conditions.

Northwestern Minnesota

Northwestern Minnesota is dominated by the Glacial Lake Agassiz Lacustrine Plain, more commonly known as the Red River Valley. This area consists of a nearly level plain of uniform soil and subsoil material. The soils are high in organic matter and have clayey and silty texture. Soils are generally poorly drained. The eastern portion of the Red River Valley is comprised of a series of ancient beach ridges with coarse-textured soils.

Groundwater in the northwestern region is typically found in buried, confined lenses. Surficial aquifers are usually low yielding due to the fine aquifer materials. Some coarser-textured aquifers in the southern portion of the Red River Valley, along the beach ridges or in alluvial areas, can be used as sources of water supply.

Agriculture in the Red River Valley is intensive, with the principal crops being wheat, barley and soybeans. Other important crops, though grown on substantially less acreage, are potatoes, sugar beets and sunflowers. Wheat, barley and soybeans generally receive one herbicide application per growing season, while potatoes, sugar beets and sunflowers commonly receive multiple applications of insecticides, fungicides and herbicides. Post-emergence applications of 2,4-D and MCPA on small grains, as well as a diverse group of other compounds such as triallate, trifluralin and bronate, are commonly used.

Eight wells were sampled in five counties in the Red River Valley. Wells were generally completed deep beneath the water table, with a median water column in the monitoring wells of 18 feet and a range of 5 to 35 feet. A summary of the well-site information is presented in Table 4.

Pesticides and nitrate-nitrogen were not detected in any of the eight wells sampled. Soil, climatic and pesticide use characteristics do not provide a high potential for movement of pesticides or nitrate to groundwater. It was anticipated that the combination of low aquifer recharge potential and high organic matter, fine-textured soils and fine-textured subsoils would result in a limited impact of pesticides on the groundwater in this region. The few wells sampled were not necessarily located in the most susceptible regions of the northwest nor did the wells available for sampling have screens located near the water table. Both of these factors may have influenced pesticide and nitrate-nitrogen detections in this region; however, the results are consistent with the initial evaluation that the northwest region would be less susceptible.

Southwestern and South Central Minnesota

The undulating prairies of southwestern Minnesota are a result of multiple glacial advances which left outwash, till, moraines and narrow meltwater channels. These features have had a major influence on the formation of soils in this region. Typical of the region are fine- or loamy-textured soils overlying loamy calcareous subsoil with moderate to poor drainage. Alluvial valleys commonly feature coarse-textured soils with excessive drainage characteristics.

The surficial aquifers are principally alluvial, although some drift aquifers are present. Yields in most alluvial aquifers are adequate for irrigation. The alluvial aquifers are typically unconfined, hydraulically connected to streams, and responsive to spring and fall recharge.

Agriculture in the southwest is dominated by dryland corn and soybean production. These two crops account for approximately 85 percent of the planted acreage, with corn grown on an estimated 45 percent of the land. Other crops are alfalfa, wheat and oats. Irrigation occurs in the narrow alluvial valleys where coarse-textured soils predominate. Corn, soybeans and wheat typically receive a single herbicide application, though tank mixes of two or more products are not uncommon. Post-emergence application of a second herbicide is also a common practice. Herbicides which are commonly used include: cyanazine, alachlor, atrazine, metolachlor, EPTC, 2,4-D, dicamba and trifluralin. Insecticides are not used extensively in this region.

A diversity of geomorphic and soil conditions was represented at the 17 well sites sampled in the southwest. Seven wells were situated in alluvial areas, with the remaining wells in moraine or drift areas. Thirteen sites contained layers of silt- or clay-textured soil or subsoil, although the depths were not thick enough to be considered a confining layer. Soil textures near the wells ranged from sandy loam to clay loam, although the majority of the sites were associated with fine-textured soils. A summary of well-site descriptions is presented in Table 5.

Only four of the 17 sites contained detectable levels of pesticides. Atrazine was detected once in three wells. Pentachlorophenol and atrazine were detected in the deepest well sampled (45 feet). None of the pesticides appeared in repeat samples. Nitrate-nitrogen was detected in seven wells. Only one well exceeded 10 mg/l nitrate-nitrogen. This exception was a 30-foot, tile-cased drinking water well located on a farm with a livestock operation.

The few pesticide detections in the southwest may be a function of the diversity of geomorphic settings, the thickness and presence of silt- and clay-textured soils and subsoils or the depth of the well screens into the aquifer. Although some atrazine use was reported in past years near monitoring wells, growers reported that atrazine rate and frequency of use have been reduced due to carry-over problems associated with the calcareous soils.

There was a general absence of elevated nitrate-nitrogen concentrations in the wells sampled in the southwest. Silt- and clay-textured soil and subsoil may have influenced movement of nitrate to the groundwater. Vertical stratification of the nitrate may also have occurred. The sampling techniques utilized limited the opportunity to detect nitrate-nitrogen at more than a short distance above or below the well screen.

Southeastern Minnesota

The karst region of southeastern Minnesota is one of the regions in the State most susceptible to groundwater contamination. Variable depths of permeable, loess-derived silt that range from hundreds of feet to less than two feet thick, overlie carbonate bedrock with fractures, solution channels and sinkholes. The soils are silty- or loamy-textured, have medium organic matter content, and are typically well drained. In the northernmost portion of the region, the carbonate bedrock is overlain by coarse-textured soils and subsoils with low organic matter and clay content. Soils in this region are often moderately to excessively drained.

Several major aquifers are located in the southeast. The upper carbonate and St. Peter, if present, are separated by a confining layer. The St. Peter and Prairie du Chien-Jordan may be hydraulically connected. The Prairie du Chien-Jordan may be unconfined or confined depending upon location. Beneath the Prairie du Chien-Jordan lie the Franconia-Ironton-Galesville and the Mt. Simon-Hinckley aquifers, which are separated by confining layers.

Rapid vertical drainage through soils and subsoils in this region is compounded by rapid vertical movement through karst formations. Hallberg et al. (1984) suggested that infiltration through the soil in areas similar to southeastern Minnesota may deliver the greatest mass of pesticides to the groundwater. The upper carbonate, St. Peter and Prairie du Chien-Jordan aquifers can be impacted by direct movement of surface water runoff into sinkholes. Regionally, sinkholes may be important contributors to pesticide movement to groundwater. In Winona County alone, Dalgleish and Alexander

(1984) inventoried 535 sinkholes and estimated that a total of over 700 may exist in the county.

Corn, the dominant crop in the region, is grown on nearly half the crop acreage. Hay, soybeans and oats account for approximately 19, 18 and 10 percent of the remaining cropland, respectively. Corn and soybeans receive the majority of the pesticide applications. Alachlor, atrazine, cyanazine, dicamba and 2,4-D are the most widely used herbicides. Insecticides, such as terbufos, fonofos, phorate and chlorpyrifos, are commonly used for control of corn rootworm. Fungicides are seldomly used in the area. The majority of the pesticides are applied in the spring as pre-plant, pre-emergent or early post-emergent applications.

Twenty-one wells were sampled in southeastern Minnesota (Table 6). Since there are few established observation or monitoring wells in the area, private water supply wells were selected for sampling. Wells in Dakota, Mower and Olmsted Counties were selected based on recommendations from local officials and on previous nitrate-nitrogen analysis. Wells in Winona County were chosen from a list of wells that had been part of the Garvin Brook Watershed Study (Garvin Brook RCWP, 1985). In most cases, information on the wells was limited to an owner-reported total depth. Well casing depth was available for a few of the Winona County wells. Except for one shallow sand point well in Dakota County, well depths ranged from 50 to over 400 feet and terminated in either the upper carbonate or the Prairie du Chien-Jordan aquifers.

Analytical results from the well water sampling indicate that 13 of the 21 wells contained measurable concentrations of a pesticide in at least one of the four samples taken from each well (Table 7). Atrazine was detected in all 13 wells that contained a pesticide and in all the samples that contained pesticides. Four wells contained atrazine on all four sampling occasions. Cyanazine and alachlor were detected only once in the wells in which they were present. Dicamba was found in all four samples taken from one well.

Figure 7 presents the distribution of atrazine detections for southeastern Minnesota. The majority of the detections were less than 1 µg/l.

Although pesticide presence fluctuated, the concentrations of the pesticides detected in each well tended to be relatively constant. Wells having samples with atrazine concentrations greater than 0.2 µg/l usually had atrazine detected in subsequent samplings. In wells having samples containing atrazine at less than 0.2 µg/l, the reproducibilty of detection at the next sampling averaged 50 percent.

Most of the wells selected in the southeast were not associated with an obvious potential point source. However, because of the karst features and the location of most wells in farmyard settings, potential point sources could not be totally excluded. Two wells were located near possible point sources. These wells contained the highest atrazine concentrations and the only dicamba findings. Pesticide concentrations exceeded 1.0 µg/l in both wells in every sample collected. In contrast, wells without an obvious potential point source nearby exceeded 1.0 µg/l in only two of 75 samples.

Pesticides were detected in nine of the ten wells in Winona County. The large proportion of wells containing pesticides may be a result of the wells being located in the area where the Prairie du Chien-Jordan aquifer is likely to receive regional recharge water. In Winona County, wells were sampled that terminated in the Jordan sandstone. Although the number of wells sampled in the Prairie du Chien limestone was too small to show statistically significant relationships, there may be a slight difference in water quality between the limestone and sandstone, even though they are hydraulically connected. Wells cased into the limestone had slightly higher pesticide concentrations than wells cased into the sandstone.

In Olmsted County, soil conditions varied from one well site to another. The only well that contained pesticides in more than one sample was located in an area containing many nearby sinkholes and very shallow soil. This particular well was 83 feet deep and terminated in the Galena portion of the upper carbonate aquifer. The other well in which a pesticide was detected was located nearby and was only 50 feet deep, but contained atrazine in only one of the three samples collected. The two wells that did not contain pesticides were located in areas that typically have a layer of loamy glacial till between the soil and the limestone bedrock.

Dakota and Mower Counties each had one well in which atrazine was detected. The Mower County detection was unusual in that the well was 150 feet deep and located in a region of deep, loamy soils. In Dakota County, one shallow sand point well in a heavily irrigated area contained atrazine in two samples. Wells in Dakota County that were finished in the Prairie du Chien-Jordan aquifer did not contain detectable concentrations of pesticides.

All but two wells in the southeast contained measurable nitrate-nitrogen concentrations, with seven of the 21 wells exceeding the drinking water standard of 10 mg/l. Nitrate-nitrogen concentrations fluctuated in some wells and remained relatively constant in others.

Nitrate-nitrogen was detected in all but one well in which pesticides were found. Nitrate-nitrogen concentration and pesticide concentration were not directly correlated. However, at higher nitrate-nitrogen concentrations, the number of detections of atrazine and other pesticides increased (Figure 8). The average nitrate-nitrogen concentration of samples without pesticides was 6.2 mg/l compared to an average nitrate-nitrogen concentration of 12.9 mg/l for those samples with detectable concentrations of pesticides.

Central Minnesota

The central Minnesota region included a wide geographic area with diverse soil, agronomic and climatic conditions. The majority of wells sampled in central Minnesota were in unconfined, surficial sand and gravel aquifers associated with outwash plains. The outwash plains, formed as a result of debris deposition from the meltwater streams of stationary glaciers, are commonly associated with coarse-textured, well-drained soils with a low water holding capacity. These soils tend to be loamy sands or sandy loams with low organic matter content and low clay content. Soil series representative of outwash regions include Hubbard, Esterville, Menahga, and Sioux. The subsoil is usually composed of sand and gravel.

Shallow, unconfined aquifers typically exhibit a high hydraulic conductivity and are a readily available source of water. Water tables are commonly less than 30 feet beneath the soil surface.

Agriculture is the principal land use in central Minnesota. Corn and soybeans are grown on approximately 36 and 22 percent of the crop acreage, respectively. Small grain and hay account for the majority of the remaining acreage. Crops such as potatoes or sugar beets are grown on small, but locally concentrated, acreage. Irrigation is common in central Minnesota and accounts for the majority of the estimated 300,000 to 500,000 irrigated acres in the State.

Commonly used herbicides are atrazine, alachlor, metolachlor, 2,4-D, dicamba, metribuzin, and trifluralin. Insecticides such as terbufos, fonofos and carbofuran are used by some growers for corn rootworm control. Aldicarb is used to a limited extent on some potato acreage. Insecticides or fungicides are applied to sweet corn, potatoes, and sugar beets. Pesticides are commonly applied by ground sprayers at planting or by aerial application after the crop development.

A total of 54 wells were sampled at 45 sites in central Minnesota. At nine of the sites, two wells were located immediately adjacent to each other but at different depths in the aquifer. These adjacent sites are discussed in detail in the following section, though data presented in this section includes information and results from both wells at these nine sites. Table 8 summarizes information from central Minnesota wells.

The 54 wells included 45 water table observation wells, six drinking water wells, and three irrigation wells. The median depth of observation wells and potable wells was 23 feet with a range of 7 to 60 feet. The majority of wells were 11 to 30 feet deep. (Figure 9). The median water table depth of the observation wells (water table measurements were not available for drinking water or irrigation wells) was 12 feet with a range of 2 to 42 feet. The majority of the water table levels, taken as a mean over the duration of the study, were between 6 and 15 feet beneath the surface (Figure 9).

Five herbicides, one insecticide and one wood preservative were detected in central Minnesota wells (Table 9). Pesticides were present in 34 of the 54 wells sampled and at 31 of the 45 sites. Most pesticide detections were less than 1 µg/l (Table 9) and most samples contained only one pesticide.

The most frequently detected pesticide was atrazine, which accounted for 78 percent of the total pesticide detections. Atrazine was detected at 29 of the 45 sampling sites and in 30 of the 54 wells sampled in central Minnesota. The median atrazine concentration was 0.32 µg/l and most detections were less than 1 µg/l (Figure 10.). Atrazine concentrations greater than 3 µg/l were measured in all samples collected from three wells. The highest concentrations measured in the survey for atrazine and alachlor, 42.4 and

2.81 µg/l, respectively, were detected in a single sample from a central Minnesota well. A sample collected from the same well four months later contained atrazine and alachlor at 9.1 and 0.15 µg/l, respectively.

Generally, atrazine demonstrated persistence once it was found. Of the 29 wells in which atrazine was detected, 15 wells contained atrazine in three or more of the four samples taken from each well. Once atrazine was detected in the central Minnesota wells, 78 percent of the time the detection would be confirmed in the next sample. Only 5 percent of the initial detections were not confirmed in the subsequent sample but were detected in a later sample.

Alachlor was the second most frequently detected pesticide in the central Minnesota region. It was detected in seven samples collected from six wells. Only one well had alachlor present in consecutive samples. In six of the seven samples in which alachlor was detected, atrazine was also detected. In the six wells in which both alachlor and atrazine were found, four of the wells demonstrated a continued atrazine presence without a continued alachlor presence.

Aldicarb was detected in two observation wells adjacent to irrigated potato fields. One well was twelve feet deep with the water table at 6 feet. The first three samples from this well had levels of 9.0, 30.6 and 19.0 µg/l, followed by a fourth sample in which no aldicarb was detected. Four different pesticides were detected in this well during the course of the survey. The other well in which aldicarb was detected was 43 feet deep and screened at 20 feet. Aldicarb was detected twice at concentrations of 0.5 and 0.7 µg/l.

Pesticides other than atrazine repeated in only 57 percent of the subsequent samples. Metribuzin, cyanazine and pentachlorophenol did not repeat in any well. Alachlor repeated once in one of the seven wells in which it was detected. Simazine and aldicarb repeated in the wells in which they were found. The well with simazine and the well with three aldicarb detections (the fourth sample contained pentachlorophenol) were the only two wells in which a non-atrazine pesticide was detected on all four sampling occasions.

Wells in which pesticides were detected were examined with regard to well depth, water table depth and depth of the well beneath the water table. Well depth was related to pesticide detections in that the majority of detections occurred in wells less than 30 feet deep (Figure 11). Also, eight of the ten wells that contained a pesticide on all four sampling occasions were less than the median depth of 22 feet. A correlation was not observed between pesticide occurrence and water table depth or well depth beneath the water table. In areas with coarse-textured subsoil, relatively minor differences in the depth to the water table should have little impact on the capability of a pesticide to move to the groundwater. While the depth of the well beneath the water table would be expected to have significant effects on the detection and concentration of pesticides in groundwater, those differences were not noted in this portion of the study.

Analysis of the nitrate-nitrogen concentrations with respect to well depth, water table depth and depth of the screen beneath the water table did not indicate any relationships. Sixteen wells contained no detectable levels of nitrate-nitrogen. An approximately equal distribution of wells with concentrations of nitrate-nitrogen at less than 1 mg/l, 1 to 10 mg/l and greater than 10 mg/l was observed. The lack of a direct relationship between nitrate and well characteristics indicates the site-specific nature of nitrate contamination in shallow, unconfined aquifers. Evidently a number of factors are involved in the distribution of nitrate within shallow unconfined aquifers.

Atrazine concentrations were not related to nitrate-nitrogen concentrations in central Minnesota wells. Figure 6 illustrates the lack of a linear relationship between detectable concentrations of nitrate-nitrogen and atrazine.

Pesticide presence was related to nitrate-nitrogen concentration. Pesticides were more likely to be found at higher nitrate-nitrogen concentrations (Figure 12). However, nitrate-nitrogen was not always a good indicator of pesticides, since pesticides were present in some wells where nitrate-nitrogen was not present. Conversely, pesticides were not present in some wells where nitrate-nitrogen concentrations were high.

The presence of an elevated or high nitrate-nitrogen concentration at a point in an aquifer indicates that the point is impacted by a nitrogen source. This nitrogen source may or may not be related to a pesticide source. Therefore, the presence of nitrate only indicates the potential for a pesticide to be present providing the pesticide is also capable of utilizing the same pathway as the nitrate.

The methodology employed in this survey was not sufficient to determine the interactions of the complex sets of factors that affect nitrate and pesticide movement to groundwater.

Adjacent Observation Wells

Two adjacent observation wells located within two feet of each other were sampled at nine sites in central Minnesota. These wells were screened at different depths in unconfined sand and gravel aquifers. Simultaneous sampling of adjacent wells permitted the examination of vertical differences in the aquifer with regard to pesticide and nitrate-nitrogen occurrence and concentration.

Vertical differences in nitrate-nitrogen concentrations were observed by Myette (1984) in unconfined surficial aquifers. Myette concluded that nitrate-nitrogen concentrations were highest near the water table and that little mixing occurred near the source of nitrate unless the groundwater was disturbed by pumping.

Well logs indicated that subsoil materials ranged from fine sand to gravel at all sites; however, two sites contained 5-foot layers of silty or clayey material. Six of the nine adjacent well sites were located in proximity to irrigated cropland. The mean depths for the shallow and deep wells were 17 and 28 feet, respectively. Well screen depth beneath the water table averaged 6 feet for the shallow wells and 17 feet for deep wells. Summary information about the sites is contained in Table 10.

The data from these sites indicate that significant vertical differences in pesticide and nitrate-nitrogen presence and concentration occur in unconfined, surficial aquifers. The degree of the differences varied from site to site and emphasized the site-specific nature of aquifer contamination by pesticides and nitrate. Three general types of situations were observed at the adjacent observation wells.

The first situation was observed at two of the nine sites where no pesticides were detected in any samples. However, the shallow wells had higher nitrate-nitrogen concentrations than did the deeper wells. Average nitrate-nitrogen concentrations were 7.4 and 1.9 mg/l for the shallow and deep wells, respectively.

The second situation occurred at four sites. The shallow wells at these sites contained more pesticides and had greater pesticide concentrations, more pesticide detections, and higher nitrate-nitrogen concentrations. The shallow wells averaged 14.5 mg/l nitrate-nitrogen while the deep wells averaged 1.1 mg/l nitrate-nitrogen. The shallow wells contained pesticides in eleven of sixteen samples. Atrazine was detected in all four shallow wells at average concentrations of 15.0, 0.67, 0.41 and 0.19 μg/l. Alachlor was detected three times in two shallow wells and cyanazine was detected once in a shallow well. Two deep wells contained atrazine in only two of sixteen samples at an average concentration of 0.14 μg/l. No other pesticides were detected.

The remaining three sites had more prevalent pesticide contamination in the deep well. At one site, nitrate-nitrogen was detected only once in the deep well, while atrazine was detected in three of four samples at an average of 0.15 μg/l. A second site contained nearly equal nitrate-nitrogen concentrations of 12.9 and 16.4 mg/l for the shallow and deep wells, respectively, but metribuzin was detected only in the deep well in one of the four samples. At the third site, the deep well contained atrazine in all four samples. The shallow well at this site had atrazine in two of three samples. Concentrations averaged 0.76 μg/l atrazine and no nitrate-nitrogen in the shallow well compared to 0.18 μg/l atrazine and 24.1 mg/l nitrate-nitrogen in the deep well.

This data indicates that pesticide and nitrate-nitrogen occurrence and concentration in unconfined, surfical aquifers vary with depth. These vertical differences vary by site and by time of sampling.

Tile Line Analysis

Many soils in southern and western Minnesota have poor natural drainage characteristics. These soils typically have high organic matter and clay content which contribute to reduced permeability. To farm these soils productively, artifical drainage systems, or tile lines, are often installed. Tile line effluent under controlled conditions can reflect fertilizer and crop management practices and has been used to evaluate nitrate-nitrogen leaching losses (Randall et al., 1988).

Five tile lines were sampled from research plot areas at three University of Minnesota Experiment Stations. The tile line systems were installed at an average depth of 4 feet to facilitate effluent collection from individual small plots for research purposes. These plots were "wrapped" in plastic to a depth of 6 feet to prevent lateral movement of water from outside the plots. No surface inlets were located in the plot areas. Tile lines were installed in 1976 at Waseca and Lamberton and in 1983 at Morris. Samples were collected twice from Waseca and once from both Lamberton and Morris in the spring of 1986. There was no discharge from the tile lines in the fall of 1986 and in the spring of 1987.

Pesticide use information was obtained for the Waseca and Lamberton sites for the previous thirteen years (Table 11). The Morris sites had pesticide use information for the previous three years; however, atrazine use information was available that indicated the herbicide had been used in 1966, 1969, 1972 and 1983.

Atrazine was detected in three of the five tile lines sampled. No other pesticides were detected. Detection of atrazine in the tile lines was associated with atrazine use. Atrazine was present in the Waseca tile lines at concentrations of 0.59 and 0.80 µg/l in samples obtained on April 8 and at concentrations of 0.94 and 0.98 µg/l in samples collected on June 8. Atrazine was used in 10 of the last 13 years at Waseca and in each of the last eight years. At the Morris sites, atrazine was detected in one tile line at a concentration of 0.23 µg/l. It should be noted, however, that atrazine was used in 1983 which also was the year of tile line installation. Subsurface contamination by surface soil containing atrazine residue may be the source of atrazine in the tile line effluent.

Several other pesticides were used at each site, though none were detected in the tile lines. Alachlor, cyanazine, carbofuran and terbufos were used at all sites to varying degrees. Overall, alachlor was the most frequently used herbicide (twelve of thirteen years at Waseca); however, it was not detected in the tile line effluent.

Soil characteristics related to poor natural drainage, such as high clay and organic matter content, also are important factors in pesticide adsorption and degradation. These factors interact with the chemical characteristics of various pesticides differentially and may provide a partial explanation for the nondetection of pesticides, other than atrazine, in the tile lines.

METHODS: MDH PESTICIDE SURVEY

Well Selection

Wells serving public water supplies (PWS) were selected for sampling by the MDH in order to address public exposure to pesticides in drinking waters. Public water supplies are defined as systems which provide piped water for human consumption to at least 25 persons or 15 service connections for 60 days or more of the year. Public water supplies serving year-round residents include municipal systems, mobile home park systems, and apartment complexes. Other PWS, which serve transient populations, include office buildings, factories, schools, churches, restaurants, service stations, resorts and campgrounds. A total of 400 PWS wells, including 224 municipal wells, were selected for sampling in 77 counties.

Wells were generally selected for sampling based on their apparent susceptibility to pesticide contamination. A well was assumed to be susceptible if pesticides were used in the area and the well/well site was characterized by one or more of the following: 1) karst topography; 2) surficial sand and gravel aquifers overlain by coarse-textured soils; 3) shallow depth to bedrock (less than 50 feet); 4) known water quality problems, particularly high or fluctuating nitrates; 5) proximity to facilities which handle bulk quantities of pesticides; and 6) proximity to irrigated cropland. Wells regarded as most susceptible to pesticide contamination were located in the karst region in southeastern Minnesota and in the surficial sand and gravel aquifer areas in central and southwestern Minnesota. Most sampled wells were located in these sensitive areas.

Some wells were selected outside of the most sensitive areas in order to provide areal coverage of the State's agricultural regions and diverse cropping practices. Many of these wells were regarded as less susceptible to pesticide contamination. Few wells were sampled in northeastern Minnesota due to the limited agricultural activity in the area.

More than half of the wells were selected prior to initiation of sampling. These wells were selected based on recommendations provided by MDH district offices, city and county health departments, the Minnesota Pollution Control Agency, Minnesota Geological Survey, Agricultural Extension Service and others. Soils and geological maps, well records and historical water quality data were also used in the site selection process.

The remainder of the wells included in the survey were selected in the field as the survey progressed. These sites were chosen to include geographic areas not adequately covered in the initial well selection and to provide additional data on aquifers of particular interest, i.e., the karst formations and surficial sand and gravel aquifers.

Sample Collection

Timing. Four hundred initial and 125 follow-up samples for pesticide and nitrate analyses were collected from the selected wells between May 1986 and June 1987 (Figure 13). Most initial and follow-up samples were collected during the 1986 growing season (May through October) and during the spring of 1987 (April through June). A few samples were collected during each of the intervening months (November 1986 through March 1987). Sampling was scheduled such that all areas under study were visited several times during the survey. Timely collection of these samples was achieved with the assistance of MDH field staff.

Due to funding limitations, a follow-up sample was collected from only those wells in which pesticides were detected in the initial sample. Follow-up samples were also collected from several wells where initial sample results were inconclusive. The time elapsed between collection of initial and follow-up samples ranged from two weeks to several months, depending on the time required for laboratory analyses, travel distances, availability of the well for sampling, and other factors.

Site descriptions and well data were compiled for each sampled well and recorded on specially prepared survey forms (Figure 14). Maps indicating well location, land use, and observed pesticide sources were prepared in the field. Information on well construction and hydrogeology was obtained for most wells from well owners, well logs, MDH records or other resources. Pesticide use practices in the vicinity of the wells were determined through interviews with local farmers, pesticide dealers, and/or commercial applicators at 153 of the 400 well sites.

Sampling Protocol. Samples were collected from a point on the water supply system as near as possible to the well and prior to any treatment, if possible. Water samples were obtained after evacuation of two to three casing volumes of water or after operation of the well pump for 10-15 minutes. The sample tap was flushed and samples were collected in 1-liter, amber glass bottles with Teflon-lined caps. Separate bottles were used to collect samples for chlorinated acid herbicides and for base/neutral extractable pesticides. Samples for aldicarb analysis were collected from 13 wells in identical bottles and sent to the MDA laboratory for analysis. A sample for nitrate-nitrogen analysis was collected from each well in a 125-ml polypropylene bottle. All samples were immediately packed in ice and returned to the laboratory as soon as possible, usually within 72 hours.

Laboratory Analysis

All samples, except those for aldicarb analysis, were analyzed at the MDH laboratory in Minneapolis. Samples were stored at 4°C prior to extraction. Samples were usually extracted within seven days of collection, and analyzed within 21 and 40 days of collection for base/neutral and acid extracted pesticides, respectively.

Base/Neutral Pesticides. Base/neutral pesticide samples were extracted at a neutral pH with 15 percent (by volume) methylene chloride in hexane and analyzed by gas chromatography. Analysis for five base/neutral pesticides was performed using a Varian Vista 6000 gas chromatograph. Extracts for these analytes were run simultaneously through DB-5 and SPB-35 capillary columns connected to a Varian Thermionic Specific Detector, which was specific for nitrogen and phosphorous. Analysis for the remaining 17 base/neutral pesticides was performed using a Tracor Model 570 gas chromatograph. Extracts for these analytes were run simultaneously through DB-5 and DB-WAX capillary columns connected to a Varian Thermionic Specific Detector, which was specific for nitrogen and phosphorous. In both procedures, the second column was used to confirm the presence of compounds detected with the first column.

Chlorinated Acid Herbicides. Samples to be analyzed for chlorinated acid herbicides were acidified in the laboratory and then extracted with methylene chloride. The resulting extract of chlorinated acids, acid esters and salt was hydrolyzed with potassium hydroxide, extracted with methylene chloride and concentrated. The acids were converted to pentafluorobenzyl esters by derivatization with pentafluorobenzyl bromide and calcium carbonate. Isooctane was added and the sample was concentrated for injection. Identification of the esters was made by gas chromatographic separation using a Hewlett-Packard Model 5880A gas chromatograph. Each sample was run simultaneously through DB-1701 and DB-5 capillary columns connected to Ni-63 electron capture detectors. The second column was used to confirm the presence of compounds detected with the first column.

Nitrate-Nitrogen. Nitrate-nitrite nitrogen was determined using a Technicon Auto Analyzer II, with a copper-cadmium reductor column, to measure absorbency following color development with sulfanilamide and N-1-napthylethylenediamine dihydrochloride. The method reporting limit was 0.4 µg/l. Nitrite concentrations are usually negligible in groundwater samples and the results are therefore presented as nitrate-nitrogen for purposes of this report.

Quality Control. The following standard quality assurance/quality control practices were used. Method blanks were analyzed daily to safeguard against contamination of glassware and/or reagents. Laboratory spiked samples were analyzed with each sample batch to monitor method performance for all compounds. Each sample analyzed for base/neutral pesticides was also spiked with methoxychlor to monitor extraction efficiency.

Field blanks accompanied most samples and were extracted and analyzed with the samples. Spikes and duplicates were each collected and analyzed with approximately ten percent of the samples to monitor analytical accuracy and precision, respectively. The following average percent spike recoveries (and standard deviations) were obtained for the compounds most frequently detected in the survey field samples: atrazine, 92.7 (8.5); alachlor, 102.9 (32.0); and 2,4-D, 84.7 (19.8). The spike concentrations were 0.26 µg/l for atrazine; 0.10 and 0.20 µg/l for alachlor; and 0.19, 0.78 and 3.18 µg/l for 2,4-D.

Reporting Results. Well owners were notified in writing of analytical results. Four wells in which pesticide concentrations exceeded RALs established in January 1988 are scheduled for resampling in spring 1988. Well owners are being notified that final recommendations on water use will be based on the outcome of the 1988 sampling. In wells with a nitrate-nitrogen concentration exceeding the drinking water standard (10 mg/l), the MDH advised that water not be consumed by infants under six months of age.

A brochure on pesticides in groundwater (Freshwater Foundation, 1986) was sent to all owners of wells in which pesticides were detected. A brochure providing information on water quality and proper well construction and location (MDH, 1983) was sent to all noncommunity PWS well owners where nitrate-nitrogen concentrations exceeded 1.0 mg/l.

RESULTS AND DISCUSSION: MDH PESTICIDE SURVEY

Pesticides were detected in 114 (28.5 percent) of 400 sampled wells. Pesticides were detected in wells in 48 counties spanning most of the study area, but were most commonly found in southwestern, southeastern, and central Minnesota (Figure 15). Few occurrences of pesticides in well water were observed in northwestern and south central Minnesota.

A total of 12 different pesticides, all of which were herbicides, were detected in the survey (Table 12). Atrazine was the most commonly detected compound and was found in 107 wells. Atrazine was detected in initial samples in every month except February 1987, when only three initial samples were collected. Alachlor and 2,4-D, the next most frequently occurring pesticides, were found in eight and seven of the sampled wells, respectively. Nine other herbicides were each detected in three or fewer wells. None of the insecticides or fungicides included in the survey were detected.

A single pesticide was observed in 100 of the 114 contaminated wells. Atrazine was the only pesticide observed in 94 of these wells. Six other wells had one of four pesticides (propachlor, 2,4-D, picloram, or alachlor) as the sole contaminant.

Multiple pesticides were detected in 14 wells. A total of 11 different pesticides was detected in the 14 wells, with atrazine being detected in 13 of these wells.

Observed pesticide concentrations were usually low. Atrazine concentrations were less than 0.10 µg/l in 69 of the 107 wells with atrazine results above the detection limits, and exceeded 1.0 µg/l in only seven wells. The highest concentrations of atrazine were found in the three areas where pesticides were most commonly detected: the southwest, the southeast, and central Minnesota.

At the time the field work and laboratory analyses were completed, no contaminants exceeded the RALs in use at that time. However, four wells had contaminants at levels exceeding the new RALs established in January 1988. In three wells, atrazine concentrations exceeded the RAL, 3.0 µg/l, in both the initial and follow-up samples. In a fourth well, a single sample contained four pesticides whose combined concentrations exceeded the recommended limit for drinking water containing multiple pesticides.

Measurable concentrations of the initially identified pesticide occurred in 65, 57, and 50 percent of the follow-up samples for atrazine, 2,4-D, and alachlor, respectively. Positive follow-ups were also observed for dicamba, picloram, MCPA, and metribuzin. Follow-up samples were below detection limits for the five other pesticides detected in initial sampling.

Pesticide occurrence in follow-up samples is dependent on several factors, including time elapsed between sampling events, pesticide mobility, pesticide persistence, rainfall, and the rates of groundwater movement in the vicinity of the well. Because each well was sampled only once or twice, an assessment of changes in pesticide occurrence and concentration over time could not be made in this survey.

Aquifer Analysis

Pesticide results were evaluated based on well construction and source aquifer. Well construction information was obtained from several sources including well owners/operators, MDH records, well logs and soils and geological maps. Based on this information, it was determined that 282 wells were completed in unconsolidated aquifers, 92 wells were completed in sedimentary bedrock, and eight wells were completed in igneous or metamorphic bedrock. The aquifer(s) supplying the remaining 18 wells could not be determined. Pesticides were not detected in any of these 18 wells.

Unconsolidated Aquifers. Two hundred eighty-two wells which terminated in unconsolidated glacial, alluvial, or lacustrine deposits were included in this classification. Twelve different pesticides were detected in a total of 79 of these wells. Atrazine was detected in 74 wells. Ten of the 14 wells with multiple contaminants were completed in unconsolidated formations.

Aquifers in unconsolidated formations can be grouped into two broad categories: 1) surficial, unconfined aquifers, which are generally viewed as more susceptible to contamination from the land surface; and 2) buried, confined aquifers, which are isolated from the land surface by an impervious layer, such as clay, and are generally regarded as less susceptible to contamination. However, information on well construction was usually not sufficient to permit a distinction between wells completed in surficial, unconfined aquifers and wells completed in buried, confined aquifers. Therefore, well casing depth was evaluated as a potential index of well vulnerability to pesticide contamination.

Casing depth was available for 179 wells finished in unconsolidated formations. Pesticides were found in 46 of these wells. The median casing depth for contaminated wells, 48 feet, was 24 feet shallower than the median casing depth for wells in which pesticide was not detected (Table 13). Pesticides were detected in wells cased as deep as 233 feet. Wells in which pesticide was detected in both the initial and follow-up samples tended to have shallower casings than wells with only a single pesticide occurrence.

The relationship between casing depth and pesticide occurrence is further illustrated in Figures 16 and 17. Pesticide occurrence was most common in wells with the shallowest casing depths and declined as depth increased. Forty-three percent of wells cased less than 50 feet deep were contaminated at least once, while only 18 percent of the wells deeper than 50 feet were contaminated.

Atrazine concentrations also declined as depth increased (Figure 18). The median concentration was 0.12 µg/l for wells cased less than 50 feet deep and 0.04 µg/l for wells cased to 50 feet deep or more.

The influence of casing depth on vulnerability of a well may be reduced under certain conditions. Wells with inadequate grout or damaged casing may allow water from very shallow depths to enter the well without percolating through the unconsolidated materials for the entire depth of the casing. In this survey, there was no means by which to evaluate the integrity of the well grout or casing.

Sedimentary Bedrock Aquifers. Ninety-two sampled wells obtained water from sedimentary bedrock formations. Fifty-six of these wells were located in nine southeastern counties which comprise most of the karst region in Minnesota (Dakota, Dodge, Fillmore, Goodhue, Houston, Mower, Olmsted, Wabasha, and Winona Counties). Pesticides were detected in 32 sedimentary bedrock wells, including 24 wells in the nine southeastern counties. Atrazine was detected in 30 wells at concentrations ranging from 0.02 to 5.5 µg/l. Alachlor was detected in three wells and picloram, propachlor, and dicamba were each detected in one well. Two wells had a single contaminant other than atrazine and four wells had multiple contaminants.

Casing depth was available for 73 of the 92 wells completed in sedimentary bedrock. Pesticide occurrence in sedimentary bedrock wells did not appear to be related to casing depth. Pesticides were detected throughout most of the range of sampled casing depths (Table 14). Casing depth may be a poor indicator of water quality for several reasons. Wells with damaged casing or inadequate grouting may be drawing water from depths much shallower than the casing depth. In addition, well records and other geologic information indicated that most sampled wells were cased into the first bedrock encountered in drilling or into formations which were hydraulically connected to overlying bedrock. Under these conditions, there may be little impediment to downward migration of pesticides other than the overlying unconsolidated materials. "Filtration" of percolating water will be determined, at least in part, by the thickness of this unconsolidated mantle, i.e., depth to bedrock.

Results did suggest a relationship between pesticide occurrence and depth to bedrock (Figure 19). Pesticides were detected in 41 percent of the wells encountering the first bedrock at depths less than 100 feet, but in only ten percent of the wells encountering the first bedrock at depths greater than or equal to 100 feet. Pesticide occurrence did not appear to be influenced by depth to bedrock when that depth was less than 100 feet.

Pesticide occurrence in specific bedrock formations is presented in Table 15. Formations are listed with the youngest formation at the top of the table and the oldest formations at the bottom. In the upper carbonate formations (Cedar Valley through Galena), pesticides were detected in 46 percent of the wells with depth to bedrock less than 100 feet, but were not detected in any of the ten wells with depth to bedrock equal to or greater than 100 feet. In the lower carbonate (Prairie du Chien) and adjoining sandstone formations (St. Peter and Jordan), pesticides were detected in 48 percent of the wells with depth to bedrock less than 100 feet. Pesticide was detected in one of four wells in these formations which had depths to bedrock greater than 100 feet. Pesticides were detected in only two of 17 wells completed in older cambrian and precambrian formations and were not detected in any of the four wells completed in Cretaceous formations.

<u>Igneous and Metamorphic Bedrock Aquifers.</u> Eight of the sampled wells were completed in igneous or metamorphic bedrock aquifers. Six wells were

in the Sioux quartzite in south central and southwestern Minnesota, one was a granite well in Morrison County, and one was a granite well in the Minnesota River Valley in Chippewa County. Atrazine, the only pesticide detected, was found in two Sioux quartzite wells in Pipestone County and the granite well in the Minnesota River Valley.

The three contaminated wells occurred where depth to bedrock was less than 35 feet. Depth to bedrock was greater than or equal to 35 feet for the five clean wells. While only a few wells were sampled, the occurrence of contamination where depth to bedrock is shallow is consistent with findings in sedimentary bedrock wells.

Pesticide Sources

Pesticides in groundwater were assumed to come from two possible sources: 1) diffuse, or non-point, sources, resulting from land application of pesticides; and 2) point sources, such as pesticide mixing, rinsing, disposal, or storage sites or backsiphonage incidents. All sampled wells were located in agricultural areas and most wells were within one quarter mile of crops which typically receive pesticide applications. Therefore, potential non-point pesticide sources existed in the vicinity of essentially all sampled wells. At most well sites, however, pesticide use information was not sufficient to allow examination of the nature of the relationship between normal pesticide use and well water contamination.

Many sampled wells were located in proximity to potential point sources of pesticide contamination, such as bulk pesticide storage and handling facilities Fifty-seven wells were located within one quarter mile of identified potential point sources, including nine wells within 100 feet of potential point sources. Pesticides were detected in five of these nine wells and in 17 of 48 wells located between 100 feet and one quarter mile from a potential point source.

Six of 14 wells with multiple contaminants and five of seven wells with atrazine concentrations greater than 1.0 µg/l were located within one quarter mile of potential pesticide point sources.

Several factors must be considered when interpreting these results. First, all the wells located near pesticide point sources were also close to nonpoint sources. It was not possible in this study to isolate a single pesticide source for any sample in which pesticides were detected. Second, many sampled wells may also have been located near unidentified point sources. These wells need to be included to provide a complete analysis of point source data. Finally, the implied link between pesticide point sources and well water contamination could not be substantiated without detailed investigations of the potential point sources, which were beyond the scope of this survey.

Nitrate-Nitrogen and Pesticides

Samples collected at 395 sites were analyzed for nitrate-nitrogen. Nitrate-nitrogen was detected above the reporting limit, 0.4 mg/l, in 187 wells (47.3 percent), and exceeded the drinking water standard, 10 mg/l, in 28 wells (7.1 percent) (Figure 20). The maximum nitrate-nitrogen concentration was 36 mg/l. Nitrate-nitrogen concentrations exceeded 10 mg/l in 11 wells in the central sand plains, 9 wells in the southwest, and 3 wells in the southeast.

Nitrate-nitrogen analyses were conducted primarily to determine if there was a relationship between nitrate-nitrogen and pesticide occurrence in groundwater. If such a relationship existed, the relatively inexpensive nitrate-nitrogen analysis could be used as a surrogate for the expensive pesticide analyses.

A clear relationship between pesticide and nitrate occurrence was not observed in this survey. Only 82 of 187 wells (43.3 percent) with detectable nitrate also contained detectable concentrations of pesticide (Table 16). Pesticides were detected in 32 wells in which nitrate was not detected, indicating that nitrate cannot be used as a reliable indicator of pesticide occurrence

Survey results did indicate that pesticides occurred more frequently in wells with higher nitrate-nitrogen concentrations. Pesticides were found in 60.7 percent of wells with nitrate-nitrogen concentrations greater than 10 mg/l, compared to a 17.4 percent pesticide occurrence in wells with nitrate-nitrogen detected at less than 1.0 mg/l.

Nitrate data were also examined to see if there was a relationship between nitrate-nitrogen concentration and pesticide concentration. The scatter of the data in Figure 21 shows no apparent relationship between pesticide and nitrate-nitrogen concentration.

The lack of a clear relationship between pesticide and nitrate occurrence in well water may be due, in part, to the respective sources of these products. While pesticides and nitrates may both occur in groundwater as a result of land-applied treatments, nitrates may also come from many other sources unrelated to pesticides, such as septic systems, animal feedlots or barnyards.

COMMON DISCUSSION

These surveys were intended to provide baseline information on the occurrence and extent of agricultural pesticide contamination in groundwater and drinking water in Minnesota. Although the full extent of pesticide contamination is unknown, the results of these surveys indicate that several pesticides are present in groundwater, especially in hydrogeologically sensitive areas of the State.

Combined pesticide results taken from both surveys are presented in Table 17. One or more pesticides were detected in 165 (33 percent) of the 500 wells sampled. Pesticides were observed more frequently in observation and private drinking water wells than in public drinking water wells. This difference is most likely attributable to the shallower depths of many of the observation and private drinking water wells and to their closer proximity to fields receiving pesticide applications.

Fifteen pesticides, including thirteen herbicides, one insecticide and one wood preservative, were detected in the surveys. Atrazine, the most commonly detected pesticide in each survey, was found in 154 (31 percent) of the 500 wells sampled and in over 90 percent of the wells which tested positive for pesticides. Alachlor, the next most commonly occurring compound in each survey, was found in 17 wells. Each of the remaining thirteen pesticides was detected in seven or fewer wells.

Although the percentage of wells with detectable levels of pesticides was relatively high, the concentrations detected were usually low. Eighty-four percent of all pesticide occurrences were at concentrations less than 1.0 µg/l. Levels exceeding the RALs were observed in samples collected from ten wells, including four public drinking water wells and one private drinking water well.

At the low concentrations typically observed in these surveys, the public health concerns focus on potential chronic health effects. Chronic toxicity information for many pesticides is limited. Although this body of information has improved significantly in recent years, it is difficult to associate specific health effects with exposure to low levels of pesticides in drinking water.

Pesticides were detected in wells in 51 counties, but were most commonly found in wells completed in the karst formations in southeastern Minnesota, the shallow, outwash sand and gravel aquifers in central Minnesota and the shallow, alluvial sand and gravel aquifers in southwestern Minnesota. Few pesticide occurrences were observed in northwestern and south central Minnesota.

The widespread occurrence of pesticides, primarily atrazine, at low concentrations in certain areas indicates that groundwater contamination may result from normal pesticide use as well as from spills, leaks, back-siphonages and other point sources.

While pesticides were observed more frequently in wells in certain areas of the State, the potential for contamination in a specific well is determined by a complex set of factors, including the contaminant source, chemical properties, local groundwater vulnerability, local agricultural practices and well construction. These factors vary considerably from area to area and from well to well.

The baseline information generated in these surveys has significantly expanded our knowledge of pesticide contamination in Minnesota groundwater and drinking water. Nevertheless, it is important to recognize the limitations of the surveys. A limited number of wells and pesticides were studied during a relatively short time frame under unusual precipitation conditions. As a result, these surveys do not provide a comprehensive statewide assessment of the extent of groundwater contamination by pesticides.

RECOMMENDATIONS

The occurrence of certain pesticides in groundwater, the unknown human health implications resulting from exposure to low levels of pesticides in drinking water, and the many unresolved questions related to the movement and fate of pesticides in the environment raise issues which need to be addressed. These issues have been the subject of considerable agency and legislative attention. The MDA is in the process of implementing the 1987 Pesticide Control Law which significantly broadened the Department's duties and responsibilities regarding pesticides and included requirements to address pesticide impacts on water quality. The MDH Safe Drinking Water initiative before the 1988 legislative session includes a request to fund ongoing monitoring of public water supplies for pesticides, and a request for support of an expanded groundwater program will be included in the next biennial budget request. The Environmental Quality Board's Water Resources Committee is currently working on a pesticide and nutrient management strategy aimed at protecting the State's groundwater and surface water. Efforts such as these must be continued and additional information must be gathered in order to develop programs and policies which adequately protect water resources and public health.

On the basis of these surveys and a broader range of concerns about pesticides, we offer the following recommendations:

Monitoring

1. Pesticide monitoring programs or activities should be developed which include:

- statewide ambient groundwater and surface water sampling to establish baselines and trends;

- public water system sampling to assess public exposure to pesticides in drinking water;
- intensive area-specific and pesticide-specific studies to further define pesticide occurrence, extent and trends in hydrogeologically sensitive areas of the State;
- sampling near spill sites and bulk pesticide storage and handling facilities to assess the impacts of those activities on water quality;
- selected private well sampling near known or suspected contamination sites; and
- selected private well sampling based on representative conditions, such as source aquifer, soils, hydrogeologic characteristics, well construction and pesticide use.

2. Public and private laboratory analytical capabilities need to be developed for additional pesticides and pesticide breakdown products and more public and private laboratory capacity is needed to accommodate larger numbers of samples. A laboratory certification program should be developed to ensure accurate, reproducible pesticide results from public and private laboratories.

3. Interagency agreements and technical work groups should be established to ensure coordinated planning and implementation of pesticide monitoring programs. Standard data collection and management protocols should be established.

4. A statistically designed pesticide use survey, capable of determining use and trends at the county or subcounty level, should be conducted on an annual basis.

Research

1. Research is needed to determine pesticide and soil characteristics which affect leaching, adsorption and persistence in Minnesota.

2. Research is needed to determine pesticide degradation pathways and breakdown products in Minnesota's soils and waters.

3. Applied research should be conducted to develop management practices which reduce pesticide leaching.

4. Risk assessment efforts should be expanded so that new health effects and exposure information can be evaluated and appropriate health advisories issued.

Education and Information

1. Information should be made available to pesticide applicators and dealers which addresses pesticide handling, mixing and storage near wells.

2. Educational programs and information related to pesticide products and their use should be expanded to include health and environmental components.

3. Groundwater vulnerability mapping should be conducted at the State and local level. County geologic and hydrologic mapping needs to be accelerated.

Regulation

1. Pesticide regulatory and enforcement activities should be increased to address major point sources of pesticide contamination in groundwater and drinking water.

2. Private and commercial applicator training programs should be approved for applicator certification only if they include an acceptable groundwater component.

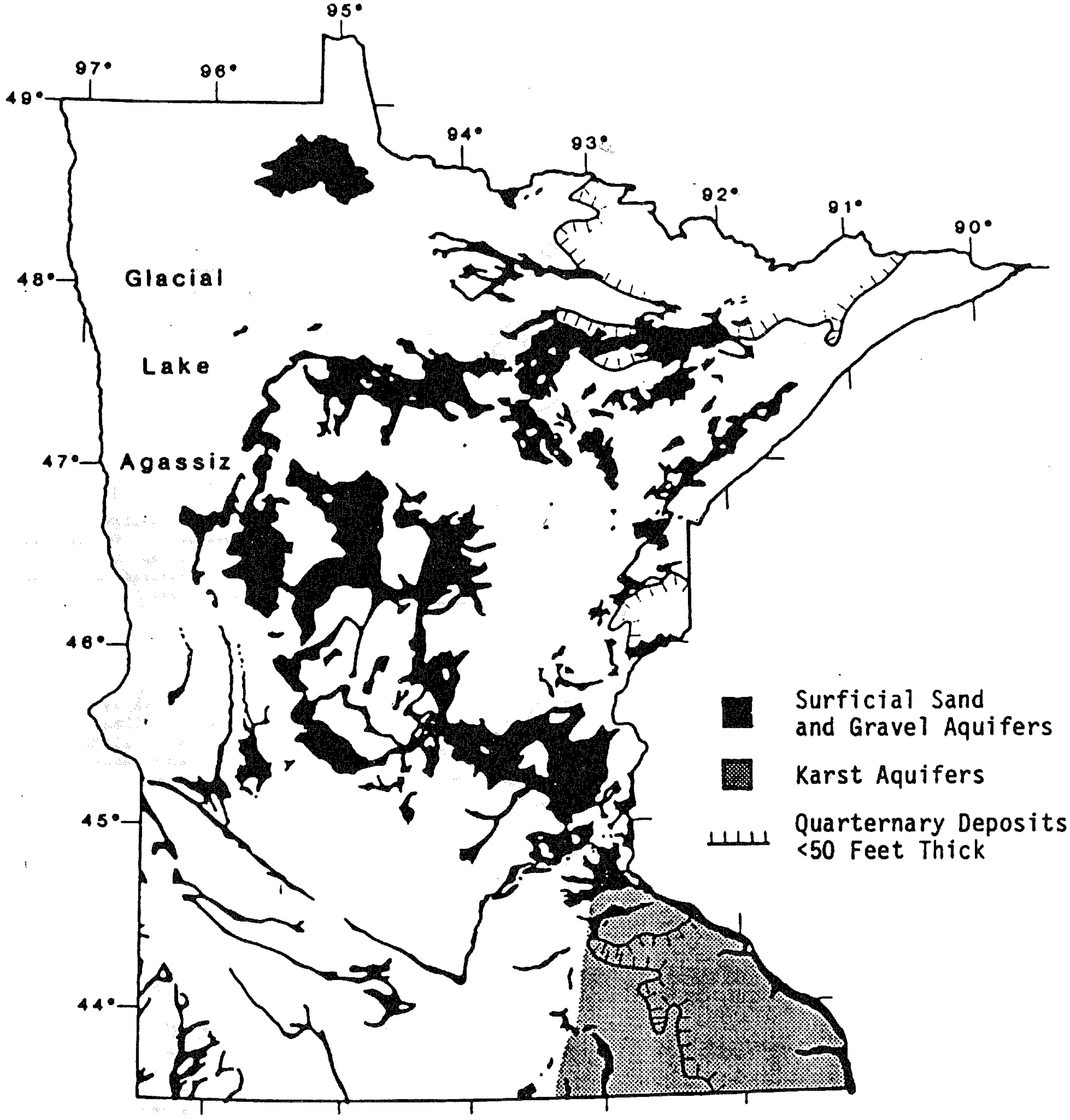
3. The water well program should be expanded to ensure that new wells are properly sited, constructed and maintained, thereby reducing the potential

for pesticide contamination. Abandoned wells should be properly sealed to eliminate potential routes of pesticide movement between and within aquifers.

4. A State pesticide regulatory management plan, including procedures for modifying pesticide use, should be developed. Provisions of the plan would be implemented when specific situations require controls to prevent further degradation of groundwater quality.

FIGURE 1

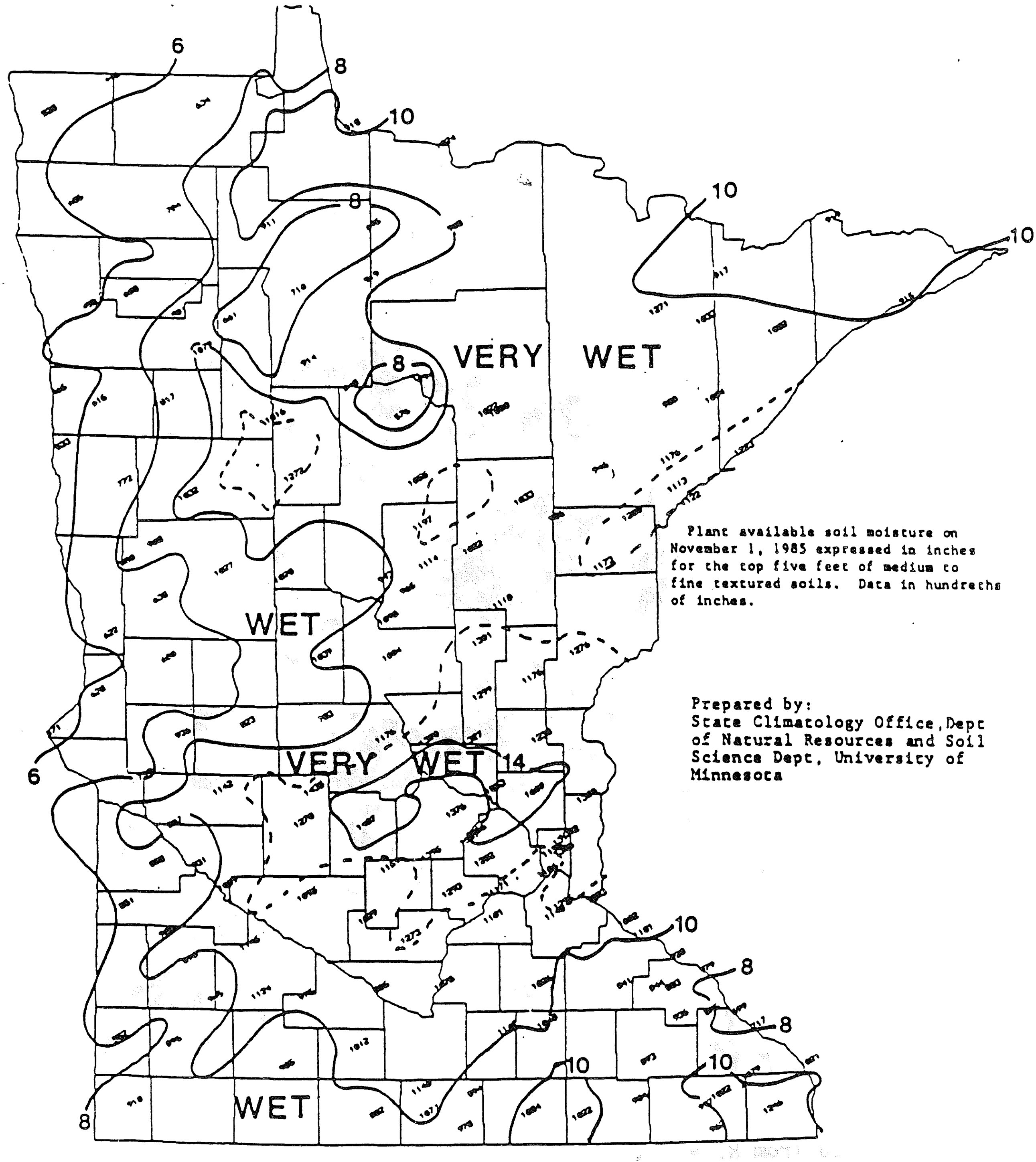
SURFICIAL SAND AND GRAVEL AQUIFERS
AND KARST AQUIFERS IN MINNESOTA



Modified from H. W. Anderson, *In* Adolphson, D. G., J. F. Ruhl, and R. J. Wolf, 1981. *Designation of Principal Water-Supply Aquifers in Minnesota*. U.S. Geological Survey Water-Resources Investigations 81-51, 24 p.

FIGURE 2

SOIL MOISTURE, NOVEMBER 1, 1985

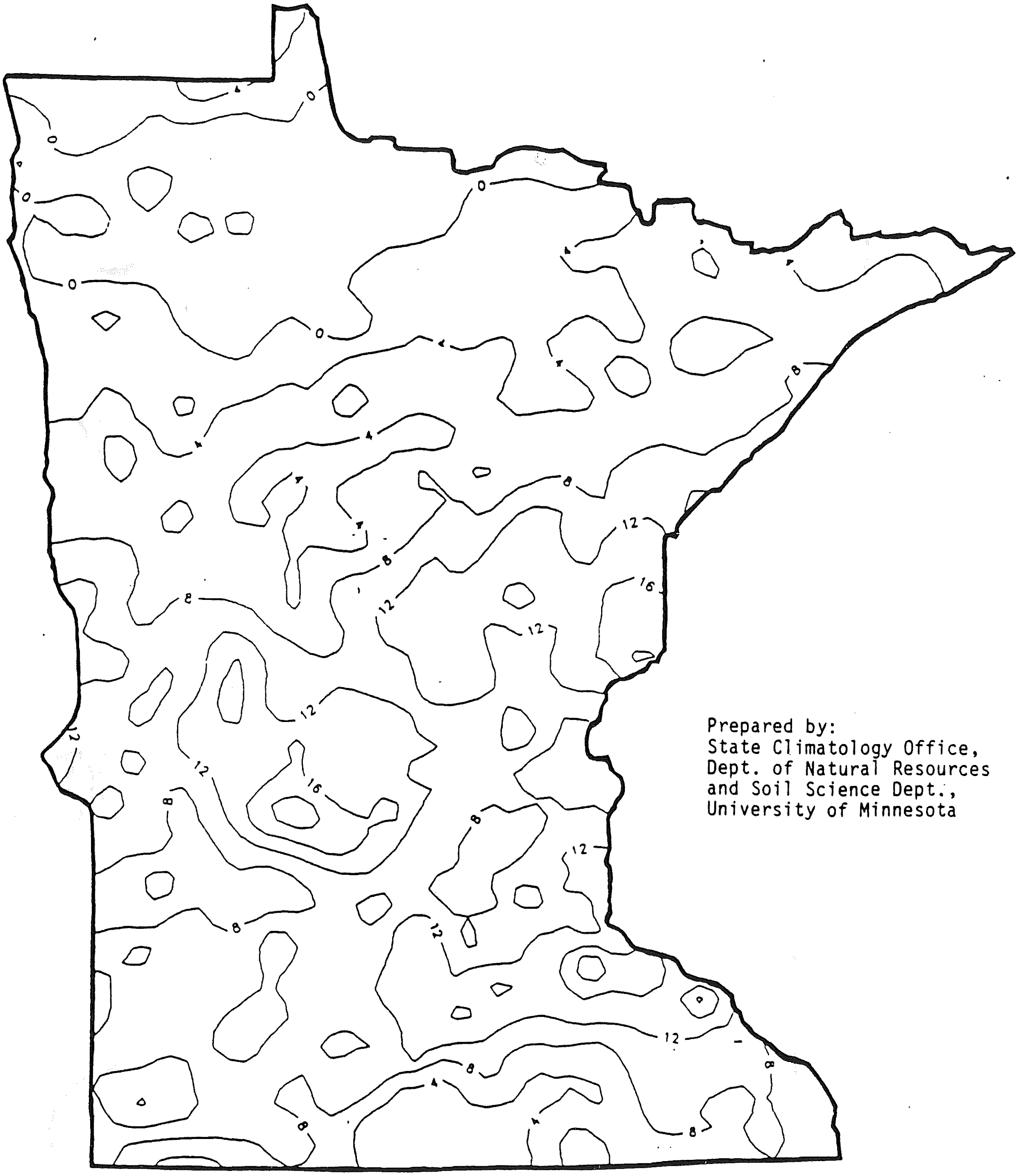


Plant available soil moisture on November 1, 1985 expressed in inches for the top five feet of medium to fine textured soils. Data in hundreths of inches.

Prepared by:
State Climatology Office, Dept
of Natural Resources and Soil
Science Dept, University of
Minnesota

FIGURE 3

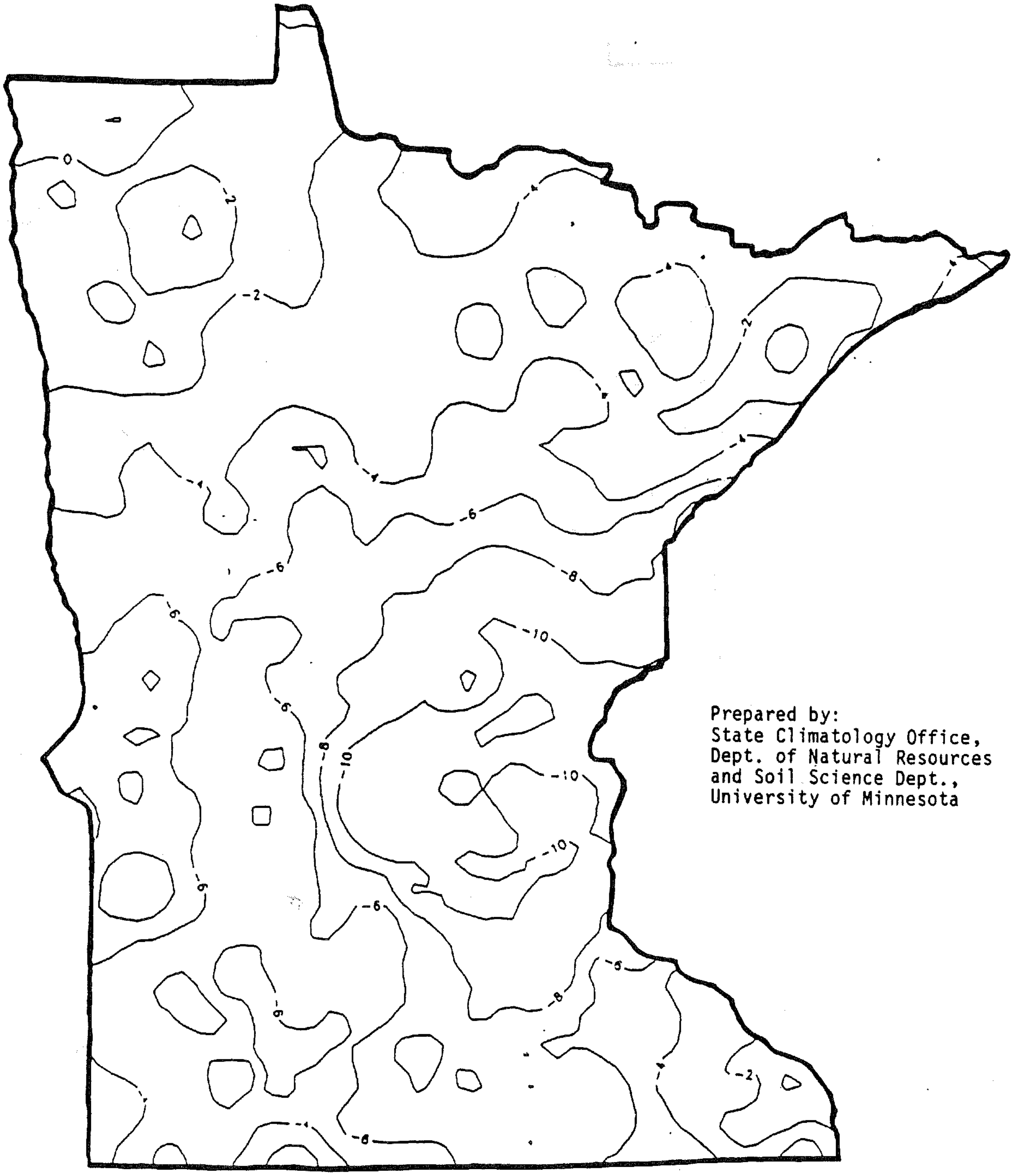
HYDROLOGIC YEAR PRECIPITATION
OCTOBER 1985-SEPTEMBER 1986
DEPARTURE FROM 1951-80 NORMALS, INCHES



Prepared by:
State Climatology Office,
Dept. of Natural Resources
and Soil Science Dept.,
University of Minnesota

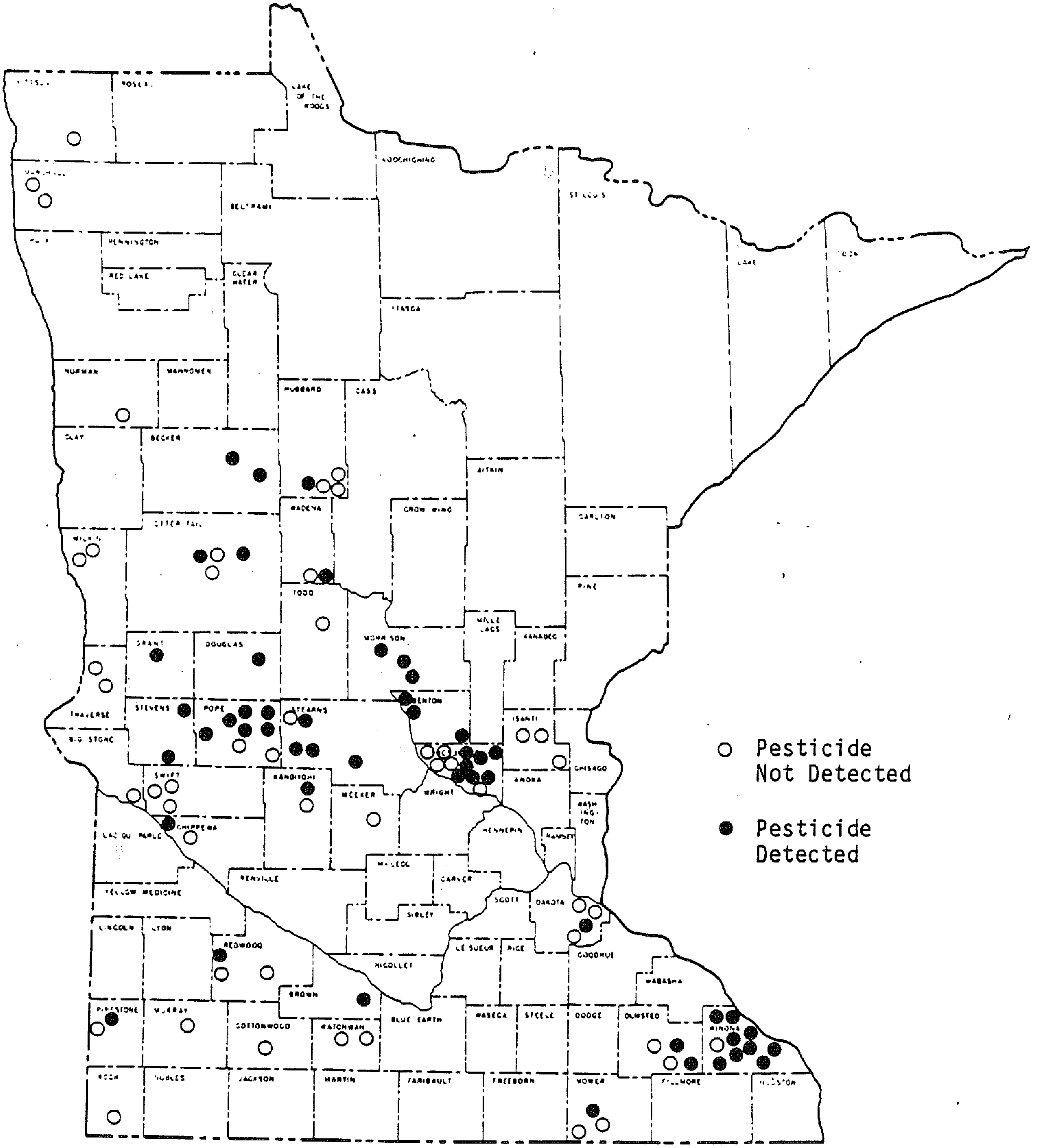
FIGURE 4

HYDROLOGIC YEAR PRECIPITATION
OCTOBER 1986-JUNE 1987
DEPARTURE FROM 1951-80 NORMALS, INCHES



Prepared by:
State Climatology Office,
Dept. of Natural Resources
and Soil Science Dept.,
University of Minnesota

FIGURE 5
OCCURRENCE OF PESTICIDES
MDA SURVEY



Minnesota Department of Health

FIGURE 6

ATRAZINE CONCENTRATION VS. NITRATE CONCENTRATION OBSERVATION AND PRIVATE WELLS

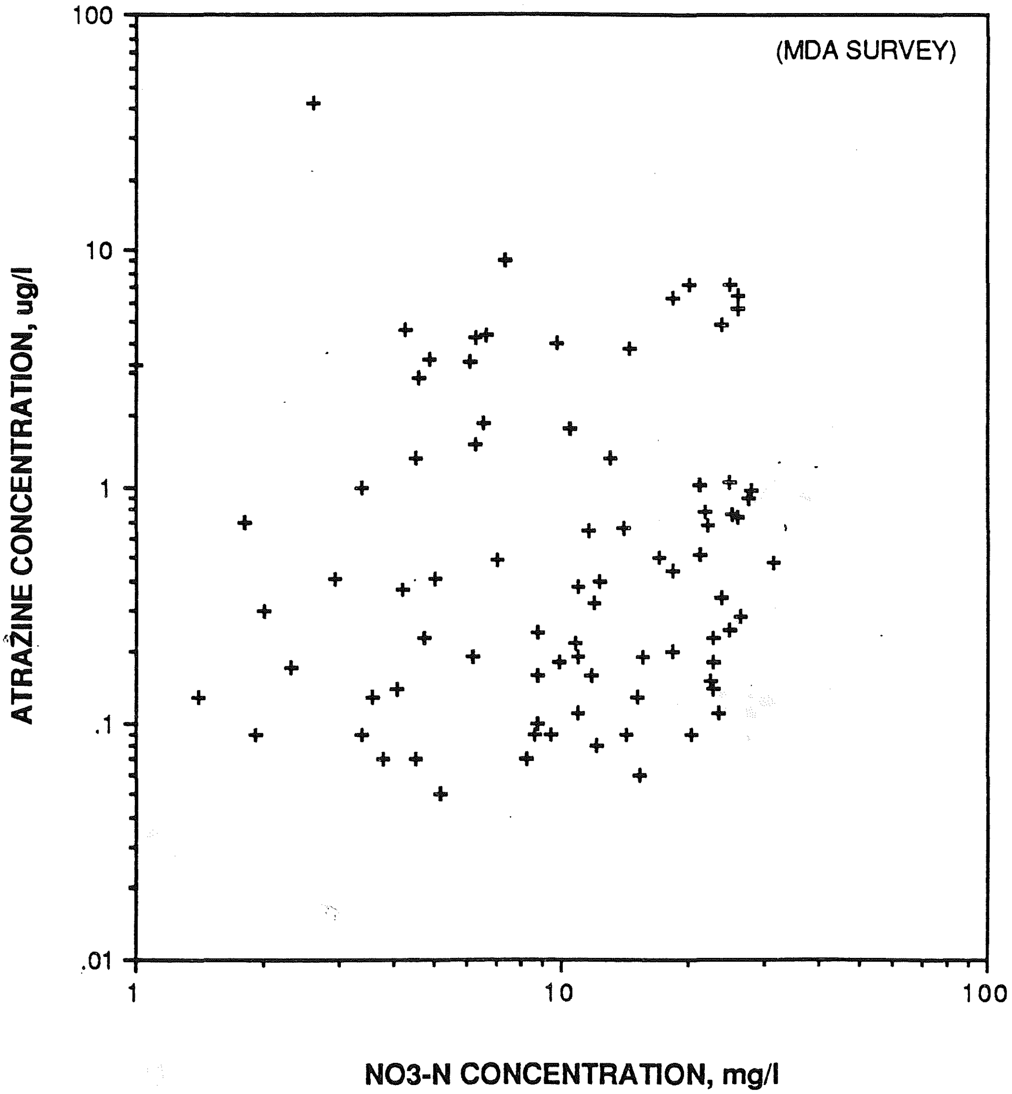


FIGURE 7

DISTRIBUTION OF ATRAZINE CONCENTRATIONS PRIVATE WELLS IN SOUTHEAST MINNESOTA

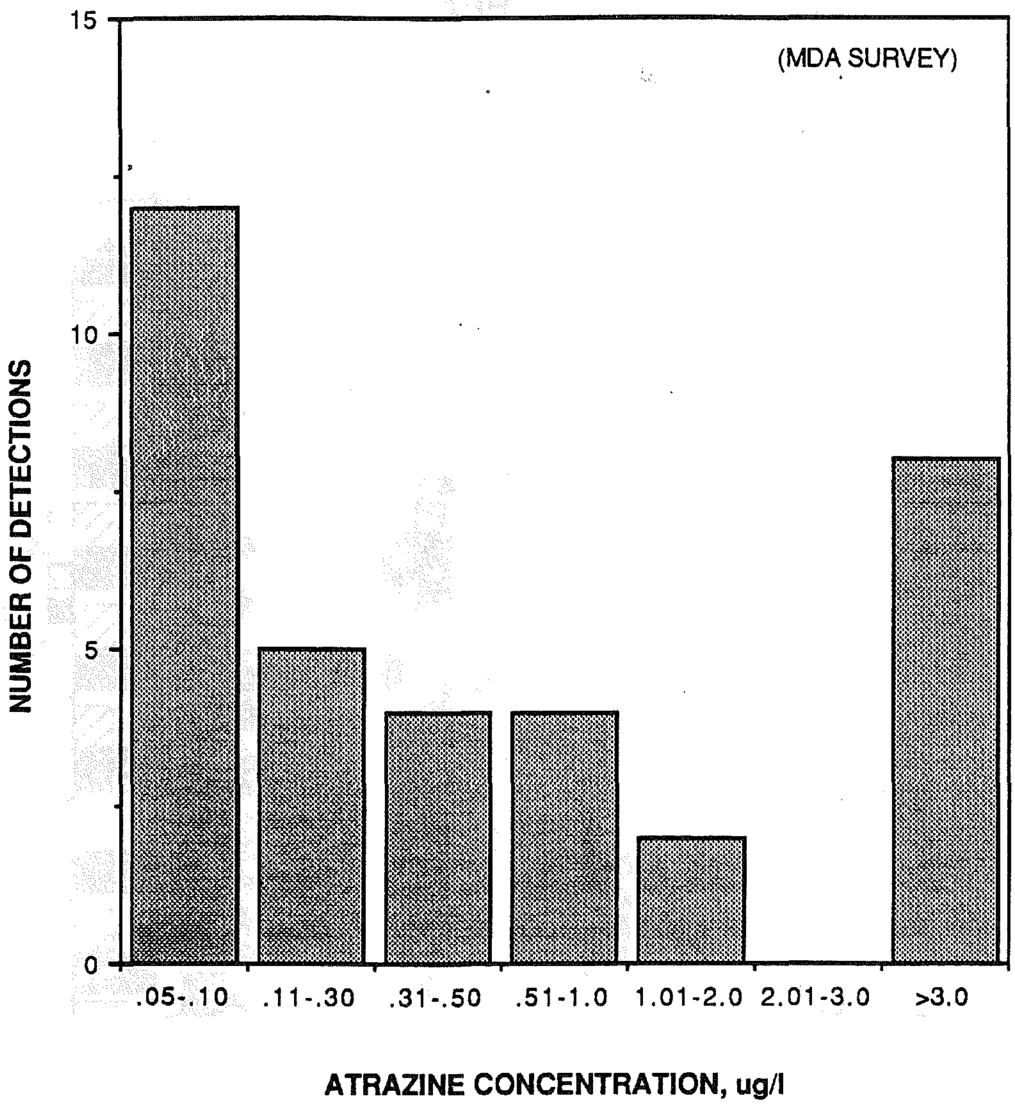


FIGURE 8

ATRAZINE OCCURRENCE VS. NO3-N CONCENTRATION
PRIVATE WELLS IN SOUTHEAST MINNESOTA

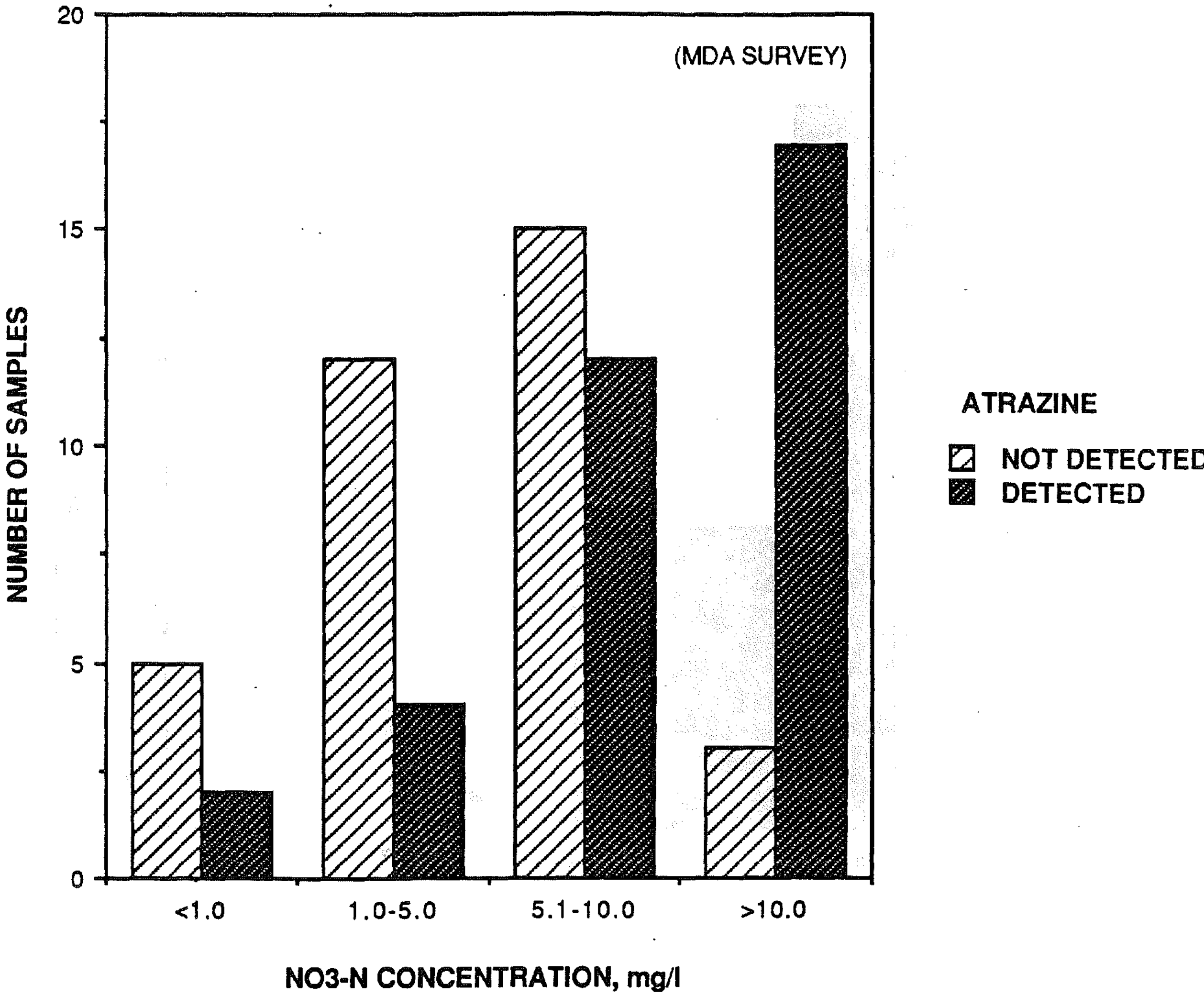


FIGURE 9

DISTRIBUTION OF WATER TABLE AND WELL DEPTHS
CENTRAL MINNESOTA

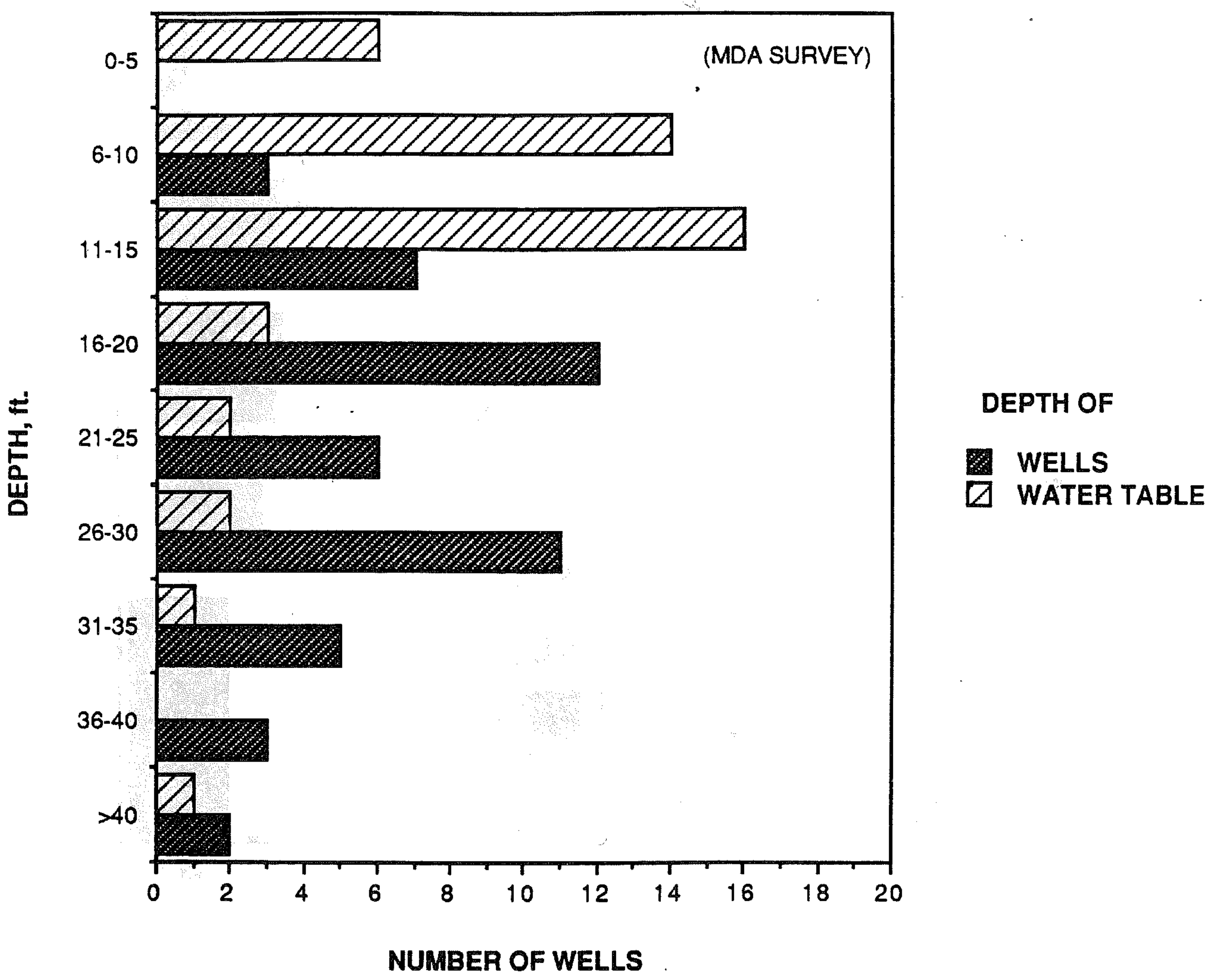


FIGURE 10

DISTRIBUTION OF ATRAZINE CONCENTRATIONS WELLS IN CENTRAL MINNESOTA

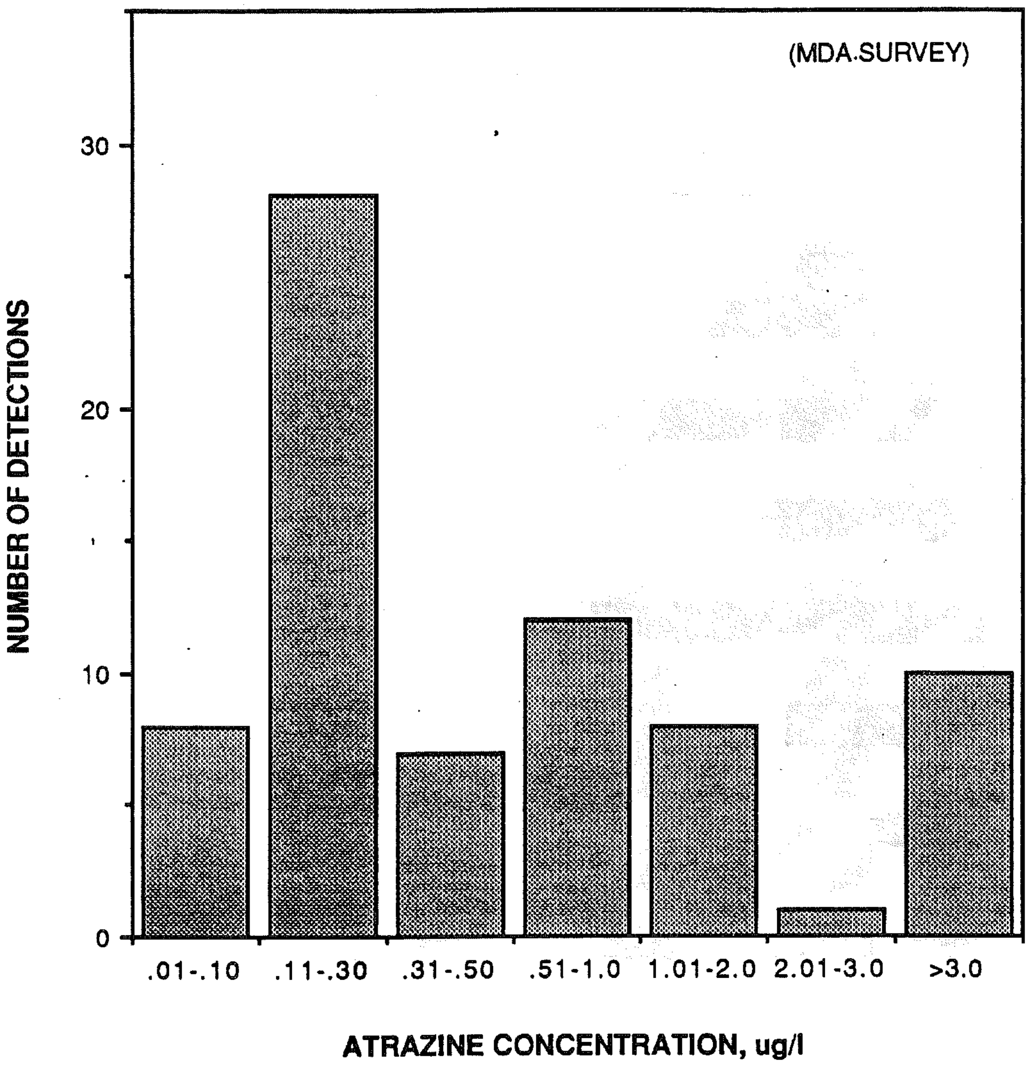


FIGURE 11

FREQUENCY OF PESTICIDE OCCURRENCE VS. WELL DEPTHS CENTRAL MINNESOTA

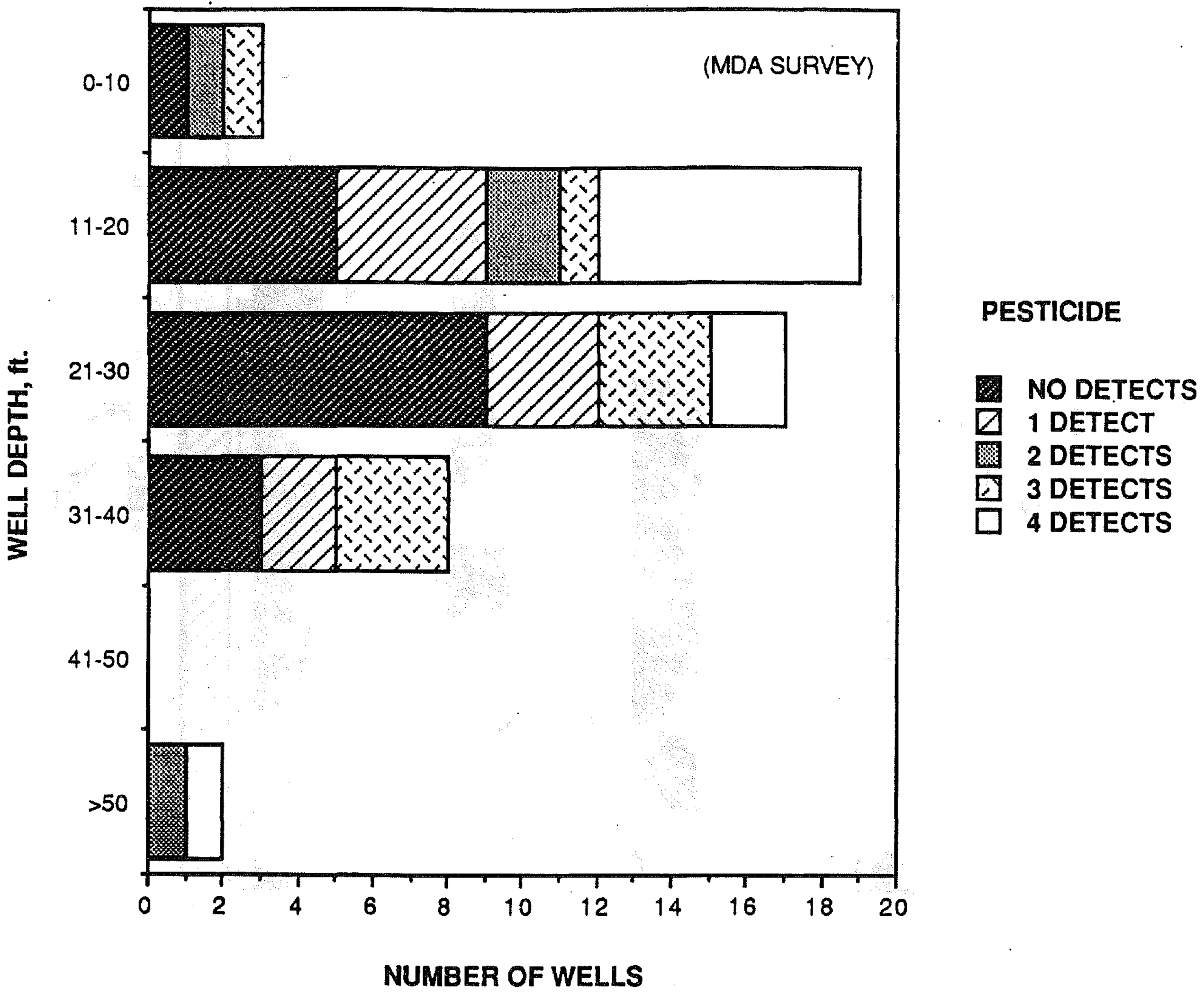


FIGURE 12

PESTICIDE OCCURRENCE VS. AVERAGE NO3-N CONCENTRATION WELLS IN CENTRAL MINNESOTA

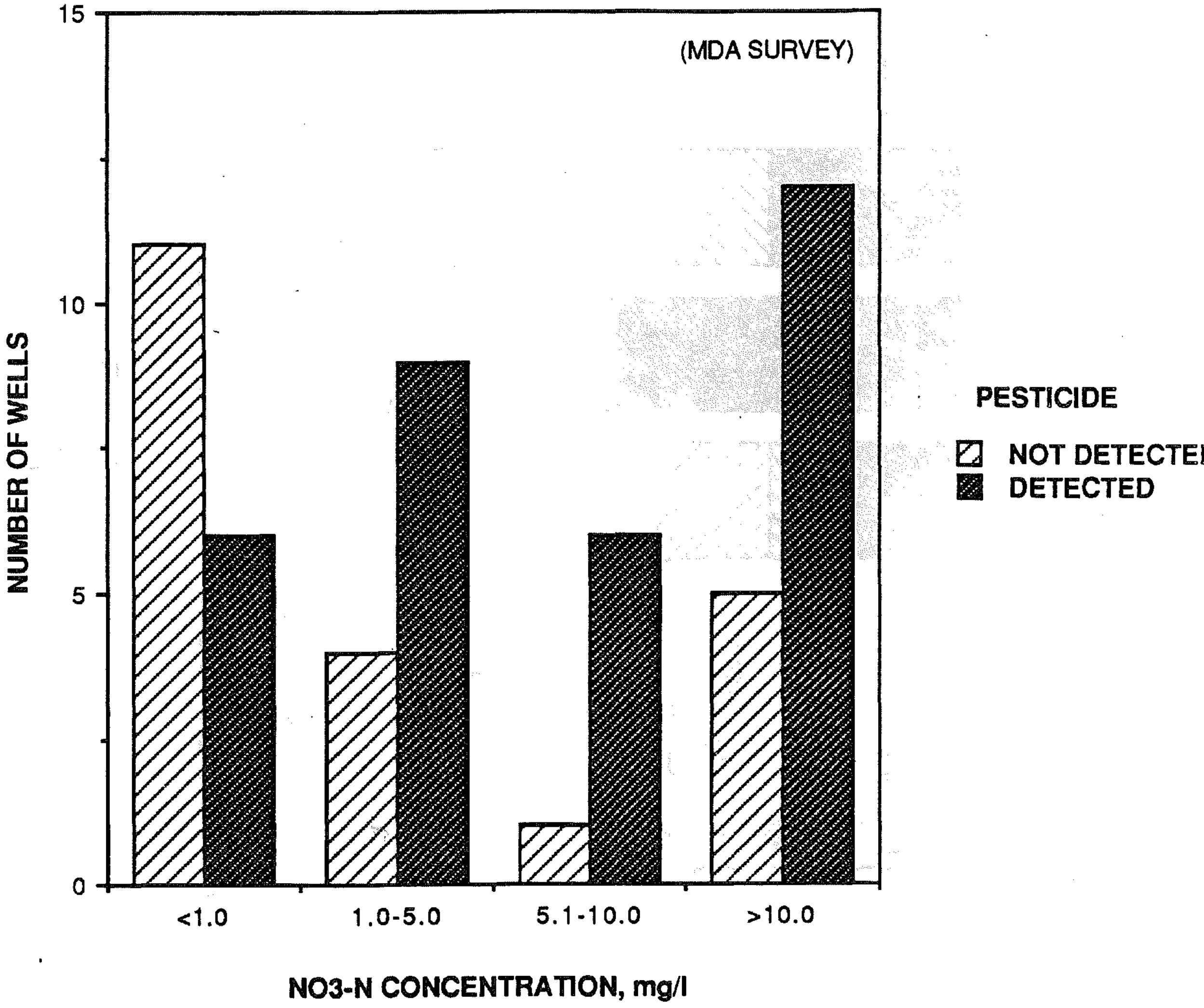


FIGURE 13

SAMPLING DISTRIBUTION BY MONTH
PUBLIC WELLS

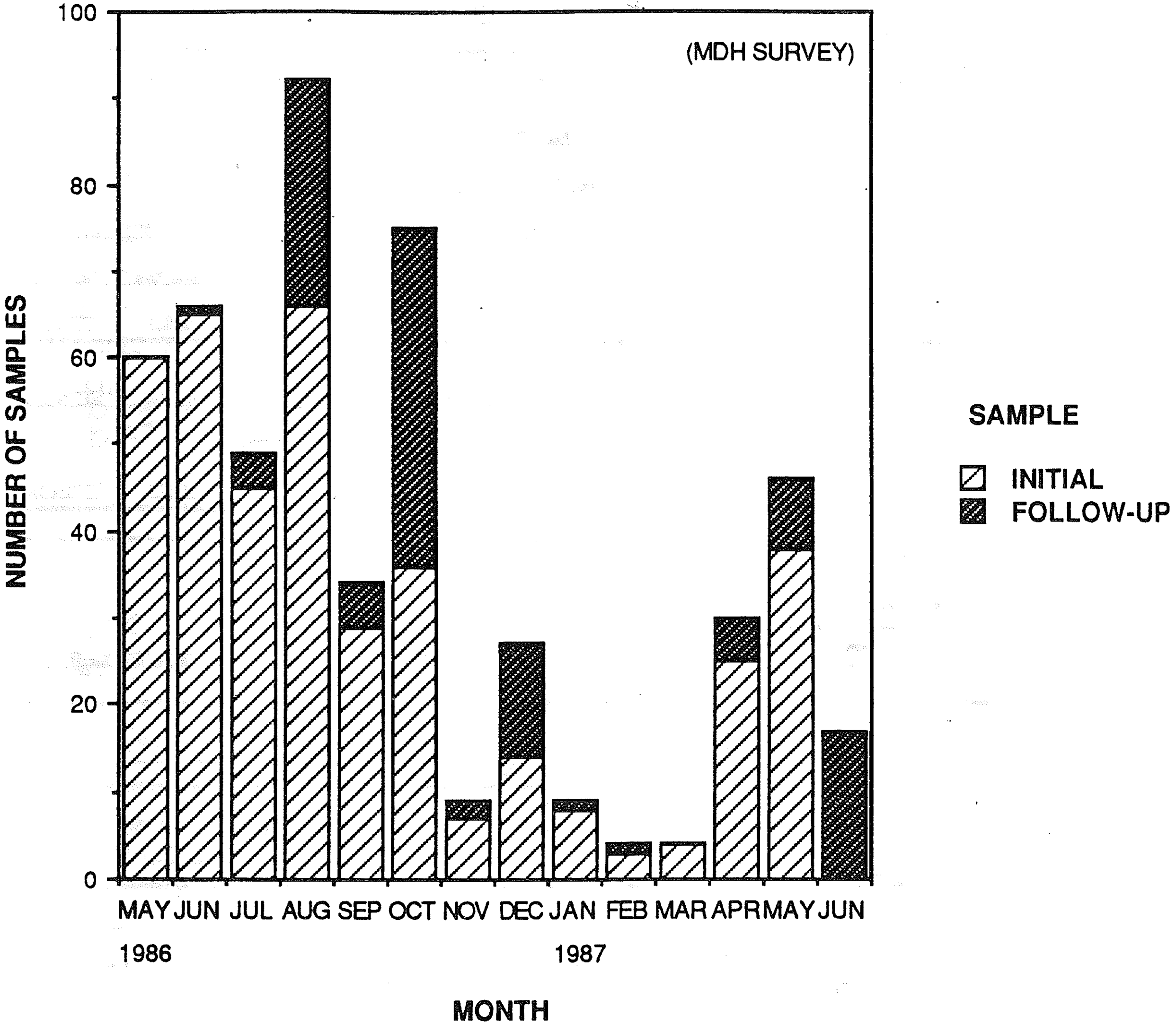
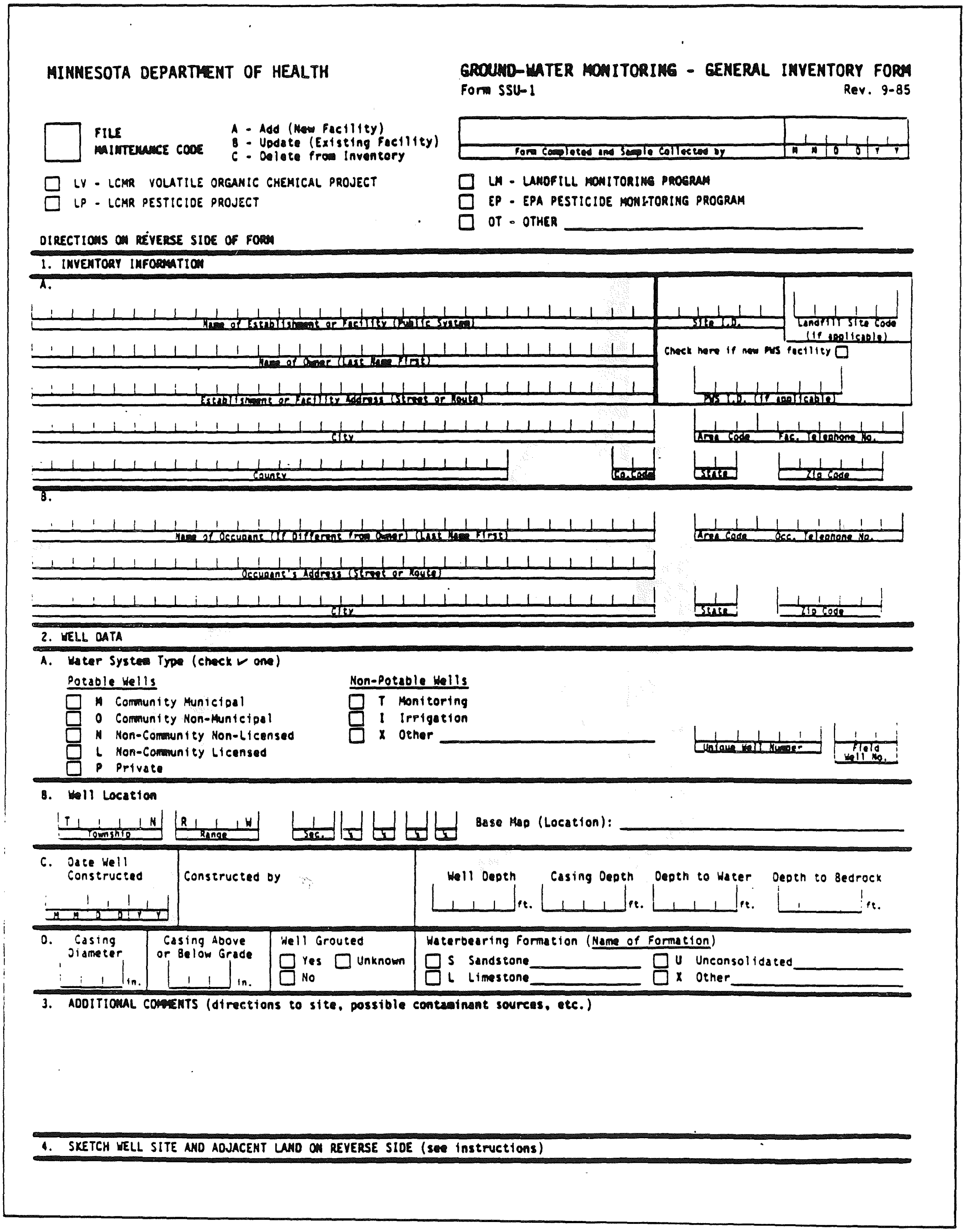


FIGURE 14
GROUNDWATER MONITORING GENERAL INVENTORY FORM
MDH SURVEY



MINNESOTA DEPARTMENT OF HEALTH

GROUND-WATER MONITORING - GENERAL INVENTORY FORM
Form SSU-1
Rev. 9-85

☐ **FILE MAINTENANCE CODE**
A - Add (New Facility)
B - Update (Existing Facility)
C - Delete from Inventory

Form Completed and Sample Collected by ______ M M D D Y Y

☐ LV - LCMR VOLATILE ORGANIC CHEMICAL PROJECT
☐ LP - LCMR PESTICIDE PROJECT
☐ LM - LANDFILL MONITORING PROGRAM
☐ EP - EPA PESTICIDE MONITORING PROGRAM
☐ OT - OTHER ______

DIRECTIONS ON REVERSE SIDE OF FORM

1. INVENTORY INFORMATION

A.

Name of Establishment or Facility (Public System)
Site I.D.
Landfill Site Code (if applicable)
Name of Owner (Last Name First)
Check here if new PWS facility ☐
Establishment or Facility Address (Street or Route)
PWS I.D. (if applicable)
City
Area Code Fac. Telephone No.
County
Co. Code
State
Zip Code

B.

Name of Occupant (If Different from Owner) (Last Name First)
Area Code Occ. Telephone No.
Occupant's Address (Street or Route)
City
State
Zip Code

2. WELL DATA

A. Water System Type (check ✓ one)

Potable Wells
☐ M Community Municipal
☐ O Community Non-Municipal
☐ N Non-Community Non-Licensed
☐ L Non-Community Licensed
☐ P Private

Non-Potable Wells
☐ T Monitoring
☐ I Irrigation
☐ X Other ______

Unique Well Number
Field Well No.

B. Well Location

T N Township
R W Range
Sec.
¼ ¼ ¼ ¼
Base Map (Location): ______

C. Date Well Constructed M M D D Y Y
Constructed by
Well Depth ft.
Casing Depth ft.
Depth to Water ft.
Depth to Bedrock ft.

D. Casing Diameter in.
Casing Above or Below Grade in.
Well Grouted ☐ Yes ☐ Unknown ☐ No
Waterbearing Formation (Name of Formation)
☐ S Sandstone ______
☐ L Limestone ______
☐ U Unconsolidated ______
☐ X Other ______

3. ADDITIONAL COMMENTS (directions to site, possible contaminant sources, etc.)

4. SKETCH WELL SITE AND ADJACENT LAND ON REVERSE SIDE (see instructions)

FIGURE 15
OCCURRENCE OF PESTICIDES
PUBLIC WELLS, MDH SURVEY

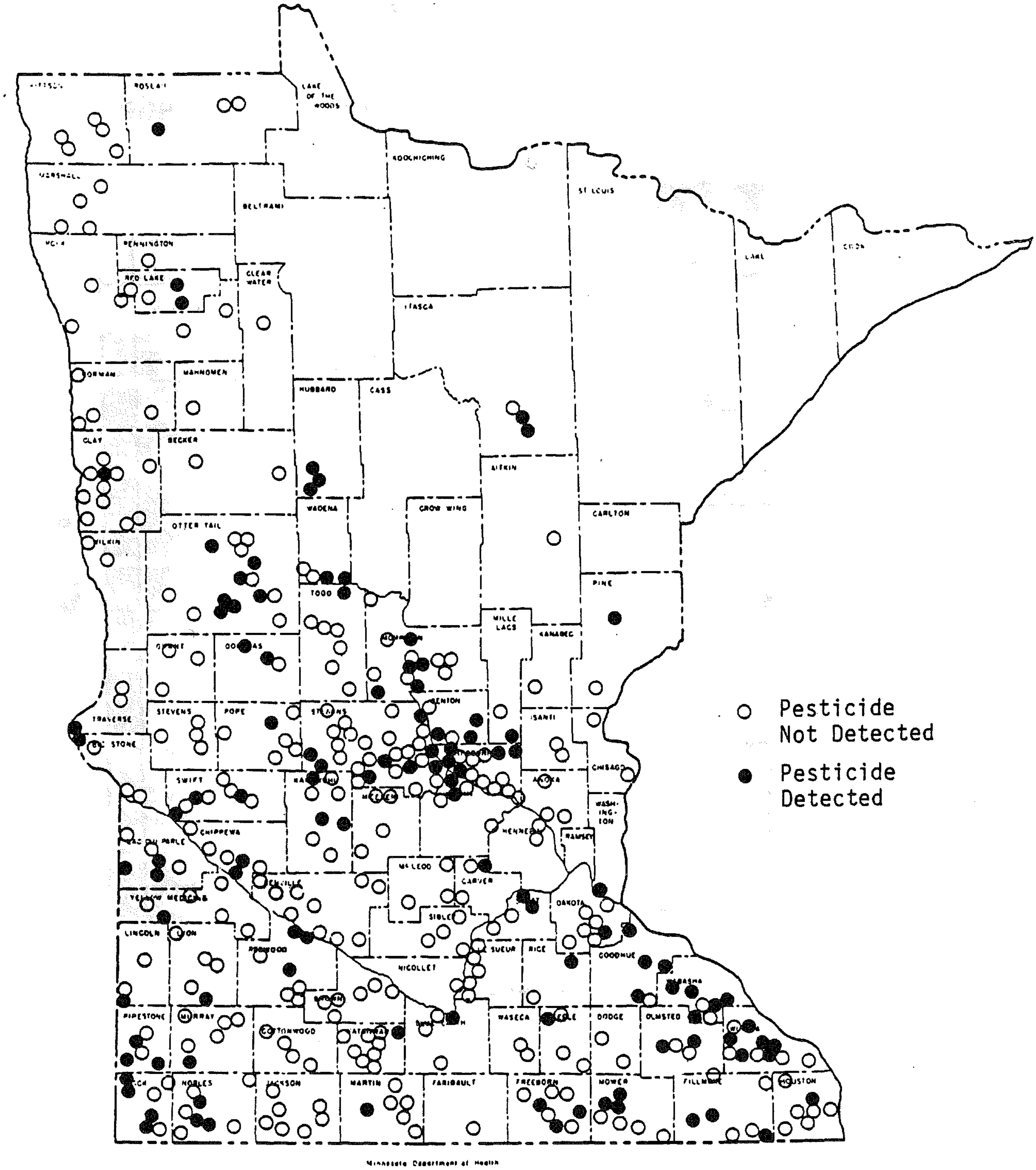


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FIGURE 16

PESTICIDE OCCURRENCE VS. CASING DEPTH PUBLIC WELLS IN UNCONSOLIDATED AQUIFERS

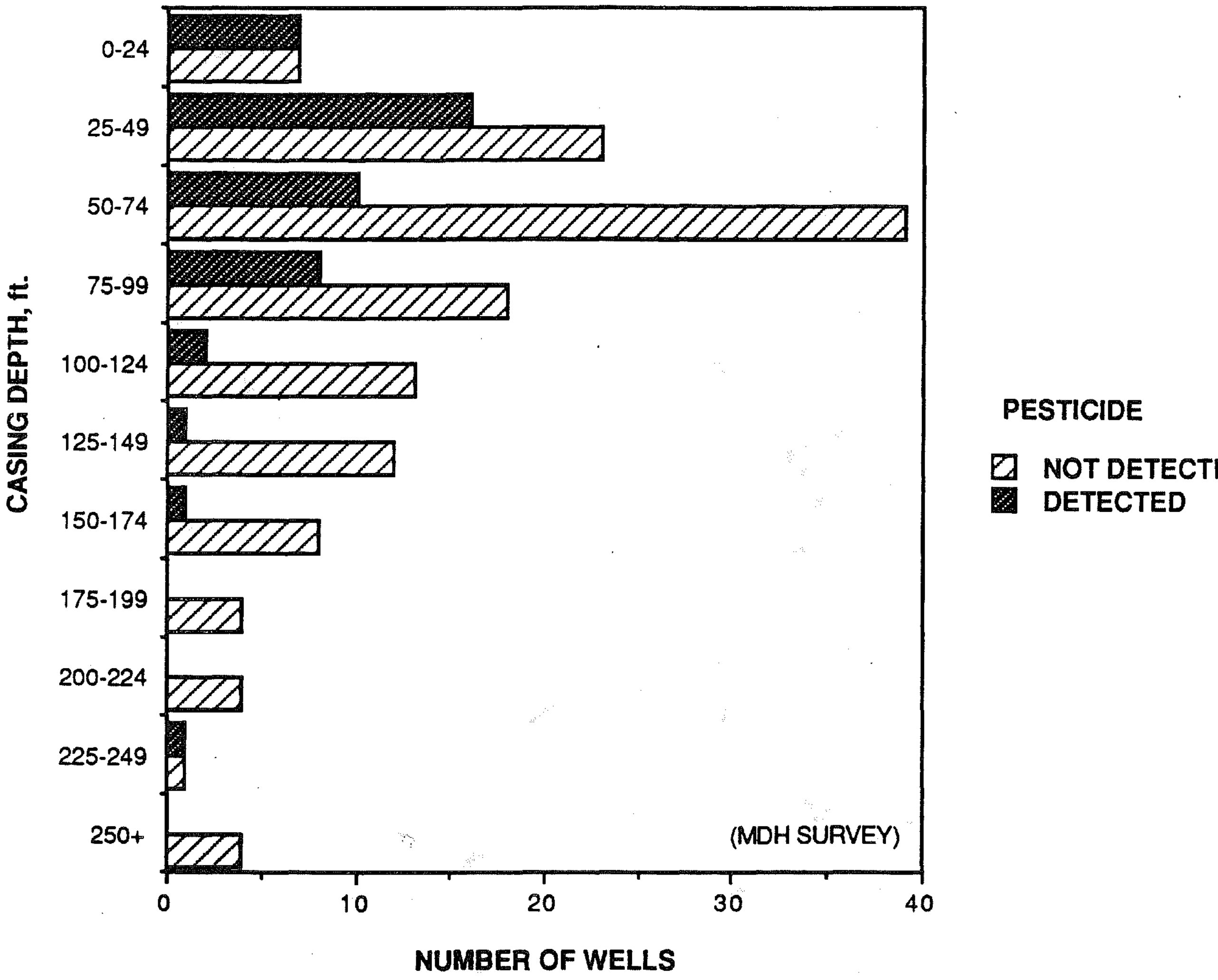


FIGURE 17

PESTICIDE OCCURRENCE VS. CASING DEPTH PUBLIC WELLS IN UNCONSOLIDATED AQUIFERS

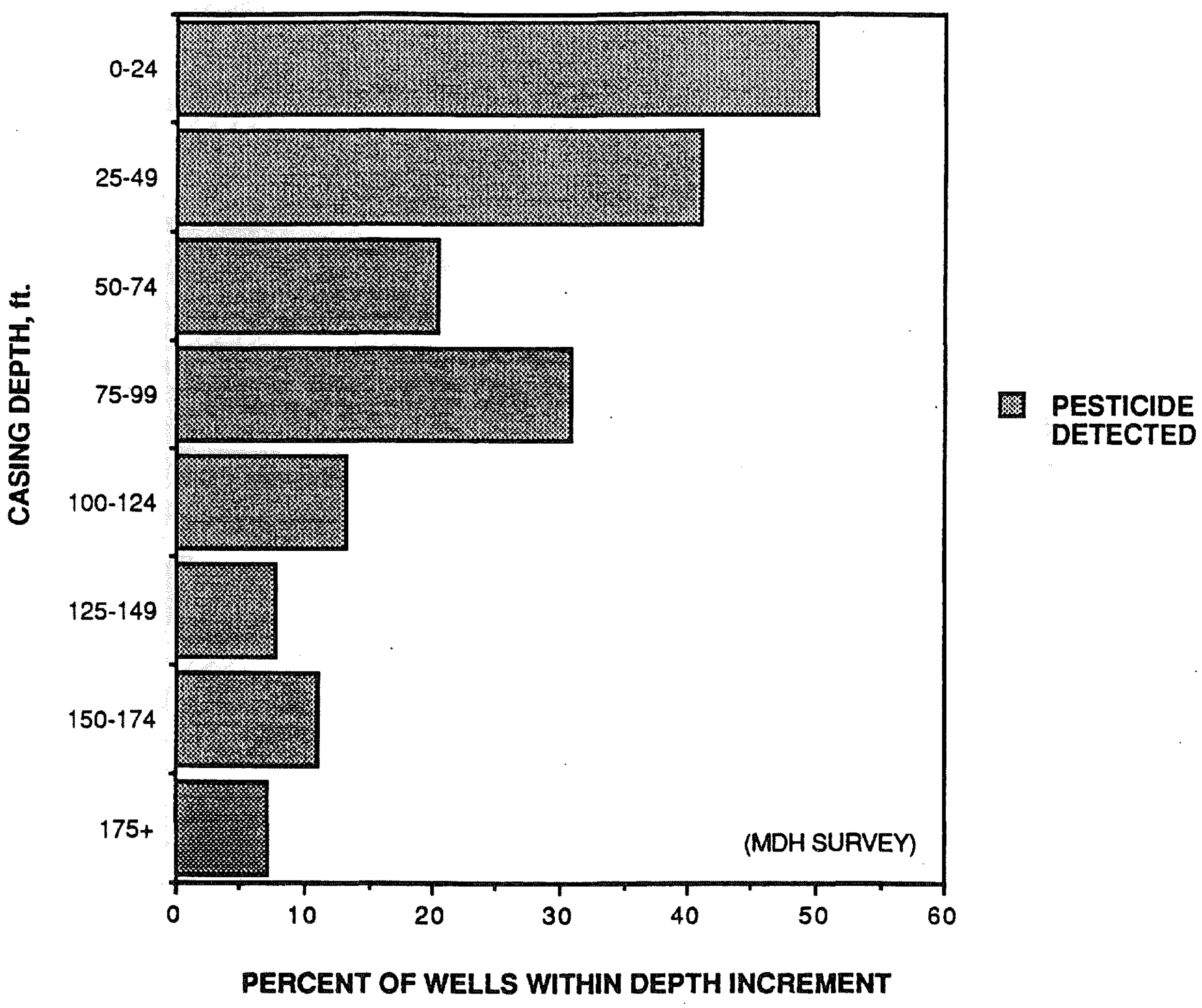


FIGURE 18

ATRAZINE CONCENTRATION VS. CASING DEPTH PUBLIC WELLS IN UNCONSOLIDATED AQUIFERS

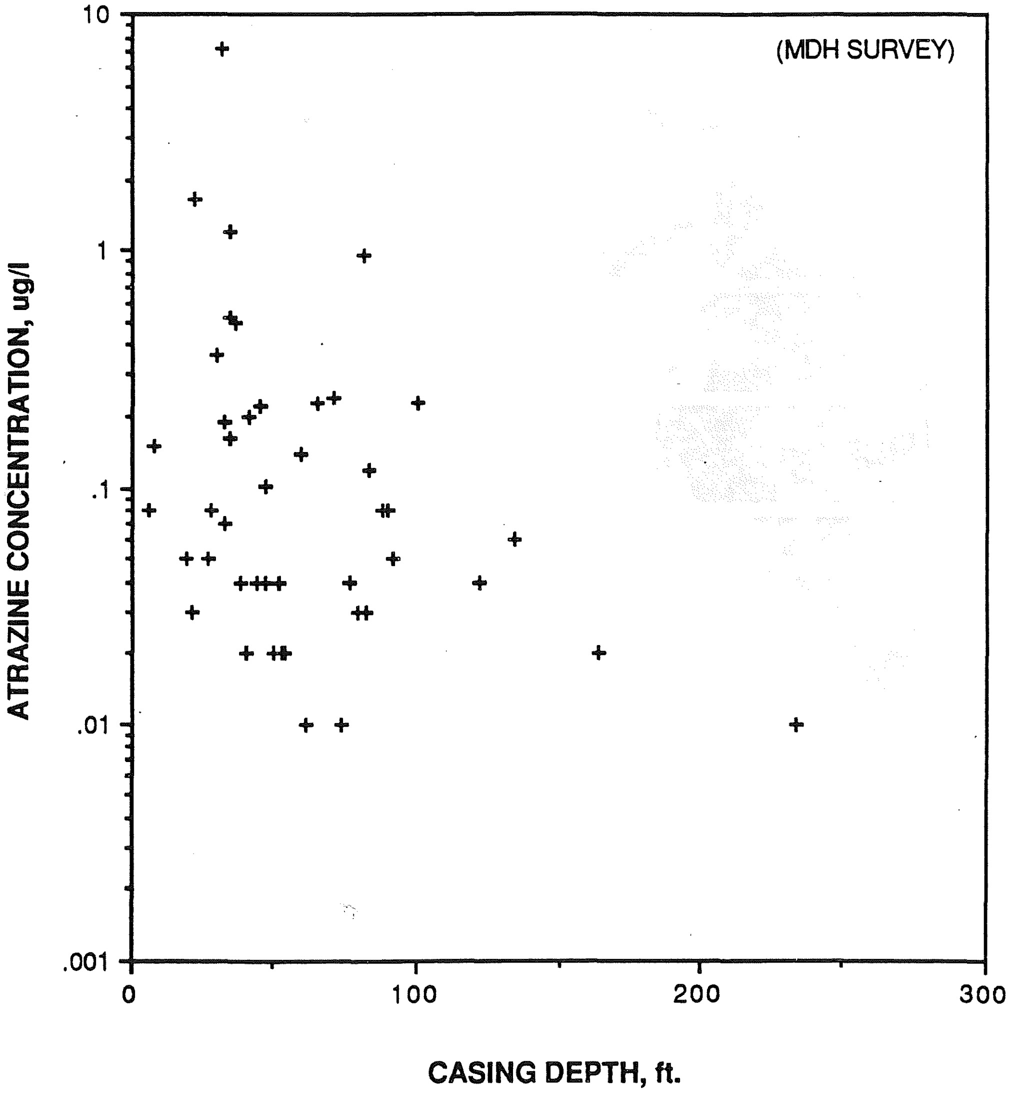


FIGURE 19

PESTICIDE OCCURRENCE VS. DEPTH TO BEDROCK PUBLIC WELLS IN SEDIMENTARY BEDROCK AQUIFERS

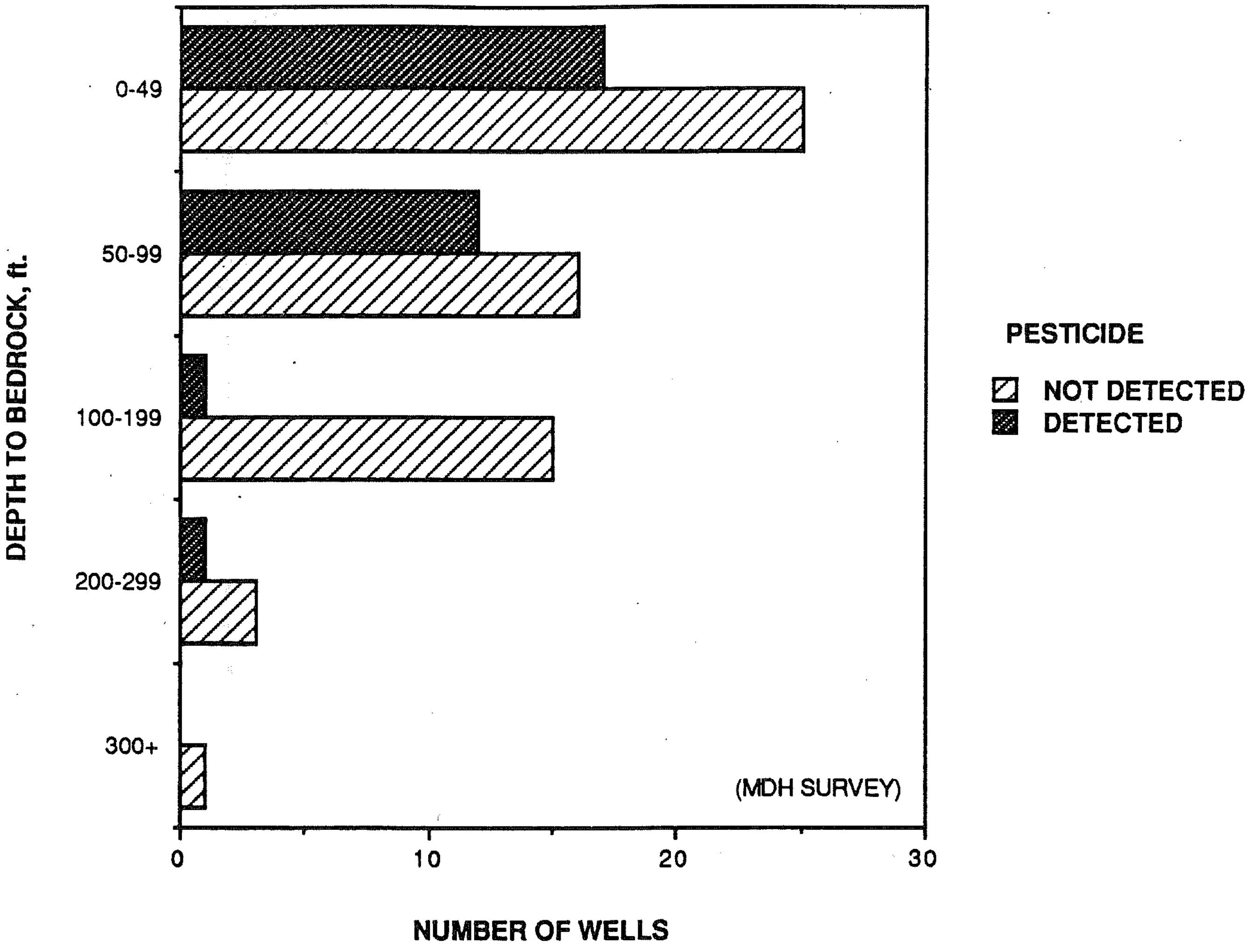
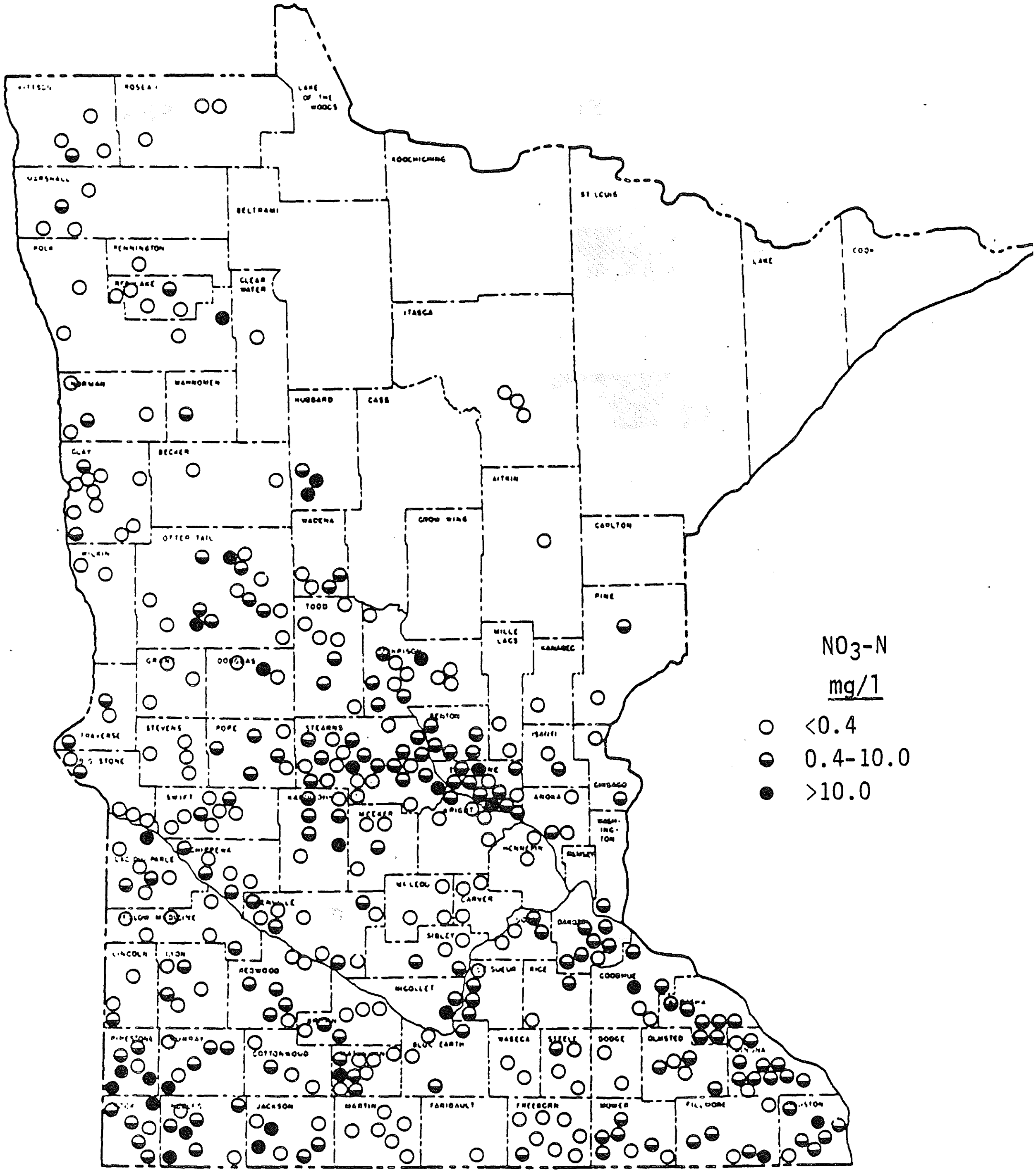


FIGURE 20
OCCURRENCE OF NITRATES
PUBLIC WELLS, MDH SURVEY



Minnesota Department of Health

FIGURE 21

ATRAZINE CONCENTRATION VS. NITRATE CONCENTRATION PUBLIC WELLS

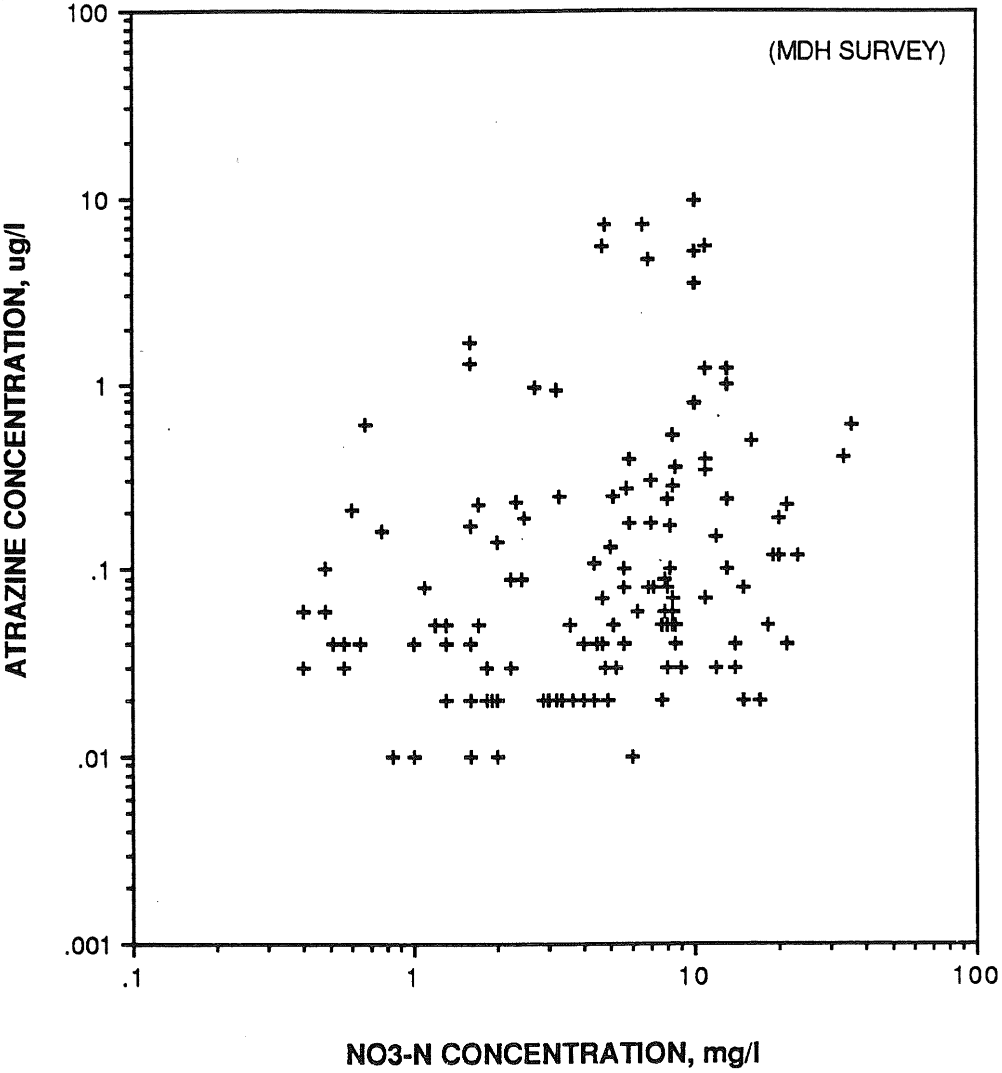


TABLE 1
PESTICIDE ANALYTES
MDA SURVEY

Pesticide	Analytical Method	Reporting Limit (µg/l)	Recommended Allowable Limit (µg/l)
Herbicides			
Alachlor	BN	0.16	6.
Atrazine	BN	0.05	3.
Butylate	BN*	0.79	50.
Chloramben	ACID	1.60	105.
Cyanazine	BN	0.12	9.
Dicamba	ACID	0.18	9.
EPTC	BN*	0.24	35.
Linuron	BN	0.17	44.
MCPA	ACID	0.27	3.6
Metolachlor	BN	0.56	10.
Metribuzin	BN	0.17	175.
Picloram	ACID	1.80	490.
Propachlor	BN	0.10	92.
Simazine	BN	0.08	35.
Trifluralin	BN	0.02	2.
2,4-D	ACID	0.21	70.
Insecticides			
Aldicarb	N-M	0.5	9.
Aldicarb Sulfone	N-M	0.5	
Aldicarb Sulfoxide	N-M	0.5	
Carbaryl	N-M	0.5	700.
Carbofuran	N-M	0.5	36.
3-OH Carbofuran	N-M	0.5	
Chlorpyrifos	BN	0.24	21.
Disulfoton	BN	0.82	0.3
Fonofos	BN	0.16	14.
Methyl Parathion	BN	0.10	2.
Phorate	BN	0.49	0.7
Phosphamidon	BN	0.70	-
Fungicide			
Pentachlorophenol	BN	0.28	220

BN: Base neutral extraction with electron capture and nitrogen-phosphorus detection
ACID: Chlorinated acid herbicide procedure
N-M: N-methylcarbamate pesticide procedure
*: No response with electron capture detection

TABLE 2

PESTICIDE ANALYTES
PUBLIC WELLS, MDH SURVEY

Pesticide	Analytical Method	Reporting Limit (µg/l)	Recommended Allowable Limit (µg/l)
Herbicides			
Alachlor	BN-ECD	0.05	6.
Atrazine	BN-NPD	0.01	3.
Butylate*	BN-NPD	0.01	50.
Chloramben	ACID	0.05	105.
Cyanazine	BN-ECD	0.5	9.
Diallate	BN-ECD	0.12	10.
Dicamba	ACID	0.04	9.
EPTC*	BN-NPD	0.01	35.
Linuron	BN-ECD	0.4	44.
MCPA	ACID	0.05	3.6
Metolachlor	BN-ECD	0.13	10.
Metribuzin	BN-ECD	0.02	175.
Picloram	ACID	0.04	490.
Propachlor	BN-ECD	0.2	92.
Simazine	BN-ECD	0.3	35.
Trifluralin	BN-ECD	0.03	2.
2,4-D	ACID	0.04	70.
2,4,5-T	ACID	0.04	21.
2,4,5-TP	ACID	0.05	10.
Insecticides			
Aldicarb	MDA	0.5	9.
Carbaryl*	BN-NPD	0.05	700.
Carbofuran*	BN-NPD	0.05	36.
Chlorpyrifos	BN-ECD	0.05	21.
Dimethoate	BN-ECD	0.2	140.
Disulfoton	BN-ECD	0.45	0.3
Fonofos	BN-ECD	0.03	14.
Methyl Parathion	BN-ECD	0.02	2.
Phorate	BN-ECD	0.10	0.7
Terbufos	BN-ECD	0.2	0.18
Fungicide			
PCNB	BN-ECD	0.02	49.

BN-ECD: Base neutral extraction with electron capture detection
BN-NPD: Base neutral extraction with nitrogen-phosphorus detection
ACID: Chlorinated acid herbicide procedure
MDA: Analysis performed for MDH by MDA
*: Confirmatory analytical method not available until September 12, 1986

TABLE 3

OCCURRENCE OF PESTICIDES
MDA SURVEY

Pesticide	Wells with Detections*	Samples with Detections	Median (μg/l)	Range (μg/l)
Atrazine	47	112	0.38	0.01-42.4
Alachlor	8	9	0.37	0.16- 2.81
Metribuzin	4	4	0.41	0.12- 0.78
Cyanazine	3	3	0.22	0.18- 2.90
Simazine	1	4	1.40	0.49- 2.58
Dicamba	1	4	0.66	0.53- 0.86
Aldicarb	2	5	9.0	0.50-30.6
Pentachlorophenol	3	3	0.58	0.42- 0.64

*One or more pesticides were detected in 51 (51%) of 100 sampled wells.

TABLE 4

SUMMARY OF WELL-SITE INFORMATION FROM NORTHWESTERN MINNESOTA MDA SURVEY

Counties (wells):	Kittson (1), Marshall (2), Norman (1), Traverse (2), and Wilkin (2)
Geomorphic Regions: (wells)	Agassiz Lacustrine Plain, Red River Valley (8)
Soils:	Fargo, Hegne, Rolliss, Valler, and Beardon
General Description:	Intense small grain agriculture on poorly drained, high clay and organic matter soils
Pesticides Used:	2,4-D, MCPA, triallate, bromoxynil and trifluralin
Crops:	Small grain, soybeans, and sugar beets
Well Depth:	Median 23 ft.; Range 10-43 ft.
Water Table:	Median 5 ft.; Range 3-8 ft.
Pesticides Detected:	None

TABLE 5

SUMMARY OF WELL-SITE INFORMATION FROM SOUTHWESTERN AND SOUTH CENTRAL MINNESOTA MDA SURVEY

Counties (wells):	Big Stone (1), Brown (1), Chippewa (2), Cottonwood (1), Murray (1), Pipestone (2), Redwood (3), Rock (1), Swift (3), and Watonwan (2)
Geomorphic Regions: (wells)	Appleton-Clontarf Outwash Plain (6), Blue Earth Till Plain (6), Minnesota Outwash Plain (1), Southwestern Coteau (4)
Soils:	Maddock, Esterville, Darfur, Estelline, and Barnes
General Description:	Intensive corn and soybean dryland farming on loamy-textured, high organic matter soils; some local regions of irrigated corn production
Pesticides Used:	Trifluralin, 2,4-D, cyanazine, alachlor and dicamba
Crops:	Corn and soybeans
Well Depth:	Median 19.0 ft.; Range 8-45 ft.
Water Table:	Median 10.0 ft.; Range 5-20 ft.
Pesticides Detected:	Atrazine, pentachlorophenol

TABLE 6

SUMMARY OF WELL-SITE INFORMATION FROM SOUTHEASTERN MINNESOTA MDA SURVEY

Counties (wells): Dakota (4), Mower (3), Olmsted (4), Winona (10)

Geomorphic Regions: Cannon Valley Outwash (2), Mississippi Valley Outwash (2), Harmony Plainview Uplands (10), Claremount-Lyle Plains (3), Rochester Drift Plain (1), Red Wing-LaCrescent Uplands (3)

Soils: Mt. Carroll, Port Byron, Ostrander, Kasson, Hubbard

Pesticides Used: Atrazine, alachlor, cyanazine, 2,4-D, dicamba

Crops: Corn, soybeans, alfalfa

Pesticides Detected: Atrazine, alachlor, dicamba, cyanazine

TABLE 7

OCCURRENCE OF PESTICIDES
SOUTHEASTERN MINNESOTA
MDA SURVEY

Pesticide Name	Wells with Detections	Samples with Detections	Median (µg/l)	Range (µg/l)
Atrazine	13	35	0.32	0.05-7.18
Alachlor	2	2	0.21	0.19-0.23
Cyanazine	1	1	0.18	N.A.
Dicamba	1	4	0.67	0.53-0.86

TABLE 8

SUMMARY OF WELL-SITE INFORMATION FROM CENTRAL MINNESOTA MDA SURVEY

Counties (wells):	Becker (2), Douglas (1), Hubbard (4), Wadena (2), Benton (3), Morrison (3), Grant (1), Isanti (3), Kandiyohi (2), Pope (8), Stearns (5), Meeker (1), Sherburne (12), Stevens (2), Todd (1), Otter Tail (4)
Geomorphic Regions: (wells)	Anoka Sand Plain (3), Alexandria Moraine Complex (1), Belgrade-Glenwood Outwash Plain (13), Big Stone Moraine (1), Crow Wing Outwash Plain (5), Detroit Lakes Outwash Plain (1), Mississippi Outwash Plain (13), Osakis Till Plain (2), Park Rapids-Staples Outwash Plain (12), St. Croix Moraine (1)
Soils:	Hubbard, Esterville, Dorset, Sioux
General Description:	Corn, soybean and potato production on coarse-textured low organic matter soils frequently associated with irrigation
Pesticides Used:	Atrazine, alachlor, trifluralin, metolachlor, 2,4-D, dicamba, aldicarb, terbufos, carbaryl, metribuzin, cyanazine
Crops:	Corn, soybeans, potatoes, small grains
Well Depth:	Median 22.9 ft.; Range 7-60 ft.
Water Table:	Median 11.9 ft.; Range 2-42 ft.

TABLE 9

OCCURRENCE OF PESTICIDES
CENTRAL MINNESOTA
MDA SURVEY

Pesticide	Wells with Detections	Samples with Detections	Median (μg/l)	Range (μg/l)
Atrazine	30	74	0.38	0.01-42.4
Alachlor	6	7	0.39	0.16- 2.81
Aldicarb	2	5	9.0	0.50-30.6
Metribuzin	4	4	0.41	0.12- 0.78
Simazine	1	4	1.40	0.49- 2.58
Pentachlorophenol	2	2	0.53	0.42- 0.64
Cyanazine	1	1	0.22	N.A.

TABLE 10

SUMMARY OF WELL-SITE INFORMATION FROM ADJACENT WELLS MDA SURVEY

Counties:	Sherburne (4), Stearns (2), Isanti (1), and Kandiyohi (1)
Soil:	Hubbard, Zimmerman, Sverdrup
General Description:	Coarse-textured soils and subsoils, often with irrigation nearby
Shallow Well Depth:	Mean 17.1 ft.; Range 10-23 ft.
Deep Well Depth:	Mean 28.0 ft., Range 22-37 ft.
Shallow Water Table Depth:	Mean 5.8 ft.; Range 2-9 ft.
Deep Water Table Depth:	Mean 16.7 ft.; Range 12-20 ft.

TABLE 11

SOIL TYPE AND FREQUENCY OF PESTICIDE USE
TILE LINE SAMPLING SITES
MDA PESTICIDE SURVEY

Site Location	Tile Line	Soil Type	Pesticide Use (years)**
Morris	1	Nutley clay	Alachlor (2) Cyanazine (2) EPTC (1) MCPA (1)* Terbufos (1) Carbofuran (1)*
Morris	2	Nutley clay Hammerly loam Barnes loam	Alachlor (3) Cyanazine (3) Glyphosate (1)* MCPA (1)* Terbufos (1) Carbofuran (1)
Lamberton	1	Webster loam	Alachlor (5) Cyanazine (9) EPTC (3) Propachlor (4) Carbofuran (8)* Terbufos (5)
Waseca	1	Webster clay loam	Alachlor (12) Atrazine (10) Cyanazine (2) Dicamba (1)* Propachlor (1) Carbofuran (8)* Isofenphos (1)* Terbufos (4)
Waseca	2	Webster clay loam	Same as Waseca No. 1 plus 2,4-D (1)*

*N-methylcarbamate and acid herbicide analysis not conducted.

**Pesticide use information for 3, 13, and 13 years for Morris, Lamberton and Waseca, respectively.

TABLE 12

OCCURRENCE OF PESTICIDES PUBLIC WELLS, MDH SURVEY

Pesticide	Wells with Detections*	Samples with Detections	Median (µg/l)	Range (µg/l)
Atrazine	107	177	0.06	0.01-9.70
Alachlor	8	14	0.44	0.07-4.03
2,4-D	7	12	0.22	0.07-5.70
Dicamba	3	6	0.10	0.05-0.21
Picloram	3	5	0.16	0.08-0.63
MCPA	2	4	0.26	0.13-2.20
Metribuzin	2	3	0.23	0.10-1.05
Metolachlor	2	2	0.42	0.30-0.55
Propachlor	2	2	0.35	0.20-0.50
Cyanazine	1	1	0.80	N.A.
EPTC	1	1	0.33	N.A.
2,4,5-T	1	1	0.21	N.A.

*One or more pesticides were detected in 114 (28.5%) of 400 sampled wells.

TABLE 13

EFFECT OF CASING DEPTH ON PESTICIDE OCCURRENCE
PUBLIC WELLS IN UNCONSOLIDATED AQUIFERS
MDH SURVEY

Result	Number of Wells	Casing Depth (ft.)	
		Median	Range
Pesticide Not Detected	133	72	16-380
Pesticide Detected	46	48	6-233

TABLE 14

EFFECT OF CASING DEPTH ON PESTICIDE OCCURRENCE
PUBLIC WELLS IN SEDIMENTARY BEDROCK
MDH SURVEY

Results	Number of Wells	Casing Depth (ft.)	
		Median	Range
Pesticide Not Detected	48	160	52-528
Pesticide Detected	25	185	40-455

TABLE 15

PESTICIDE OCCURRENCE IN SELECTED SEDIMENTARY BEDROCK FORMATIONS
PUBLIC WELLS, MDH SURVEY

	No. of Wells with Depth to First Bedrock:			
	<100 ft.		≥100 ft.	
Formation*	Pesticide Detected	Pesticide Not Detected	Pesticide Detected	Pesticide Not Detected
Cretaceous	0	1	0	3
Cedar Valley (DCVA)	5	3	0	0
DCVA or OMDG	0	2	0	0
Maquoketa-Dubuque-Galena (OMDG)	1	2	0	7
Decorah-Platteville-Glenwood	0	1	0	0
St. Peter (OSTP)	1	0	0	0
OSTP or OPDC	0	1	0	1
Prairie du Chien (OPDC)	6	6	0	0
OPDC or CJDN	5	4	0	0
Jordan (CJDN)	9	12	1	2
Older Cambrian and Precambrian	1	9	1	6

*Well casing terminates in the indicated bedrock formation. Some wells also extend into deeper formations.

TABLE 16

RELATIONSHIP BETWEEN PESTICIDE OCCURRENCE AND NITRATE-NITROGEN CONCENTRATION PUBLIC WELLS, MDH SURVEY

	No. of Wells with NO_3-N Concentration (mg/l):			
	<0.4	$\geq$0.4, <1.0	$\geq$1.0, $\leq$10.0	>10.0
Pesticide Not Detected	176	24	71	11
Pesticide Detected	32	10	54	17
Total	208	34	125	28
Percent with Pesticides Detected	15.4	29.4	43.2	60.7

TABLE 17

OCCURRENCE OF PESTICIDES
ALL WELLS
MDA AND MDH SURVEYS

Pesticide	Wells with Detections*	Median (µg/l)	Range (µg/l)
Atrazine	154	0.12	0.01-42.40
Alachlor	16	0.39	0.07- 4.03
2,4-D	7	0.22	0.07- 5.70
Metribuzin	6	0.32	0.10- 1.05
Dicamba	4	0.17	0.05- 0.86
Cyanazine	4	0.51	0.18- 2.90
Picloram	3	0.16	0.08- 0.63
Pentachlorophenol	3	0.58	0.42- 0.64
Metolachlor	2	0.42	0.30- 0.55
Propachlor	2	0.35	0.20- 0.50
MCPA	2	0.26	0.13- 2.20
Aldicarb	2	9.0	0.50-30.60
Simazine	1	1.40	0.49- 2.58
2,4,5-T	1	0.21	N.A.
EPTC	1	0.33	N.A.

*One or more pesticides were detected in 165 (33%) of 500 sample wells.

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APPENDIX

Herbicides

Alachlor (Lasso) - a widely used, pre-emergence herbicide used to control annual grasses and broadleaf weeds in soybeans and corn. Registered for use in 1969.

Atrazine (Aatrex) - a widely used, pre-emergence herbicide used to control weeds in corn. Registered for use in 1963.

Butylate (Sutan) - a widely used, pre-plant herbicide applied to control grassy weeds in corn. Registered for use in 1967.

Chloramben (Amiben) - a widely used, pre-emergence herbicide used to control weeds in soybeans. Registered for use in 1960.

Cyanazine (Bladex) - a widely used, pre- and post-emergence herbicide used for control of annual grasses and broadleaf weeds in corn. Registered for use in 1971. Restricted use classification.

Diallate (Avadex) - a pre-emergence herbicide used in corn, soybeans and sugar beets. Registered for use in 1963. Restricted use classification.

Dicamba (Banvel) - a widely used post-emergence herbicide used to control weeds in corn and small grains and to control brush and vines in non-crop areas. Registered for use in 1967.

2,4-D or (2,4-dichlorophenoxy)acetic acid - a widely used post-emergence herbicide used to control broadleaf weeds in corn, small grains, rangeland, pastures and lawns. Registered for use in 1948.

EPTC or S-ethyl dipropylthiocarbamate (Eptam or Eradicane) - a widely used, selective herbicide used to control annual and perennial grasses in corn and potatoes. Registered for use in 1969.

Linuron (Lorox) - a widely used herbicide used for weed control in corn and soybeans. Registered for use in 1966. Restricted use classification.

MCPA or (4-chloro-o-tolyoxy)acetic acid (Agroxone) - a widely used, post-emergence herbicide used to control annual and perennial broadleaf weeds in small grains, grassland and non-crop areas. Registered for use in 1952.

Metolachlor (Bicep or Dual) - a widely used, pre-plant and pre-emergence herbicide used in corn and soybeans. Registered for use in 1976.

Metribuzin (Lexone or Sencor) - a widely used, broad spectrum herbicide used to control grassy and broadleaf weeds in soybeans. Registered for use in 1973. Restricted use classification.

Picloram (Tordon) - a broad spectrum herbicide used to control broadleaf and woody plants in rangelands, pastures, and rights-of-way. Registered for use in 1963. Restricted use classification.

Propachlor (Bexton or Ramrod) - a widely used, pre-emergence herbicide used to control grasses and broadleaf weeds in corn. Registered for use in 1965.

Simazine (Princep) - a pre-emergence herbicide used to control grasses and broadleaf weeds in corn. Registered for use in 1957.

2,4,5-T or (2,4,5-trichlorophenoxy)acetic acid - a post-emergence herbicide used to control weeds and wood plants on industrial sites and rangeland. All uses have been cancelled.

2,4,5-TP or 2-(2,4,5-trichlorophenoxy)proprionic acid (Silvex) - an herbicide for weed and brush control. All uses have been cancelled.

Trifluralin (Treflan) - a widely used, pre-emergence herbicide used to control annual grasses and broadleaf weeds in soybeans. Registered for use in 1963.

Insecticides

Aldicarb (Temik) - a pesticide applied to soil or plants to control insects, mites or nematodes. Registered for use in 1970. Restricted use classification.

Aldicarb Sulfone - a breakdown product of aldicarb.

Aldicarb Sulfoxide - a breakdown product of aldicarb.

Carbaryl (Sevin) - a widely used, broad spectrum insecticide used on more than 1,000 different crops, trees, bushes and shrubs. Registered for use in 1958.

Carbofuran (Furadan) - a widely used, broad spectrum pesticide used to control insects, nematodes and mites in corn. Registered for use in 1969. Restricted use classification.

3-OH Carbofuran - a breakdown product of carbofuran.

Chlorpyrifos (Lorsban, Dursban or Killmaster II) - a widely used, soil insecticide used to control corn rootworms and cutworms in corn. Registered for use in 1965. Restricted use of Killmaster II.

Dimethoate (Cygon) - a systemic insecticide/acaricide used to control a wide variety of insects and mites in farm buildings, corn, soybeans and vegetables. Registered for use in 1963. All dust formulations cancelled.

Disulfoton (Disyston) - a systemic insecticide/acaricide used to control many species of insects and mites. Registered for use in 1958. Restricted use classification.

Fonofos (Dyfonate) - a widely used, pre-emergence insecticide used to control corn rootworm, wireworms, and cutworms. Registered for use in 1967. Restricted use classification.

Methyl Parathion (Metron) - a pesticide used for control of various insects. Registered for use in 1954. Restricted use classification.

Phorate (Thimet) - a widely used, soil and systemic insecticide used to control a wide range of insects in corn, soybeans and other crops. Registered for use in 1959. Restricted use classification.

Phosphamidon (Dimecron) - a systemic insecticide used against sucking insects and aphids in a variety of crops. Restricted use classification.

Terbufos (Counter) - a widely used, pre-emergence pesticide used to control rootworms, insects and nematodes in corn. Registered for use in 1974. Restricted use classification.

Fungicides

PCP or Pentachlorophenol - a wood preservative used to protect for fungus decay and termite attack. Cancelled for non-wood uses. All other uses restricted.

PCNB or Pentachloronitrobenzene - a soil fungicide and seed dressing agent used for a variety of specialty crops and lawns. Registered for use in 1954.