AGRICULTURAL IMPACT ON WATER QUALITY IN A SHALLOW CONFINED AQUIFER AND IN THE OVERLYING SATURATED GLACIAL TILL IN EASTERN NORTH DAKOTA: MOVEMENT OF PESTICIDES

By

Principal Authors

W.M. Schuh — North Dakota State Water Commission, Bismarck ND
D.L. Klinkebiel — Carrington Research Extension Center, Carrington ND
R.F. Meyer — Colorado Extension Service, Burlington CO

Contributing Authors

M.D. Sweeney — Soil Science Dept., North Dakota State University, Fargo ND
J.C. Gardner — Carrington Research Extension Center, Carrington ND
A.R. Wanek — North Dakota State Water Commission, Bismarck ND

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EXECUTIVE SUMMARY

The results of the pesticide movement portion of the Carrington RECHARGE experiment conducted from 1988 through the spring of 1993 are summarized in this Executive Summary. These conclusions are related to, and dependent on, results of complementary hydrologic and tracer analyses also performed on the Carrington site. The reader is referred to the Executive Summary of Schuh et al. (1994a) for conclusions of the hydrologic and tracer portions of the experiment.

Pesticides were detected at all sampled levels of the vadose zone, saturated till, and the surface of the Carrington aquifer in dilute quantities.

1. There were three major periods of pesticide influx. One was in July of 1989. One was in July of 1990. The other was in October of 1992. During most other periods of the experiment detections were sporadic, and most frequently not repeated at the same depth on the experiment site.

2. Times of pesticide detection usually corresponded to independent hydrologic evidence of recharge to the saturated till and to the Carrington aquifer, and to tracer peaks.

3. No pesticide detections were made in samples taken during the drought year of 1988. Hydrologic analysis indicated that there was little water movement through the root zone in that year, and that drainage waters were caused by capillary response to the receding water table, rather than to surface source influx. Also, micro-extraction procedures were used which increased detection levels.

4. The largest number of pesticide detections was in 1989. It is likely that dry conditions in 1988 impeded pesticide movement and degradation, and that early rains in 1989 caused movement and subsequent detection of pesticides in ground water.

5. Agricultural practices and rotations least susceptible to pesticide movement in recharge water on the Carrington site would likely be those which prevent runoff and concentration of water in microtopographic low areas. Such practices would include those offering earlier and denser stem and leaf canopies, and those enhancing random surface roughness and residue cover. Also, crops with earlier canopy growth, and earlier root proliferation and soil-water use would be expected to more effectively prevent movement of water below the root zone during spring and early summer periods characterized by higher probabilities of rainfall.

6. Pesticide detections were less for years in which wheat was planted, than for years in which soybeans and sunflowers were planted.

7. Most pesticide concentrations detected were below levels of toxicologic concern under current standards.

8. Pesticide detections were ephemeral and limited to brief recharge periods.

9. There is no evidence of pesticide accumulation in the Carrington aquifer or in the saturated till beneath the experiment site..

10. General pesticide screenings in road ditches and drainageways several hundred feet northwest and southeast of the experiment plot, indicated no detections of any pesticides during the entire period of the experiment.

In summary, recharge to the saturated till at 2.5 to 4.0 m (8 to13 ft.), and to the Carrington aquifer underlying the till at about 6.8 m (22 ft.), is highly complex, and includes concentrated flow caused by surface runoff and concentration of water in microtopographic low areas. Water cycling through the soil and vadose zone also includes waters recharged to the water table at other more active surface recharge sites. This water redistributes laterally at the water table, and then moves upward into neighboring sites under force of capillarity. Recharge is also strongly influenced by enhanced hydraulic gradients caused by pumping of the aquifer. Both tracers and pesticides move in recharge waters to virtually all depths, with tracer concentrations and pesticide detections usually corresponding to the hydrologic evidence of water movement. Except for one year (which followed a drought year), pesticide concentrations were usually sporadic and poorly replicated at depth and between depths. Almost all detected pesticide concentrations were below levels of current toxicologic concern.

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INTRODUCTION

In the fall of 1987 an experiment was initiated on the lands of the Carrington Research Extension Center Station, in Foster County North Dakota (Figure 1), to investigate the relationship between ground-water recharge and the movement of contaminants on a level agricultural field, using common cropping practices for East Central North Dakota. Five years of monitoring were undertaken between the spring of 1988 and the spring of 1993. Components of the experiment included (1) year-round water-level monitoring of the Carrington aquifer and of the overlying saturated till; (2) root- and vadose-zone water balance measurements during the frozen period of the year; (3) local root-zone and vadose-zone water balance and drainage determinations during the non frozen portion of the year; (4) monitoring for changes in basic water quality constituents; (5) tracking the movement of surface applied tracers in relation to movement of recharge waters; and (6) tracking the movement of applied pesticides. Results of hydrologic analysis and tracer movement have been reported by Schuh et al. (1994a). The purpose of this report is to present pesticide detection data, and to discuss the results of pesticide sampling in relation to local hydrology and tracer movement.

ACKNOWLEDGMENTS

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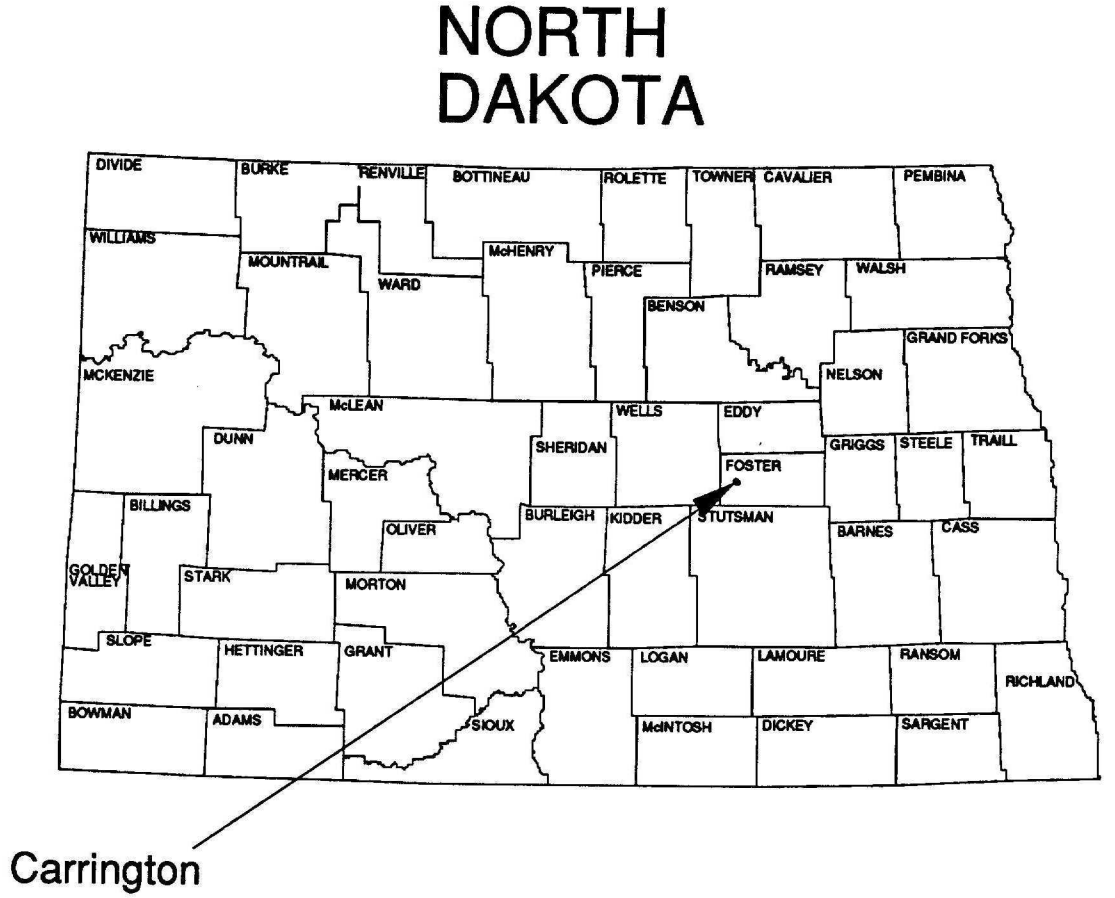

Figure 1. Map of experiment location.

LOCATION AND NUMBERING SYSTEM

The location and numbering system used in this report is based on the public land classification system used by the U.S. Bureau of Land Management. The system is illustrated in Figure 2. The first number denotes the township north of a base line, the second number denotes the range west of the fifth principal meridian, and the third number denotes the section in which the well or test hole is located. The letters A, B, C, and D designate, respectively, the northeast, northwest, southwest, and southeast quarter section, quarter-quarter section, and quarter-quarter-quarter section (10-acre tract). For example, well 147-067-4ADD is located in the SE 1/4 SE 1/4 NE 1/4 sec. 4, T. 147 N., R. 67 W. Consecutive terminal numerals are added if more than one well or test hole is located within a 10 acre tract.

CLIMATE

The climate of Foster County North Dakota is continental, having cold winters and hot summers. The onset of cold weather usually begins in early November. The frost usually leaves the soil in mid April. The moisture regime is borderline between semi-arid and sub-humid, with a long-term average annual precipitation of about 48 cm (19 inches).

GEOLOGY AND SURFACE DRAINAGE FEATURES

The landscape near Carrington ND was formed by the deposition of approximately 30 m (100 ft.) of glacial drift in late Wisconsonian time, on top of bedrock shale of the Cretacious Pierre formation (Bluemle 1965, Wanek and Meyer 1989). The Carrington aquifer (Figure 3) was formed by the deposition and elutriation of sand and gravel between a bedrock ridge oriented northwest to southeast near Carrington and a glacial boundary of similar orientation north of Carrington. The Carrington aquifer was later covered with about 12.3 m (40 ft.) of glacial till in a later (Grace City Phase) ice advance. Overall till particle-size distribution (excluding fractions coarser than sand) is about 33-percent sand, 45-percent silt, and 22-percent clay. However, the till is extremely heterogeneous, and frequently includes sand and gravel varves and lenses imbedded within masses of predominantly finer materials.

Land surface in Foster County near Carrington is a low relief type, having semi-integrated drainage, and formed in glacial ground moraine along a corridor between the Missouri Coteau and an

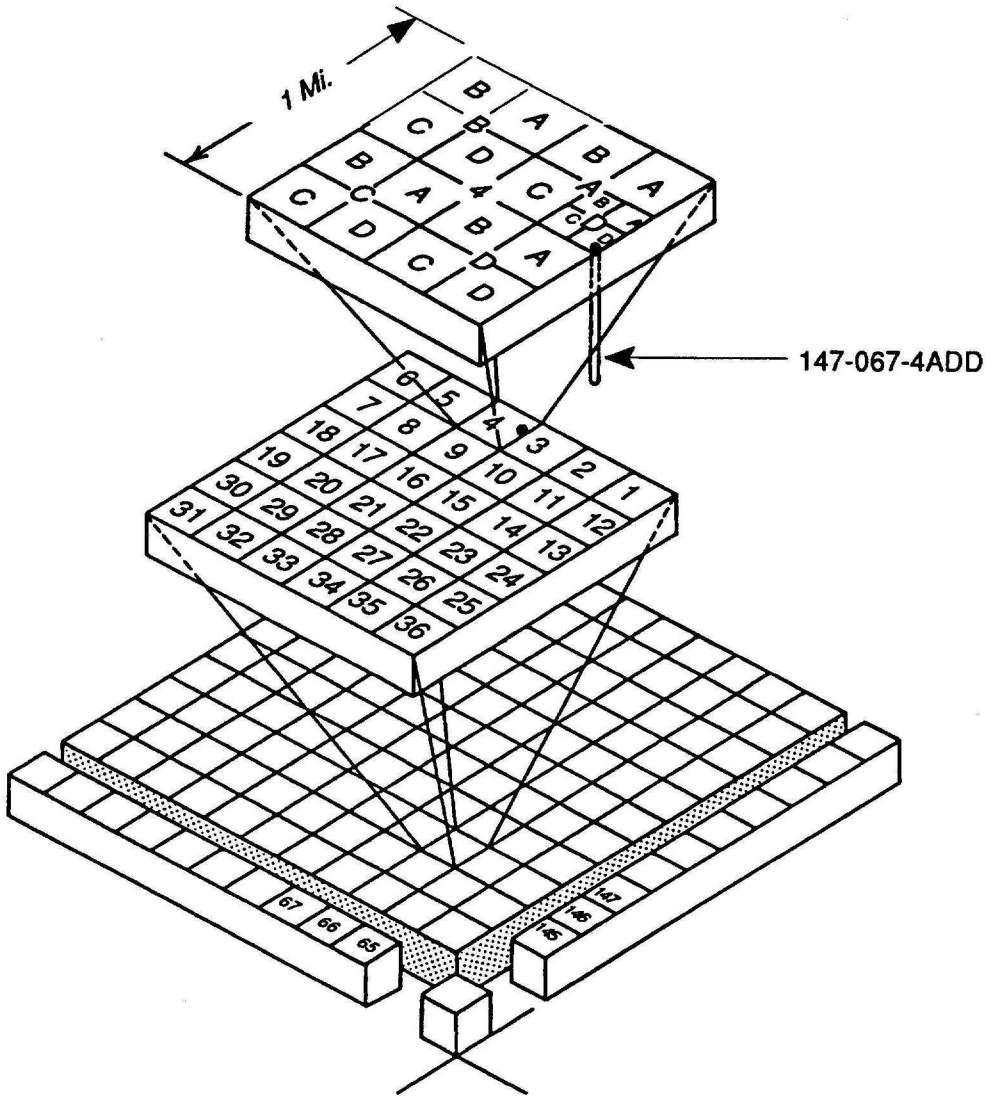

Figure 2. Map location and numbering system used in this report (from U.S. Bureau of Land Management).;

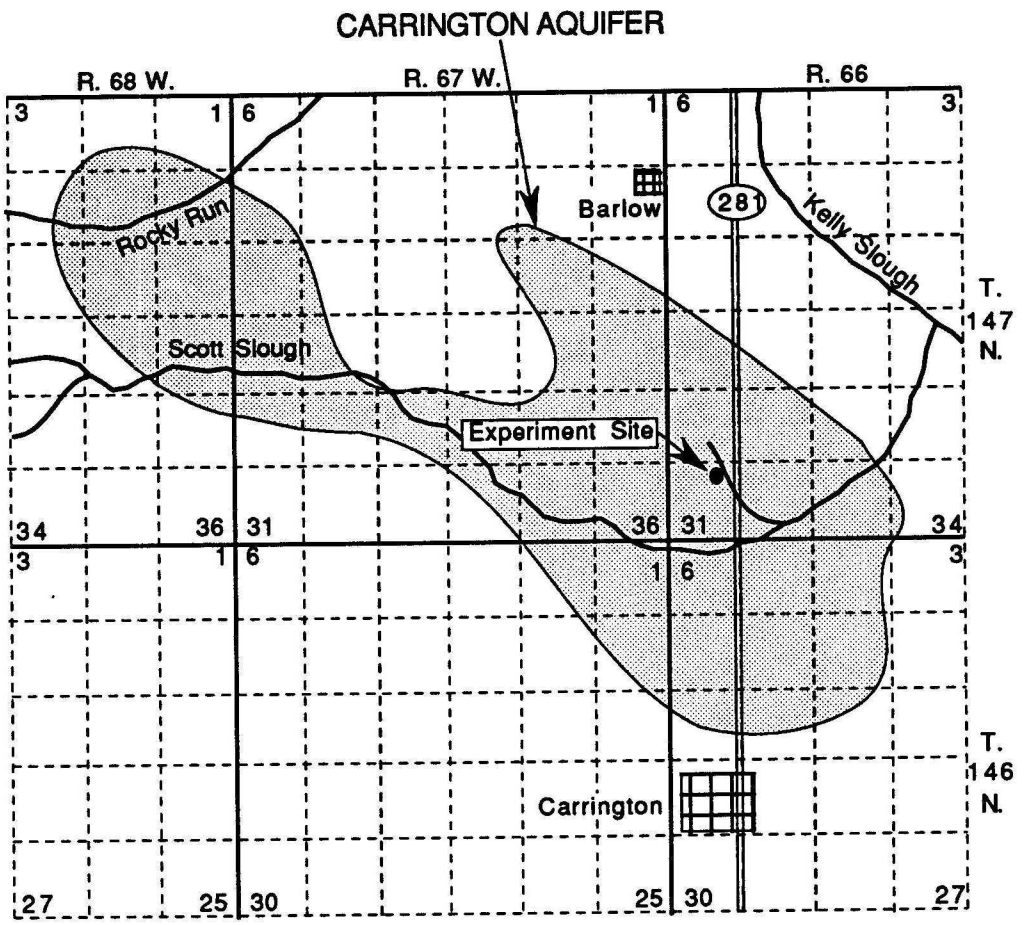

Figure 3. Map illustration of the Carrington aquifer.

older relic coteau to the east. It is thus somewhat atypical of the prairie pothole topography common to the region. Surface topography generally slopes east at 3 m (10 ft.) per mile. Scotts Slough, a glacial-marginal surface drainage feature cuts a channel about 7.6-m (25-ft.) deep and 213-m (700-ft.) wide through glacial till overlying the aquifer. Despite its name designation as a slough, it is actually an underfit stream valley, and functions hydrologically as both a creek and a slough. Rocky Run, a similar feature, cuts across the northwest end of the aquifer. Kelly Slough, a broad channel located about two miles northeast of the Carrington aquifer, is a third surface drainage feature related to both Scotts Slough and Rocky Run (Figure 3.)

HYDROLOGY

The Carrington aquifer is a buried sand and gravel deposit approximately 19.3-km (12-miles) long, 6.4-km (4-miles) wide, and 9- to 18-m (30- to 60-ft.) thick. Its long axis is oriented northwest to southeast. The aquifer is unconfined along its southwest flank, but otherwise confined with an artesian head of up to 9-m (30-ft.) above the top of the aquifer. Although confined, pumping can draw down the aquifer water level creating an unconfined zone around the well. An irregular till/aquifer interface results in localized confined/unconfined areas. A 97-h aquifer test performed using an irrigation well one half mile southwest of the Carrington experiment site indicates an aquifer transmissivity of 1,486 m^2 (16,000 $ft.^2$) per day and a storativity of 0.03. The sand and gravel is 12-m (40-ft.) thick at the aquifer test site, so the hydraulic conductivity is 120-m (400-ft.) per day.

In addition to domestic and livestock use, permitted water use from the Carrington aquifer is approximately 2,570 cubic decameters (2,090 acre-ft.) per year, including 400 cubic decameters (325 acre ft.) used as the municipal supply by the City of Carrington, and the remainder used for irrigation on 19 quarter sections in 1992.

The potentiometric surface of the Carrington aquifer indicates an overall flow direction toward the east. However, localized flow gradients indicate possible discharge points along Rocky Run and Scotts Slough. Wanek and Meyer (1989) have hypothesized that most recharge to the Carrington aquifer is from precipitation. For most of the aquifer, waters have to pass through about 9 m (30 ft.) of till after infiltration before reaching the aquifer. However, in some cases Scotts Slough cuts through the till and provides a direct hydraulic connection from the surface to the aquifer. There are also areas of lesser till thickness where recharge from surface infiltration may be enhanced. Sand- and gravel-filled fractures in the till may help to enhance the rate of recharge in some areas. According to Wanek and Meyer (1989) only a small amount of water in the Carrington aquifer is lost to evapotranspiration, and this likely occurs in the area occupied by Scotts Slough.

WATER QUALITY

Water from the Carrington aquifer is of the calcium-magnesium bicarbonate type. Total dissolved solids concentration (TDS) varies between 400 and 800 mg/L, and the sodium adsorption ratio (SAR) is generally less than 2. The water is hard (7.0 to 10.5 grains per gallon) and high in iron (0.3 to 5 mg/L, usually around 1 mg/L) for domestic use. Organic compounds are rarely detected. Waters near the periphery of the aquifer are sometimes higher in TDS (up to 1,200 mg/L), and some waters near to or in contact with the Pierre Formation have high sodium and chloride concentrations and TDS concentrations as high as 2,420 mg/L (Wanek and Meyer 1989).

PESTICIDE IN GROUND WATER IN NORTH DAKOTA

Non point source pesticide contamination of ground water in the United States and Canada varies greatly with climate, local conditions and land and water use practices. A recent ranking of states for pesticide leaching vulnerabiliy ranked North Dakota 37th (Kellogg et al. 1994). The percent of North Dakota crop land in the high risk category (1 percent) was the lowest of the lower 48 continental states; and the percent of North Dakota crop land in the lowest risk category (52 percent) was fourth highest, exceeded only by South Dakota, Texas, and Arkansas. General conclusions of Kellogg et al. (1994) were that the highest risk was in the mid west, and southeast coastal plain states. Irrigated land in the west was also cited as high risk for pesticide leaching. In addition to leaching potential, aquifer characteristics must be considered. These include depth to ground water, confined or unconfined status of aquifers, depth of buried aquifer systems and the nature of overlying materials, aquifer size, aquifer flow rates, location and nature of recharge sites, and the amount, timing, and location of water withdrawal from the aquifer.

In order to meet monitoring requirements of the U.S. Environmental Protection Agency (USEPA) and state legislative mandates, many states have been conducting surveys to evaluate the overall status of pesticide contamination. Examples of some results are as follows. 1. California is ranked 20 th on the Kellogg leaching potential list. 42.8 percent of California crop land is listed as high risk, and only 28.2 percent is listed as low risk. However, most land in California is not used for agriculture, and land that is in crop production is used for high value irrigated crops. Between 1986 and 1992, 5.4% of 17,713 California wells sampled and tested were reported to have confirmed detections of at least one pesticide. The pesticide most commonly detected was simazine, followed by diuron and atrazine. Of 273 compounds tested 68 were detected at least once (Maes et al., 1992). Of 2,324 additional wells sampled in 46 counties in 1993, about 3% were reported to have detections of at least one pesticide. Most wells sampled were from public supplies, and 2 percent of these had detections (Maes et al., 1992). Private wells had about 9% detections, and 31 percent of irrigation and industrial production wells were found to have detections. However, there were only 35 production wells sampled. All detections reported were below U.S. Environmental Protection Agency (EPA) maximum contaminant level (MCL - where applicable) or health advisory levels (HAL - where MCL is not available). In Washington, a pilot survey of 81 wells known to be highly susceptible to contamination resulted in 23 wells with at least one of 46 pesticides tested detected. Washington is ranked 30th in overall leaching vulnerability on the Kellogg index.

In Canada, Miller et al (1992) have reported that dicamba, 2,4-D, mecoprop, MCPA, diclofop-methyl, and bromoxynil were all detected repeatedly in wells sampled near Tabor, Alberta. Replications of detections per sampling varied from as little as 6% for diclofop-methyl to as much as

94% for 2,4-D. 2,4-D was the most commonly detected herbicide. However, all detections reported were below EPA-MCL . An Ontario well survey cited in the Canadian Water Quality Guidelines for trifluralin (Kent et al. 1992) has indicated that trifluralin is seldom detected in wells, and that a single relatively large detection of trifluralin occurred at a well site used for mixing chemicals (indicating a likely point source).

Minnesota, which borders North Dakota on the east, is ranked 27 on the Kellogg index, and has 22.3 percent of crop land in the high risk category, and 33.7 percent in the low risk category. A survey of pesticides in 500 Minnesota wells found detections in 33 percent of the wells sampled (Klasius et al. 1988). The most common detected pesticide was atrazine (31% of wells tested), and the second most common was alachlor. Only ten of the wells (0.5%) were above Minnesota RAL (recommended allowable limits). Of these wells, five were monitoring wells, one was a private well, and four were public water supplies. Most detections were in vulnerable areas, such as Karst and outwash plains with shallow unconfined aquifers. A survey of 18 wells sampled in the Anoka Sand Plains resulted in detections of atrazine in 11 wells. Few detections were made in South Central or Northwestern Minnesota, where the predominant soils are of fine glacial till or lacustrine origin (Klasius et al. 1988).

Other States bordering North Dakota are ranked by the Kellogg index as having low vulnerabillity to pesticide leaching (South Dakota [40] and Montana [45]). Average annual precipitation east of the Red River generally exceeds potential evapotranspiration, indicating a net leaching environment; potential evapotranspiration approximately equals precipitation near the Red River, and progressively exceeds precipitation as the moisture regime grades from sub humid to semi-arid in the eastern part of the state.

In eastern South Dakota Bischoff (1991) monitored detections of alachlor, atrazine, carbofuran, dicamba, fonofos, metolachlor, MCPA, pendimethalin, terbufos, trifluralin, and 2,4-D for a wheat and corn rotation under moldboard plow and no till tillage practices, and for alfalfa. The soil type was a Poinsett silt loam. The water table was at approximately 2.5 to 3 m below land surface. Samples were taken from 0.6 m (2 ft.), 1.2 m (4 ft.), 1.8 m (6 ft.) and 4.5 m (15 ft.). All of the tested pesticides were detected in at least one depth in 1989. Average number of detections per sample decreased approximately linearly from approximately 5.5 at 0.6 m (2 ft.) to 2.5 at 4.5 m (15 ft.). These techniques limited sampling to the time of water influx following storms, which was the time of highest detection probability.

A survey of three shallow unconfined aquifers in south-eastern and north-central South Dakota from 1988 through 1993 indicated that pesticides were detected in 6% of samples in 1988, 11% in 1989, 6% in 1990, 20% in 1992, and 27% in 1993 (South Dakota Department of Environment and Natural Resources 1994). Trends in detections with climate are similar to those in North Dakota.

As in North Dakota, 1988 was a drought year with little recharge. 1993 was an abnormally wet year. Common pesticide detections were metolachlor, terbufos, fonofos, 2,4-D, and atrazine. Other pesticides detected were alachlor, dicamba, EPTC, butylate, propachlor, picloram, and bromoxynil. None of the detections were above EPA MCL or HAL. The authors stated that increased nitrates in samples corresponded to rising water tables, and that nitrates may have been dissolved from the vadose zone by rising waters. The same might have applied to pesticides in some cases.

In Montana seven pesticide compounds were detected in 229 samples taken from 1984 to 1989. These included aldicarb sulfoxide and sulfone, atrazine, simazine, 2,4-D, picloram, MCPA, and dicamba (Montana Department of Agriculture, 1989). These pesticides were found in about 25% of the tested wells. This survey was taken from wells considered to be highly vulnerable to contamination and in areas of high sensitivity to pesticide leaching. This sample set would likely comprise a worst case scenario. The Montana survey is similar In method and results to the Washington state study. A later source (Montana Department of Health and Environmental Sciences, 1994) indicated that a total of 10 pesticides have been detected in Montana ground water. In addition to those reported above, dinoseb and pentachlorophenol were cited. Of all detections, only dinoseb and pentachlorophenol were reported to be above health advisory levels. The Montana reports did not separate detections according to sources (point or non point).

Several pesticide surveys have been implemented in North Dakota. A survey or picloram concentrations in 126 private and public wells considered susceptible to contamination was conducted in 1985 (Glatt 1985). Eleven samples (8.7 %) were found to have picloram (all below 0.85 µg/L). Only four of the eleven detections were confirmed in a second sample taken later. Concentrations of confirmation samples ranged from 0.05 to 3.56 µg/L. All concentrations were below levels of human health concern based on current health advisory levels.

A survey of 92 municipal wells (analyzed for aldicarb, fenvalerate, picloram, methyl parathion, and 2,4-D) indicated that at least one pesticide was present in 10 different municipal samples (Glatt 1986). Picloram was detected in seven samples (maximum concentration of 1.46 µg/L and minimum concentration of 0.85 µg/L.). Glatt (1986) also reported possible "trace" detections of ethyl parathion, methyl parathion, and trifluralin in three separate samples. However, the certainty level of the trace detections is not high. In a survey of picloram in 126 water samples collected from public, private, and livestock wells in Rolette County, ND (Glatt 1986), 11 were found to have detections at tracel levels (< 0.02 µg/L) or higher, with a maxiumum concentration of 0.85 µg/L. A second check of the positive wells resulted in confirmations in only four of the wells (concentration range from 0.05 to 3.56 µg/L). At the time of the report, the "suggested no adverse response level" (SNARL) was 105 µg/L, and a "health guidance level" (HGL) of 250 µg/L for a 22 pound child were suggested for lifetime exposures.

Montgomery et al. (1988) conducted a survey of atrazine, simazine, alachlor, and metolachlor in 229 samples from drain tiles and monitoring wells placed on a 1 square-mile grid in a 5,000-acre irrigation test area in Dickey County, North Dakota. Alachlor and atrazine are heavily used in the sampled areas. Montgomery's well samples were taken in an area of heavy irrigation development, and from depths of 6 to 10 m (20 to 30 ft.), just above a till aquitard at the bottom of the Oakes aquifer. Results were no detections of any pesticide in the tile drains. There were no detections of atrazine, simazine, or metolachlor (at 1 µg/L) in any of the well samples. There were six detections of alachlor in the monitoring wells. However, two of the six detections were below 1 µg/L and are cited as "trace" or uncertain detections by the authors. Three of the confirmed detections were from a single well. There were no alachlor detections in neighboring wells, and the authors considered that a point source (localized spill) rather than labeled use on fields was the likely cause.

Later experiments with movement of atrazine, pendimethalin, chlorpyrifos, and phorate under irrigated corn on the Oakes (ND) sand plain in 1990 indicated that maximum leaching occurred at 11 to 49 days after application, and that no pesticides were detected in the soil below 0.9 m (3 ft.) (Hofmann et al. 1991). Experimental conditions included good management practices, and irrigation applications were applied at 75 to 80% of crop demand. Additional experiments of atrazine and bromide leaching under irrigated corn at Oakes (Komor and Emerson 1994) indicated that preferential flow contributed to deeper movement of pesticide and tracer on the Oakes sand plain. However, no atrazine was detected in the underlying shallow aquifer. Because of sandy soil, substantial irrigation, and shallow unconfined aquifers, Dickey and Sargent Counties are the only ND counties listed as high risk area in the Kellogg study.

A survey of organic compounds (including 22 commonly used pesticides) in 346 community (> 15 connections or 25 people) wells was completed in 1990. Results (Abel 1992) indicated that there were detections of at least one pesticide in less than one percent of the wells. Only two pesticides were detected. Alachlor was detected at 0.55 µg/L (EPA MCL as of 1993 was 2 µg/L), and picloram was detected in one well at 1.99 µg/L (EPA MCL as of 1993 was 500 µg/L). Thus, the few detections were well below levels of EPA mandated regulatory concern.

Murphy and Greene (1992) monitored 13 wells placed near the surface of aquifers in the coarse Denbigh Sand Hills of McHenry County, in north central North Dakota. All areas surrounding the wells were sprayed with 2,4-D and picloram. During the two year monitoring period almost all of the wells were found to have some fractional detections of 2,4-D (ranging from 0.09 to 2.09 µg/L). However, detections were several orders of magnitude below EPA MCL. Only three of the thirteen wells were found to have samples containing picloram. Detections in two of the three wells were in concentrations below 1 µg/L (picloram EPA MCL is 500 µg/L). The area of the one well with

detections above 1 µg/L (18.4 to 107 µg/L) was suspected to have been accidentally sprayed with a treatment level above labeled dose (Murphy and Greene 1992).

The Camp Grafton South military reserve located in Eddy County in East Central North Dakota overlies the shallow unconfined (and partially confined) Cherry Lake aquifer. Soils of the Camp Grafton South reserve are sandy. Picloram is sprayed for leafy spurge control. Malathion and dursban are sprayed for mosquito control on bivouac and work sites. During 1992 and 1993 water samples were taken from nine shallow wells (screened intervals varying from 2 to 12 m [7 to 40 ft.], depending on water table depth) in the Cherry Lake aquifer, one spring, and three surface water sources (two lakes and a reservoir). These samples were analyzed for 39 pesticides (Schuh, 1994). There were no detections in any of the wells or spring samples, or in the reservoir. Two area shallow lakes were found to have consistent low background levels of picloram (0.2 µg/L). Previous samples of the same lakes taken in 1986 had not indicated picloram, and later detections may have been caused by unusually large runoff from large precipitation events occurring during the flood years of 1993 and 1994 in east central North Dakota.

Beginning in 1992 an ongoing monitoring program for pesticides has been conducted by the North Dakota Health Department to satisfy base requirements of state primacy in implementing EPA-mandated ground-water protection, and pesticide in ground water protection plans. A vulnerability index has been devised and used to prioritize all major aquifers in North Dakota (Radig 1994). Beginning with aquifers having the highest indicated vulnerability, samples are being collected on an approximate one-square-mile grid from residential, production, and monitoring wells. In 1992 a total of 137 wells were sampled in the Oakes (Dickey County, southeast North Dakota), Warwick (Eddy County, east central North Dakota), and Icelandic aquifers (Grand Forks county, northeast North Dakota). All samples were analyzed for 44 pesticides commonly used in North Dakota. Only three wells (2.2 %) contained one or more pesticides. Pesticides detected were lindane, picloram, and trifluralin. Some possible (trace) indications of carbofuran presence were also noted, but confidence levels for the apparent carbofuran detection was low. Site analyses indicated that wells were likely contaminated by point sources rather than by labeled use (Radig and Bartelson 1992).

1993 and 1994 were exceptionally wet years in eastern North Dakota, and recharge was large. In 1993, 117 additional wells were sampled in the unconfined Denbigh aquifer (McHenry County, north central North Dakota), Elk Valley aquifer (Grand Forks County, northeast North Dakota), Fordville aquifer (Grand Forks County, northeast North Dakota), Lake Souris aquifer (Botteneau, McHenry, and Rollette counties, north central North Dakota), and Shell Valley aquifer (Rollette County, north central North Dakota). A total of 21 wells (18 percent) had at least one detection. All wells with detections were resampled. On resampling, 7 wells (7 percent) had confirmed detections of the same pesticides

as previously sampled (written communication, Scott Radig, November 13, 1994). There is some uncertainty of the results of one well sample in which replicated detections of ethyl parathion were found, because of repeated detections of ethyl parathion in laboratory blanks. Most confirmed detections were of picloram (six wells). There was one confirmed detection of trifluralin. The largest detections in relation to toxicological standards were detections of cyanazine (7 percent of MCL) and 2,4-D (35 percent of MCL) in one well. All other detections were only a fraction of one percent of MCL or HAL. These (1993 and 1994) results must be considered as preliminary until fully analyzed and reported by the appropriate project leaders.

In an experiment conducted over the confined Carrington aquifer in Foster County (east central North Dakota), there were no confirmed detections of pesticides used on biological, integrated management, and conventional farm management field treatments in 1992 and 1993. Samples were taken from the aquifer just below the till boundary (approximately 6 m or 20 ft. below land surface). Detections were lacking, despite hydrologic evidence of large recharge during 1993, and despite enhanced nitrate movement to the aquifer during that time (Schuh et al. 1994b).

THE CARRINGTON EXPERIMENT

OBJECTIVES

The objectives of the Carrington experiment were: (1) to investigate the detailed hydrologic processes occurring on an agricultural field farmed using rotational crops and practices common to North Dakota; (2) to describe the manner in which these hydrologic processes contribute to ground water recharge in both the saturated till and the underlying Carrington aquifer; (3) to investigate and characterize the effect of local hydrologic processes on the movement of tracers and nitrates; and (4) to investigate the movement of pesticides in relation to site hydrology and tracer movement. Objectives (1), (2), and (3) have been reported in Schuh et al. (1993a), Schuh et al. (1993b), Schuh and Klinkebiel (1994), and in a general summary report by Schuh et al. (1994a). The purpose of this report is to examine the occurrence of pesticides in relation to soil water movement and tracers.

SITE LOCATION AND CHARACTERISTICS

The experimental site (Figure 4) consists of a 30- x 30-m (100- x 100- ft.) area at 147-66-31AAB located on the land of the Carrington Research Extension Center. The site consists of coarse loamy glacial till overlying a finer fractured till with intermittent and discontinuous horizontal fractures. There are boulder lag layers about 0.31-m (1-ft.) thick at 1.5-m (5-ft.) and 4.6-m (15-ft.) depths. The stratigraphy of a test hole drilled on the experiment site is presented in Appendix Table A.1. The soil type is Heimdal loam (coarse-loamy mixed udic Haploboroll). The soil solution is saturated with respect to calcium bicarbonate, and has a pH of about 8.1 and electrical conductivity (ECE) between 800 and 1100 μmhos cm^{-1}. Parent materials between the root zone and the saturated till have higher pH values (8.1 to 8.6). Clay content varies from negligible in the sand and gravel filled fractures to as high as 25% in the soil profile. Most layers have clay content between 10 and 20%. Soil descriptions, with particle-size distribution, pH, ECE, organic matter percent, and 15-bar moisture for three locations on the experimental site are summarized on Appendix Table A.2 reported in Schuh et al. (1994a). Soil samples were taken from neutron-probe access holes.

The Carrington aquifer is confined on the experiment site at a depth of about 6.7 to 7.0 m (22 to 23 ft.). The depth to the aquifer is less than the overall (12 m [40 ft.]) average cited by Wanek (1989) for the Carrington aquifer. The shallow depth is conducive to local recharge. The water level in the glacial till varies from 3 m (10 ft.) to approximately 4.8 m (16 ft.) below land surface. The 3-m (10-ft.) depth cited was measured in the fall of 1987 following the addition of water to the site for measurement of unsaturated flow properties, and is likely non representative of the natural water

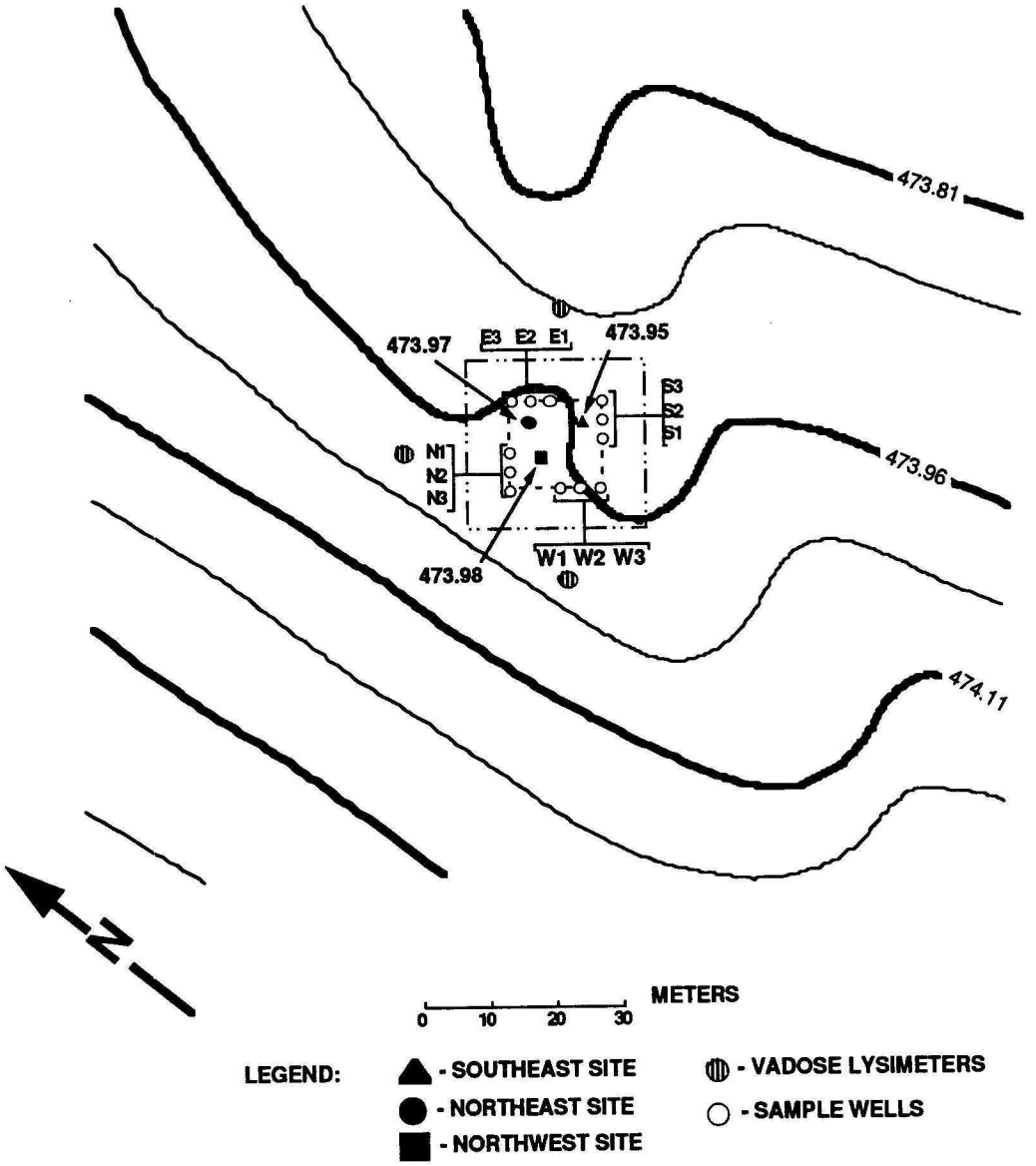

Figure 4. Site map of experimental site layout. Marked sites are locations of neutron-probe access tubes and thermocouples.

level. Two irrigation wells are located approximately 700 m (2,300 ft.) southwest of the experimental plot.

The experiment site has a slope of less than 0.4%, and is located about 176 m (600 ft.) west of a tributary to Scotts Slough (Figure 4). The overall slope of the land is in the direction of Scotts Slough, and during large rainfall and thaw events the field tends to be covered with a sheet of overflow water from fields to the west of the experiment site. The site is located approximately 150 m (500 ft.) south of a road ditch, which also provides a conduit of runoff waters to the tributary of Scotts Slough. Both the road ditch and the Scotts Slough tributary likely comprise local recharge areas. The experiment site also likely comprises a component of the extended recharge area associated with these features, receiving overflow waters in transit to Scotts Slough during large precipitation and snow-melt events. The status of the local site as an active recharge area is also enhanced by the local thinning of the till above the Carrington aquifer as described above.

SITE INSTRUMENTATION AND LAYOUT

The experiment site consists of a 12- x 12-m (40- x 40-ft.) square plot which was instrumented for full hydrologic analysis and for water quality sampling. The instrumented site was placed at the center of a 30- x 30-m (100- x 100-ft.) square buffer area. Both the experiment site and the buffer area were farmed using the crop rotation described on Table 1. Instrumentation for hydrologic measurements has been described by Schuh et al. (1994a).

Replicate sets of monitoring and sampling wells were placed on each of four sides around the perimeter of the 12- x 12-m (40- x 40-ft.) interior plot area. Each well had a 0.3-m (one-ft.) screen. Each nest of wells consisted of one well screened in the top of the Carrington aquifer at approximately 6.7 to 7.0 m (22 to 23 ft.); one well screened in the deeper saturated till at approximately 4.4 to 4.7 m (14.4 to 15.4 ft.); and one well screened in the shallow saturated till at approximately 3.3 to 3.6 m (10.8 to 11.8 ft.). The deep (Carrington aquifer) well was drilled using a forward-rotary drill rig. The annular space between the well casing and the wall of the drilled hole was filled with bentonite grout to just below the soil surface. The remainder of the annular space was filled with soil. The deep till wells were also installed using a forward-rotary drill rig. The annular space was cemented to just below the soil surface, and the remainder filled with soil. The shallow (till) wells were placed using a power auger. Granular bentonite was also placed around the shallow till well. Each well was constructed of 5-cm (2-inch) diameter rigid PVC joined using stainless steel screws. No glues were used in well construction. Each well was capped with a threaded well cap. A small air hole was drilled in the top of the cap.

Table 1. Agronomic treatments and practices for the Carrington experiment site. For pesticides, (EC) is emulsifiable concentrate, (S) is soluble. For fertilizer, DAP is diammonium phosphate. For tillage, DI is disk, CU is cultivate, RT is rotary till. Fertilizer reported (N-P_2O_5-K_2O) according to industry convention.

Year	Crop	Planting Date	Pesticide (common name)	Application Date	Active Ingrediant (lb./A)	Pesticide Form	Fertilizer lb./acre active ingrediant (N-P_2O_5-K_2O)	Application Date	Form	Tillage	Yield bu/A (*lb/A)
1980 to 1985	Alfalfa		none								
1986	wheat		diclofop	5/29	1.03	EC	70-30-0		DAP* and Urea		50
			bromoxynil	5/29	0.25	EC					
			MCPA	5/29	0.25	EC					
1987	wheat		diclofop	5/29	0.94	EC	90-30-0	4/22	DAP* and Urea		40
			bromoxynil	5/29	0.25	EC					
			MCPA	5/29	0.25	EC					
1988	wheat		diclofop	6/3	1.13	EC	0.36-0-0	9/22	Ammonium -Sulfate	1-DI, 1 CU	22
			bromoxynil	6/3	0.25	EC					
			MCPA-ester	6/3	0.25	EC					
			propicanizole	6/13	0.113	EC					
			dimethoate	6/17	0.188	EC					
			glyphosate	9/22	0.75	S					
1989	sunflower	6/1	trifluralin	6/1	0.75	EC	59-23-0	5/21	DAP and Urea	RT	1650*
			methyl-parathion	8/9	0.75	S					
1990	soybean	5/22	trifluralin	5/22	0.75	EC	8.8-42		DAP and Urea	1 CU	24
1991	wheat	4/18	diclofop	5/28	0.94	EC	30-0-522	4/18	Urea and Muriate of Potash	1-DI, 1 CU	
			bromoxynil	5/28	0.375	EC					
			MCPA	5/28	0.0625	EC					
			propicanizole	6/13	0.1125	EC					
			dimethoate	6/17	0.5	EC					
1992	sunflower	5/29	glyphosate	5/22	1	S	30-0-0	5/29	Ammonium -Nitrate		1025*
			2,4-D amine	5/22	0.15	S					
			trifluralin	5/29	0.75	EC				1-DI, 1 CU	
			ethyl parathion *	8/7	1	S					
			ethyl-methyl parathion	8/21	1	S					

* unauthorized aerial spray

When not being sampled the capped wells were always covered with two polyethylene bags, which were tied individually to the well stem with string, or fastened with tape. Bags were changed frequently. After each chemical application bags were changed immediately. Beginning in 1992, the bags were replaced with a 10-cm (4-inch) rigid PVC cover, which was placed inverted over the well stem. Wells are labeled and referenced according to relative location (N for north, E for east, S for south, and W for west) and depth (1 for shallow till wells [appr. 3.4 m], 2 for deep till wells [appr. 4.5 m]; and 3 for Carrington aquifer wells [appr. 6.8 m]), as shown on Figure 4). For example, N3 is the north replicate of the Carrington aquifer wells, while W2 is the west replicate of the deep till wells.

In the fall of 1987 vadose samplers consisting of porous 5-cm (2-inch) diameter 1-bar ceramic tips and 5-cm PVC barrels from the sampling point to the surface were installed at 30-, 60-, 91-, and 193-cm (12-, 24-, 36-, and 76-inch) levels at three sites within the plot. During 1988 these samplers were found to be inadequate because of the ease with which detritus and exterior contaminants could enter the sampler. They were replaced in the spring of 1989 with three sets of vadose samplers which were better protected against contamination. The replacement samplers consisted of 5-cm (2-inch) diameter by 15-cm (6-inch) long porous 1-bar ceramic cups, sealed on the top with a teflon plug glazed to the ceramic cup (no glues were used). A teflon pressure fitting was used to join the 0.032-cm (1/8-inch) O.D. teflon access tubing, which was extended to the surface. Above the surface the two teflon tubes were terminated in stainless-steel fluid couplers. Complementary fluid couplers were used to connect the vadose samplers to the field sampling apparatus. Photographs of the vadose sampler used and of its placement are on Figure 6B in Schuh et al. (1994a).

The vadose samplers used in this experiment were installed in April of 1989, prior to the application of chemicals for the 1989 crop season. Because small-grain pesticides had already been applied in the 1988 season, special care was taken to avoid contamination of the vadose sampler hole. Topsoil was removed to a depth of one ft. (0.3 m) and a hand auger was used to clean the hole for placement. Three vadose samplers were placed on each of three locations, north (N), east (E), and west (W) on the experiment site (Figure 4). Two samplers were placed at the 1.5-m (5-ft.) level because it was expected that the soil during the crop season would dry more quickly at the shallower depth, and that two samplers would likely be needed to provide a sufficient quantity of water for measurement of pesticides. One vadose sampler was placed at the 2.1-m (7-ft.) level. After placement of the sampler, a clean silt slurry was tremmied into the hole to help insure good hydraulic contact between the sampler and the surrounding soils. Dry clean silt was placed to approximately 0.3 m (one ft.) above the sampler. Above that depth soil augured from the hole was replaced and packed with the tremmie rod. Packing was used to insure less influx of water at the point of sampler

placement. The teflon tube was also looped, approximately 0.15-m (6 inches) below the surface, to help insure against piping down the tubing to the sampler.

AGRONOMIC PRACTICES

Agronomic practices are summarized on Table 1. During 1988 and 1989 the field surrounding the buffer area was planted to different crops than those used in the experiment. However, it was decided that a larger chemical buffer area would be desirable, and beginning in 1990 the site and the surrounding field were planted to the same crop. The introduction of soybeans into the rotation after sunflowers is not a common rotational practice. This exception was made to synchronize the measurement site with the larger field rotation.

Background field fertility was evaluated using soil tests taken in the fall of 1987, 1991, and 1992. Soil sample fertility data are shown on Appendix Table A.3 of Schuh et al. (1994a). Soil tests and fertility evaluation were made by the North Dakota State University Soil Fertility Laboratory, Fargo ND. Small nitrogen (N) applications were based on an initial high background soil nitrate-N level, probably resulting from the extended period in alfalfa production which ended in the fall of 1985. Soil samples for nitrate -N were taken from the top 0.6 m (two ft.) of soil. Potassium (K_2O) levels were high to moderately high through the spring of 1991, so that no potassium was applied. The large application of potassium in 1991 was made in the form of muriate of potash for chloride tracer application. Phosphorus (P_2O_5) levels varied from medium to high. Soil pH did not vary greatly during the experiment. pH values indicate that the topsoil soil solution is saturated with respect to calcium bicarbonate.

For most years, tillage consisted of one pass with a disc and one pass with a field cultivator to incorporate the herbicide, or to smooth the surface for planting. An exception was 1990 when a single pass with a cultivator was used to incorporate trifluralin before planting soybeans (Table 1). For two years of row cropping (1988 and 1989) the soil was also row cultivated for weed control. In 1989 there were two row cultivations. In 1990 there were also two row cultivations during the month of July. Near field apparatus, where tillage implements could not reach, attempts were made to simulate the mechanical tillage operation as closely as possible. Shovels were used (with a side twisting motion) to simulate discing, and rakes were used to simulate the field cultivator.

Pesticide applications were planned according to common weed and insect control practices. Because the objective was to monitor the movement of agricultural chemicals, planned insecticide applications were made regardless of the size of insect populations.

REVIEW OF WATER, TRACER, AND NITRATE MOVEMENT ON THE CARRINGTON RECHARGE SITE

Results of the hydrologic, tracer, and nitrate movement portions of the Carrington ground-water contamination experiment conducted from the fall of 1987 through the spring of 1993 have been reported by Schuh et al. (1994a). These can be briefly summarized as follows.

1.0 For a partially-confined aquifer, underlying a loamy glacial till at a depth of about 6.8 m (22 ft.), and with a water level in the overlying glacial till at about 2.7 to 4.0 m (9 to 13 ft.) below land surface, recharge is a highly complex process.

1.1 Spatial variability of recharge, even on apparently level terrain, is large and is governed principally by microtopographic features and climate. Variability of soil hydraulic properties on a coarse loamy glacial till did not affect local recharge as much as surface topography.

1.2 Surface positions can be characterized as "primary active", "intermediate active", and "inactive" recharge sites. Primary active sites are those through which all water reaching or cycling through the soil and vadose profile to the water table passes vertically from the surface through the root zone. Inactive sites are those through which all water draining to the water table, or cycling through the soil and vadose profile to the water table, has an initial source in ground water that moves upward under capillary force as the water table adjusts to drainage on other more active recharge sites. Intermediate active sites are those through which water moving to the water table has a source in both surface water draining vertically through the root zone; and ground water cycling upward and redraining, in response to external sources and sinks.

1.3 Water moves from inactive surface sites to sites of larger surface infiltration activity as runoff. Concentrated waters then move through the soil- and subsoil-vadose zone to the water table where they form a mound. The mound then redistributes laterally to water-table positions underlying less active sites, where capillary adjustment of rising ground water causes upflux into the vadose zone. Upflux may reach as high as the soil profile. Later, in response to pumping of the aquifer (or other sinks), capillary waters redrain in response to the receding water table.

1.4 Following a recharge event each site, or pedon, is characterized by a pattern of drainage and upflux resulting from the specific configuration of localized ground-water recharge mounds with which it interacts hydrologically.

1.5 Total cycling of water through each site profile can be quantified using appropriate water budget procedures. Such procedures must account for direct measurement of water movement through the soil zone, changes in water storage to the water table, upflux of water from the water table during redistribution events, and direct recharge to the aquifer at each site during recharge events.

1.6. There is evidence that the saturated ground water serves as a site integrator between inactive and active sites. Despite large differences in local recharge from the surface and through the soil, it appears that the total amount of water cycling through each soil and vadose profile is frequently similar for all measurement sites.

1.7. The spatial variability, and the process of surface redistribution of water described in 1.2 provides, a "non-macropore" mechanism for preferential flow to the water table, and a means for increasing solute movement from the surface. Solute movement is enhanced by (1) movement of water across the soil surface to the recharge site; (2) concentrated movement of water through the recharge site; (3) redistribution to a position underlying other surface sites; and (4) ground-water movement upward into the soil and vadose zone under capillary influence, which can enhance either deposition in non solute-laden areas or dissolution of more solute through contact in the soil zone entered. Finally, (5) solute can be "pulled" to the water table and to the aquifer through drainage of saturated till water and capillary drawdown of water in the soil and vadose zone in response to pumping, or other sinks in the area of the site.

1.8 Active pumping of the aquifer was an important influence in moving water to the aquifer. Pumping of the Carrington aquifer increased the hydraulic gradient between the saturated till and the surface of the aquifer seasonally by a factor as large as four. This, in turn, caused drawdown of the saturated till, and capillary drawdown of unsaturated capillary water in the vadose and soil zones. The result was mixing of waters in all three layers.

1.9 Upflux of water from the lower vadose profile into the upper vadose and soil zone occurs during the winter in response to freezing. Usually, the depth of frost-water accumulation was between 1.0 and 1.5 m (3.3 and 5 ft.). The average amount of water accumulation due to frost was approximately 3 to 4 cm (1.2 to 1.8 inches). Usually, frost water fully redrained as the ice thawed from the soil profile in late April. Usually, there was no infiltration beneath the soil zone during the winter.

However, during one unseasonable thaw event (February of 1992) substantial winter recharge occurred.

1.10 Hydrologic evidence indicates that the experiment site is a recharge source area for the Carrington aquifer. The experiment site lies in the transit zone for surface water moving to a tributary of Scotts Slough. The overlying till is locally less thick than for most of the aquifer, which means that impedance to recharge is locally less. In addition, the piezometric gradients of the till are orthogonal to the gradients of the underlying aquifer. Direction of flow lines in the glacial till is northeast to southwest (toward the zone of thinner till, and also toward the irrigation pump located on section 31). And finally, vertical hydraulic gradients from the till to the aquifer are increased substantially by the pressure drawdown of an irrigation well field. All of these factors likely contribute to the amount of local recharge.

2.0 Tracers applied to the field were detectable at all levels (vadose samplers at 1.5 m and 2.1 m [5 ft. to 7 ft.], saturated till samples at 3.4 and 4.5 m [11 and 15 ft.], and Carrington aquifer samples at 6.8 m [22 ft.]).

2.1 During the year of application, tracers were usually detected at virtually all levels of the measured hydrologic system, including the surface of the Carrington aquifer at 6.8 m (22 ft.). Usually, first year detections were of lower concentrations, indicating that preferential flow paths were most influential in expediting movement.

2.2 During the year of application, slightly elevated concentrations of fluoride were detected in the deep-vadose zone and in the saturated till. Because mixing in the calcium-bicarbonatic soil solution and slow movement through the unsaturated soil would be expected to cause immediate precipitation, some early fluoride movement through large pores from the soil surface to below the root zone during large storms is thought to occur. This is consistent with bromide evidence.

2.3 During years following application tracers tended to concentrate just below the root zone. After two years, concentrations similar to those in the shallow vadose zone would appear briefly during recharge periods in the saturated till. However, deep detections were ephemeral and did not remain at relatively constant levels as in the shallow vadose zone. The movement of larger concentrations of tracers at later times may indicate greater influence of intermittent quantities of bulk

flow, compared with earlier influence of preferential flow paths. This is reasonable because most of the solute is no longer at or near the surface to be washed into large pores and cracks.

2.4 Three or more years after application, appearances of tracer in the Carrington aquifer were spatially sporadic and most frequently not repeated on other site replicates.

2.5 Tracer and nitrate concentrations at all levels corresponded approximately with topographical zones of maximum surface-water concentration mapped during a storm in 1991. These observations support the conclusions of hydrologic analysis indicating the importance of microtopographic redistribution and concentration of water in determining the activity of surface sources of recharge.

2.6 Tracer and nitrate peaks were distinct and of short duration in the vadose zone, and corresponded to periods of rising water in the saturated till. However, tracer and nitrate levels in the saturated till, and particularly in the Carrington aquifer, were prolonged and corresponded as well to a slightly later period of pressure drawdown in the Carrington aquifer, which was caused by pumping the aquifer for irrigation use. Bromide movement to the aquifer was not observed during a year in which pressure drawdown was small. Tracer and nitrate data support the hydrologic analysis which indicates that pressure drawdown from pumping is an important component influencing water movement to the Carrington aquifer.

2.7 During the period from spring 1990 through spring 1993 there were only two brief periods of nitrate movement to the Carrington aquifer. There were more frequent periodic flushes of nitrate to the saturated till.

2.8 During the period from spring 1990 through spring 1993 nitrate-N never exceeded 1 mg/L on any sample from the Carrington aquifer. In the saturated till nitrate-N reached the 10 mg/L EPA-MCL level on only one site replicate for a brief period in July of 1990.

2.9 There was no indication of an upward trend of nitrate-N in either the saturated till or in the Carrington aquifer during the period from fall 1987 to spring 1993.

METHODS

Water samples were taken for analysis of halide tracers and pesticides at least three times per year, at three depths below the water table. Depths sampled were 3.3 m and 4.5 m in the saturated till (the water table varied from about 2.5 to 4 m), and 6.8 m at the top of the Carrington aquifer. For each sample depth, water samples were taken on four individual replicate sites. Results of hydrologic and tracer measurements are summarized in Schuh and Klinkebiel (1994) and Schuh et al. (1994a).

Water samples for 1988 through 1991 were taken using a PVC bailer. Each well was bailed for approximately five well volumes before sampling (about 15 bails for the 4.5 m wells and about 25 to 30 bails for the 6.8 m wells). After 1988 the 3.4 m shallow till wells were dry. To avoid cross contamination between depths, wells were sampled according to depth blocks (4.5 m and 6.8 m, four replicates each) and a different bailer (two bailers) was used for each block of four wells. Between well replicates in each block the bailer was decontaminated using multiple (three or more) distilled water washes. Washes were performed by nearly filling the bailer with clean distilled water and agitating and rotating the bailer. For each wash action, distilled water was also decanted over the outside of the bailer and over the bailer rope. Total rinse operations also included the multiple bailings of water from the well described above. Samples for tracers and inorganic analyses were taken before samples for pesticides. As a general procedure, water samples from each bailer fill were distributed as evenly as possible in the two one-liter smoked-glass sample bottles.

For 1990 and 1991 an additional rinse with reagent grade acetone and hexane, followed by an additional distilled water wash was added to the decontamination procedure. The additional distilled water wash was added to remove any possible exudates dissolved from the PVC by the solvents. For all sampling only one worker, a designated "clean" worker maintained contact with the bailer itself. The clean worker did not touch any objects that could potentially transfer contaminants. Rinse water containers, well covers, well caps, and sample bottles were all handled by a utility worker. In 1992 and 1993 decontamination procedures were further upgraded. Each well was fitted with a dedicated polyethylene bailer, which was used for bailing, and which was left suspended within the covered well. After bailing, the polyethylene bailer was placed and secured in a new clean polyethylene bag for protection from dust, and a dedicated disposable teflon bailer was used to sample the well. In all cases, stringent measures were used to avoid any contact of the sample bailers and windblown detritus or potentially contaminated objects.

Vadose samplers and their protection from dust and contamination were described previously in sections on construction of sample apparatus, and in the section on tracer sampling and movement. On each site the soil was covered with a polyethylene soil-surface cover and the sample tubes were

extended upward through the cover in slits. The polyethylene cover was discarded after each sampling. Prior to each sampling, the stainless steel pressure coupling on the field sampler and on the bottle receiver were thoroughly rinsed three times with a pressurized spray of distilled water from a laboratory wash bottle. In addition, acetone and hexane solvent wash, followed by an additional distilled water wash, was applied in 1990 through 1993. Receiver flasks were kept in the shade (in coolers), but without ice. After completion of sampling, the stoppers and lips of the glass flask were rinsed with distilled water. The stoppers were then removed and the sample water was decanted first into a polyethylene bottle for tracer analysis. Additional samples were then poured over the same position on the flask lip into two 40-ml smoked glass sample bottles. Tracer samples were decanted first to further rinse any possible organic contaminants from the flask lips.

In addition to well replicates, additional field blanks were sampled to assess the potential for inadvertant contamination. The first type of field blank used consisted of two open wide-mouthed sample bottles, filled with distilled water, placed about five feet above the ground, and left for the duration of the full sampling period. The purpose of these open bottles was to evaluate the possibility of spurious contamination of the samplers by wind-blown dust, spray drift, and detritus. Open-bottle field blanks were sampled in May and in June of 1990, April of 1991, and July of 1992. No pesticides were detected in any of the open bottle samples (Appendix B).

A second type of field blank consisted of clean distilled water poured into the clean bailer just prior to sampling each block of wells (two samples), and then decanted into sample bottles. This field blank was intended to evaluate the possibility of bailer contamination between wells. Bailer-decanted distilled water samples were taken for all sample times in 1991, 1992, and 1993 (Appendix B). In 1992 and 1993, two additional bailer-decanted samples were taken on a site adjacent to the reported site in another experiment on the same day. These samples were screened for twenty-six pesticides. These additional bailer-wash blanks offered additional assurance of samples free from field contamination.

There were no plausible detections of any of the pesticides in any of the field blanks during the course of the experiment. Open-bottle blanks, which were filled with water and left open in an exposed position approximately five feet above the ground for several hours during the course of sampling, all exhibited non detects for all target pesticides. There was one 0.02 µg/L apparent detection of bromoxynil reported by the laboratory for the 4.5 m (15 ft.) till-well blank, taken on June 11 of 1991. However, the laboratory deionized water blank run with the sample set indicated bromoxynil detection at 0.066 µg/L (Appendix B). Thus, the apparent detection for the field blank was likely caused by laboratory contamination. There were no detections of any pesticides in the well samples on the June 11 sampling date.

BAILER WATER WASH EXPERIMENT

Because decontamination of bailers within blocks of sample replicates employed water wash alone in 1988 and 1989, an experiment was conducted to examine the efficacy of water wash procedures alone for decontamination of a PVC bailer for each of the pesticides used in this experiment. The results of this experiment are reported in Schuh et al. (1993c). Each of the pesticides in the Carrington experiment were prepared in distilled water solutions of known high and low concentrations. Four wells were selected in southeastern North Dakota. The wells were sampled to establish background pesticide levels. The bailer was then filled with the spiked contaminated sample and allowed to equilibrate for about one minute. The sample was then decanted to a sample bottle. A single distilled water wash was then applied to the bailer, followed by a second sampling. Samples were also taken following multiple distilled water washes, and following an additional 15 bails in the well. Because we were concerned with any possibility of contamination, the chemists were asked to note any possible spikes, even those below routine laboratory MDL, that might indicate the presence of the pesticide in any quantity.

Results indicated that the effectiveness of decontamination was strongly related to solubility and octanol-water partition coefficient (K_{OW}) of the pesticide. Pesticides having a K_{OW} of less than 200 or a water solubility of more than 500 mg/L were found to be fully removed in a single distilled water wash. These included bromoxynil, propicanizole, and MCPA. Dimethoate results appeared to be anomalous to other data, but dimethoate recoveries were poor and results were thus unreliable. Analytes having K_{OW} of less than 2,000 or water solubility of more than 50 mg/L were found to be effectively cleaned using multiple distilled water washes alone. These include methyl parathion. Diclofop and trifluralin both had K_{OW} greater than 2,000. However, experimental results indicated that desorption of adsorbed contaminants from the PVC bailer followed the relationship

$$C/C_o \times 100 = A\, e^{0.00004\, K_{ow}} \qquad (10)$$

Where C and C_o are final and initial analyte concentrations respectively, and A is a coefficient of 0.2296 for one distilled water rinse, 0.139 for multiple distilled water rinses, and 0.0312 for multiple distilled water rinses and 15 bails of the sample well. Calculations from this relationship indicate that for diclofop and dimethoate rinse regimes would result in a decrease in detected concentrations by a factor of 50 to 100 for one distilled water rinse, 100 to 200 for multiple distilled water rinses, and about 700 to 800 for multiple distilled water rinses plus fifteen bails in the well.

SAMPLE HANDLING AND LABORATORY PROCEDURES

All samples were kept shaded immediately after sampling, and were refrigerated within approximately 90 minutes of sampling. Samples were kept overnight in a refrigerator, transported on ice to a shipping point, and shipped on ice to the laboratory using an overnight carrier. Samples were at the laboratory within one and one half days of sampling. Samples were extracted within seven days of sampling, and laboratory analyses were made within thirty days of sampling. The first two sample dates in 1989, and some of the 1988 samples were analyzed after the 30 day holding time because of laboratory logistic problems. Although we do not think it likely that the results were greatly affected, the error bias would be expected to be toward false failure to detect rather than toward false detections under such circumstances.

All 1988 experiment sample analyses taken after May were performed by the North Dakota Health and Consolidated Laboratories organics laboratory (NDHCL) using micro-extraction procedures according to EPA method 505, revision 1.0 (USEPA 1989). The term "micro-extraction" is used to describe methods for extraction and analysis of pesticides using small size (40 ml) samples. All 1988 experiment-site well samples taken during or before May, and subsequent pesticide screenings of area wells not located on the experiment site itself using macro-extraction procedures were also performed by the NDHCL. The term "macro-extraction" is used to describe methods for extraction and analysis of pesticides using larger (1 liter) samples. All macro-extraction analytes except MCPA were analyzed on a Hewlett Packard 5890 gas chromatograph using Restek Rtx-35 and J&W DB-f columns according to EPA method 508.3 (USEPA 1990a). MCPA was analyzed using a Hewlett Packard 5970 mass spectrometer, according to EPA method 515.1 (USEPA 1990b). While 1990 procedures are cited, NDHCL laboratory procedures and instrumentation prior to 1990 did not vary substantially from the cited revised reference.

After 1988 all analyses for samples taken on the experiment site were performed by Minnesota Valley Testing Laboratory in New Ulm, Minnesota. Macro-extraction procedures used for most well samples were performed according to EPA method 608.1 (Pressley and Longbottom, 1982) for base neutrals and EPA method 515 for acids (Graves, 1989). All Laboratory determinations in 1989 were made on a Hewlett-Packard 5840A gas chromatograph using a Restek Rtx-5 column. Beginning in 1990 analyses were performed using a Shimadzu 14A gas chromatograph with dual electron capture and dual flame thermionic detectors. The columns used were Restek Rtx5 and Rtx 35. Both columns were 30 m with 0.53 mm ID and 0.5 μm film. Because of larger background noise on the Shimadzu 14A unit, MDL levels were higher for bromoxynil samples taken from 1990 through 1993 than for samples taken in 1989.

It was requested that "qualitative" detections below (but near) MDL be reported to help interpret other detections above MDL. Such "qualitative" detections are noted as such when referenced in text and tables. It must be recognized that the certainty of detections in such cases has a lower probability than for detections reported above MDL. Such data is used for supporting evidence when other substantial evidence of the presence of a contaminant exists. Further details of procedure accuracy using the double column procedure for base neutral pesticides were described by Mesia et al. (1991) in an in-house report for MVTL laboratories.

Micro-extraction procedures using 40 ml water samples were based on EPA method 505, revision 1.0 (USEPA 1989), but laboratory adaptations of methodology were used. Base neutral extractions were made using methylene chloride. Acid extractions were made by adjusting the pH to 12 using NaOH, extracting the alkaline sample with methylene chloride (and discarding the extractant), acidifying the sample with H_2SO_4 to a pH of 2, and then extracting the sample with ethyl ether. Detection instruments and columns used were the same as those used for maco extractions with the exception of 1988 when a J&W Scientific DB-5 column (30-m length, .32-mm I.D., and 0.25-um film) was used instead of the Restek Rtx-5 column. Details of micro-extraction procedures have been documented by MVTL laboratory and can be referenced as MVTL method #H10023.

Soil extraction of bromoxynil and MCPA was performed using USEPA method 8150 (USEPA 1986a), and soil extractions for diclofop, dimethoate, methyl parathion, propocanizole, and trifluralin were performed using USEPA extraction 3550 (USEPA 1986b). Instrumentation was the same as for macro-extraction procedures described above. Details of soil extraction procedures have been documented by MVTL laboratory and can be referenced as MVTL method #2682 and #2640.

INTERPRETATION OF FIELD DETECTIONS

Because of the low detection levels of concern, and because of the difficult situations almost always encountered in field sampling, including possible inadvertant spray drift, wind-driven dust contamination, and introduction of volatile contaminants in rainfall, there is almost always room for conjecture and concern over the validity of sample information. Because of these difficulties, the value of field data must be examined in full context of all of the known environmental and experimental factors involved.

Of first concern is the intrinsic value of the sample itself. This is determined by the sample procedures, which are based on established sampling protocols and upon specific experimental evidence relating to the sampling procedures used. States have varying requirements, from distilled water wash alone to a protocol including wash with low phosphate soap, water rinse, distilled water rinse, solvent rinse (frequently hexane and acetone), and a final distilled water rinse (Mickham et al.

1989). On the basis of the most conservative established protocol the intrinsic reliability of the 1992 and 1993 data which used dedicated disposable bailers is considered to be of highest quality.

The use of PVC rather than teflon bailers prior to 1992 is not of concern. Considerable evidence has been published indicating that previously claimed adsorption problems with PVC were due to plasticizers and not to rigid PVC itself. In fact, a thorough literature review and experiments by Parker et al. (1989) has indicated that PVC is probably the material of choice as a sample contact material over teflon. However, they also indicate that for very short contact times there is likely no problem for either of the materials. Also, no serious problem with chromatographic blockages or false detects caused by exudates from rigid PVC have been noted (Parker et al. 1989). These experiments have also been reviewed by Schuh et al. (1993c) for assessment of sampling procedures used in this experiment.

There is some concern, however, over the water wash procedure. While EPA procedures and many state procedures specify a solvent wash for decontamination of bailers or sampling devices to assure the removal of the broadest spectrum of organic contaminants that might be adsorbed to the sample contact material, some states require only a distilled water wash (Mickham et al. 1989). In fact, concerns over the mobilization of solute from the bailer itself in solvent wash is a matter of concern to some; and an additional distilled water wash following solvent wash is preferred by many practitioners to assure lack of spurious contaminants in water samples.

The adequacy of water wash alone varies with individual analytes. Based on experimental evidence (Schuh et al. 1993c) our confidence is high in the intrinsic value of data for bromoxynil, MCPA, propiconazole, and methyl parathion, which are very effectively washed using water alone. Intrinsic value for trifluralin and diclofop is less certain before 1992, and additional information must be considered in assessing the value of these data. The greatest problem with dimethoate appears to be not cleaning from the bailer, but rather problems in extraction and recovery of sample.

Among the factors to be considered in evaluating the reliability of field detections is the rate of water wash cleaning and dilution levels described above for individual analytes. Additional factors to be considered in evaluating the reliability of samples include the following. It is stressed that each of the following field contextual criteria do not in themselves provide conclusive evidence of anything, and care is needed in their application. They can only be used as additional clues, together with other field information, in assessing the credibility of the field measurements described.

1. Field blanks are used to evaluate the likelihood of environmental contamination of the well samples. Absence of detections in field blanks on a given sampling date provide evidence that spurious detections due to environmental contamination is not a problem. Less certainly, the

absence of contaminant detections on all, or on most of the sample dates provides evidence that spurious environmental contamination of samples is not a problem in general.

2. Replication of detections between wells of a given depth supports the validity of all detections. However, the converse is not true. The lack of replication does not necessarily indicate that the isolated detection is not real. It does indicate that movement is spatially variable and sporadic, and that there is far less certainty of contaminant damage to the aquifer indicated by the detection.

3. Replication of detections between wells of different depths also supports the validity of individual detections. Such cross depth replication supports the general belief that chemical movement in response to hydrologic events is occurring.

4. Replication of detections over time supports the validity of individual detections. If a given pesticide is persistently present under a wide range of sampling conditions and environmental conditions, then the validity of the individual detections is supported, and the general belief in the likelihood of movement of that contaminant in field water is enhanced.

5. Initial presence of a pesticide in soil or water samples taken at the beginning of the experiment, particularly those present below the topsoil and deep within the root zone, provides supporting evidence that pesticide detections in deeper waters are, indeed, indicators of true presence of the pesticide.

6. Correspondence of pesticide detections to trends of solute movement indicated by experiment tracers provides supporting evidence that detections are, in fact, moving in ground water. For example, appearance of pesticides at times corresponding to peak tracer concentrations, and lack of detections at times corresponding to lower tracer concentrations provides an indicator that pesticide detections are following patterns dictated by field solute movement and are not simply spurious errors introduced by sampling procedures.

7. Replication of detections between pesticides on a given sample date provides evidence that detections are caused by hydrologic events and solute movement in ground water, and not spurious introduction caused by sampling procedures. Detection of multiple contaminants, particularly those applied at different times, is another form of replication which supports the general contention that pesticides are moving with hydrologic events.

8. The order of sampling helps to evaluate the reliability of a given pesticide detection. For example, if the same bailer is used to sample two wells, with field decontamination procedures applied between wells, the lack of a pesticide detection in the first well would indicate that the bailer was likely clean upon entry into the second well, and would support the validity of any detections in the second well.

9. The correspondence of pesticide detections with measured flux of water to the depth of detection provides supporting evidence of the plausibility of detections through describing the mechanism of movement.

While none of these nine supporting criteria can individually prove the intrinsic value and truthfulness of pesticide detections, they can collectively help to paint the whole picture of what is actually going on in the field, and help to place field detections within the proper context of field hydrologic events.

LABORATORY QUALITY CONTROL

A deionized-water (DI) quality control blank was prepared and run with each set of field samples in the laboratory. In some cases target pesticides were detected in DI. While all field detections were confirmed on a second chromatographic column from 1990 through 1993, in some cases the laboratory neglected or was unable to confirm DI blank detections. In order to assure that reported detections for field samples were not caused by laboratory contamination, a systematic screening procedure was devised for evaluating the validity of reported detections based on laboratory quality control procedures. The screening procedure is presented in Appendix C.

The data screening procedure is based on the premise that a high level of assurance that detections are not caused by laboratory contamination is desired. The laboratory problem of primary concern is that of false detections. The following screening procedures are applied.

1. All non detections in field samples are accepted, regardless of presence or absence of detections in laboratory DI blanks.

2. Where the presence of an analyte in a DI blank has been detected, and where a second channel has confirmed the detection, all field sample detections for the target analyte in the data set corresponding to the DI blank are discarded as unreliable.

3. If a field sample detection has been confirmed on a second channel, and if the deionized blank detected on a first channel has been deconfirmed on the second channel, the field detection is accepted.

4. If a field detection has been confirmed on a second channel, and if the analyte has been detected on the first channel, but no second channel was measured for the DI blank, then the field detection is discarded unless it is of much larger (about an order of magnitude) than the single lab DI detection.

Using this procedure, eight apparent field detections were discarded from the analysis because of uncertainty of source and the likelihood or possibility of laboratory contamination. The apparent detections are still presented in the Appendix B tables. But their questionable reliability has been noted.

PESTICIDE MOVEMENT AND DETECTION

Results of water sample analyses for pesticides on the Carrington RECHARGE experiment site will be discussed in three general topics. First we will examine the overall frequency of pesticide detections in general, and their relation to hydrologic and climatic conditions. Second, we will examine the occurrence and significance of detections of individual pesticides on the experiment site. And third, we will examine the significance of reported pesticide detections in relation to the context of the larger landscape and the overall recharge status of the Carrington aquifer.

INITIAL BACKGROUND PESTICIDE LEVELS

After placement of wells on the sample site during the summer of 1987, each of the four replicate sample wells [3.0 m (10 ft.), 4.5 m (15 ft.), and 6.8 m (22 ft.)] was sampled on August 11 to establish background levels of pesticides. Results are summarized on Table 2. No pesticides were detected in the shallow or deeper till wells. In the Carrington aquifer at the 6.8-m (22-ft.) depth there were two detections of alachlor at 0.15 and 0.25 µg/L, and one detection of trifluralin at 0.069 µg/L. The source of these detections was not certain. However, the shallow wells had been placed using a dry auger, while the deep wells had been placed using a foreword rotary drill rig, which can carry near surface detritus in the circulating water. Although trifluralin had not been used on the experiment site for at least seven years (before 1980), there is some evidence from soil samples taken on May 29, 1989 (before the application of trifluralin in the experiment rotation) that some residual trifluralin may have remained in the soil of the Carrington RECHARGE site. It is therefore possible that some detritus from the topsoil may have resulted in the trifluralin detection in the Carrington aquifer well. The single initial detection of trifluralin, is not necessarily related to natural field hydrologic phenomena or agricultural practices that would cause contamination under normal circumstances.

The two initial detections of alachlor, however, are more problematic. It is unlikely that they came from the local site, as alachlor was not applied on that site within record. However, the field adjacent to the experimental site (Approximately 60 m or 200 feet to the west) was planted in irrigated corn and alachlor had been applied earlier in the year in which the wells had been placed. The alachlor may have moved in the aquifer to beneath the experimental plot.

Because of detections in initial samples, a second set of samples was taken from the Carrington aquifer wells of the RECHARGE site on May 5, 1988. These samples indicated no further detections of either trifluralin or alachlor (Table 3). However, laboratory minimum detection levels were slightly higher for alachlor (0.5 µg/L compared with 0.13 initially) and trifluralin (0.1 µg/L compared with

Table 2. Results of pesticide scan for Carrington experiment site wells shortly after construction on August 11, 1987. Number after < is lab MDL.

Well	West 6.8 m	North 6.8 m	East 6.8m	South 4.5 m
Concentration	µg/L	µg/L	µg/L	µg/L
Analyte				
alachlor	< .13	**.252**	**.15**	< .13
atrazine	< 3	< 3	< 3	< 3
cyanazine	< .5	< .5	< .5	< .5
diclofop	< .7	< .7	< .7	< .7
MCPA	< 29	< 29	< 29	< 29
parathion -ethyl	< .15	< .15	< .15	< .15
parathion-methyl	< .15	< .15	< .15	< .15
pendimethalin	< .1	< .1	< .1	< .1
triallate	< .1	< .1	< .1	< .1
trifluralin	**.069**	< .06	< .06	< .06
2,4-D	< 2	< 2	< 2	< 2

Table 3. Results of pesticide scan for Carrington experiment site wells on May 5, 1988. Number after < is lab MDL.

Well	West 6.8 m	North 6.8 m	East 6.8m	South 4.5 m
Concentration	µg/L	µg/L	µg/L	µg/L
Analyte				
alachlor	< .5	< .5	< .5	< .5
atrazine	< 4.4	< 4.4	< 4.4	< 4.4
carbaryl	< .5	< .5	< .5	< .5
carbofuran	< .5	< .5	< .5	< .5
cyanazine	< .5	< .5	< .5	< .5
diclofop	< .7	< .7	< .7	< .7
fenvelerate	< 1.25	< 1.25	< 1.25	< 1.25
MCPA	< 2	< 2	< 2	< 2
metolachlor	< .88	< .88	< .88	< .88
metrabuzine	< .15	< .15	< .15	< .15
parathion -ethyl	< .2	< .2	< .2	< .2
parathion-methyl	< .15	< .15	< .15	< .15
picloram	< 1	< 1	< 1	< 1
simazine	< 5.2	< 5.2	< 5.2	< 5.2
triallate	< .1	< .1	< .1	< .1
trifluralin	<.1	<.1	<.1	<.1
2,4-D	< 2	< 2	< 2	< 2

0.06 µg/L initially), and with the later higher detection levels there would have been no detections in the earlier sample either. Thus, the earlier detections are neither confirmed nor deconfirmed. They were, however, of low concentration, and were non replicated or sparsely replicated on the first sampling.

Hydrographic Traces

Pesticide detections from June 1989 through April 1993 on the RECHARGE site are shown on Figures 5, 6, and 7 for the vadose zone, the saturated till, and the Carrington aquifer respectively. In describing methods of pesticide sampling and analysis, procedures for screening data based on laboratory quality control were described. Screening procedure results are in Appendix C. All pesticide data for the RECHARGE experiment are provided in Appendix B. Data considered to be unreliable and discarded from analysis are identified in Appendix B. All data shown on Figures 5, 6, and 7 and discussed in analysis are those that have passed the screening procedure.

Each graph also includes sample dates and a "sensitized trace" of piezometric response in the 4.5- and 6.8-m (15 and 22-ft.) wells for comparison with pesticide concentrations peaks. Sensitized traces (T_S) are dimensionless graphs of data transformed to enhance visual definition of piezometric response. They are calculated using a formula of the type

$$T_S = \frac{(h - C)}{(h_i - C)} \qquad (13)$$

where h is water level elevation, h_i is the water level elevation at the initiation of the experiment, and C is a constant selected to enhance the visual recognition of changes in water level. T_S has no quantitative meaning. It serves only to assist in visual detection of relative response. A summary of absolute piezometer levels is shown on Figure 35 in Schuh et al. (1994a). The time scale used for all pesticide data is "experiment day" (Labeled ED), which is the time in days from the initiation of the experiment on January 1, 1988.

Overall Trends in Pesticide Detections and Movement

Schuh et al. (1994a) have described the recharge hydrology of the Carrington site and its relation to bromide, fluoride, and chloride tracer and nitrate movement in detail. A summary of conclusions has been provided in the section titled REVIEW OF WATER, TRACER, AND NITRATE MOVEMENT ON THE CARRINGTON RECHARGE SITE in this report. Figures illustrating tracer and nitrate movement will not be repeated in this report. Tracer and nitrate detections discussed can be confirmed and viewed graphically on figures 35 through 40 of Schuh et al. (1994a).

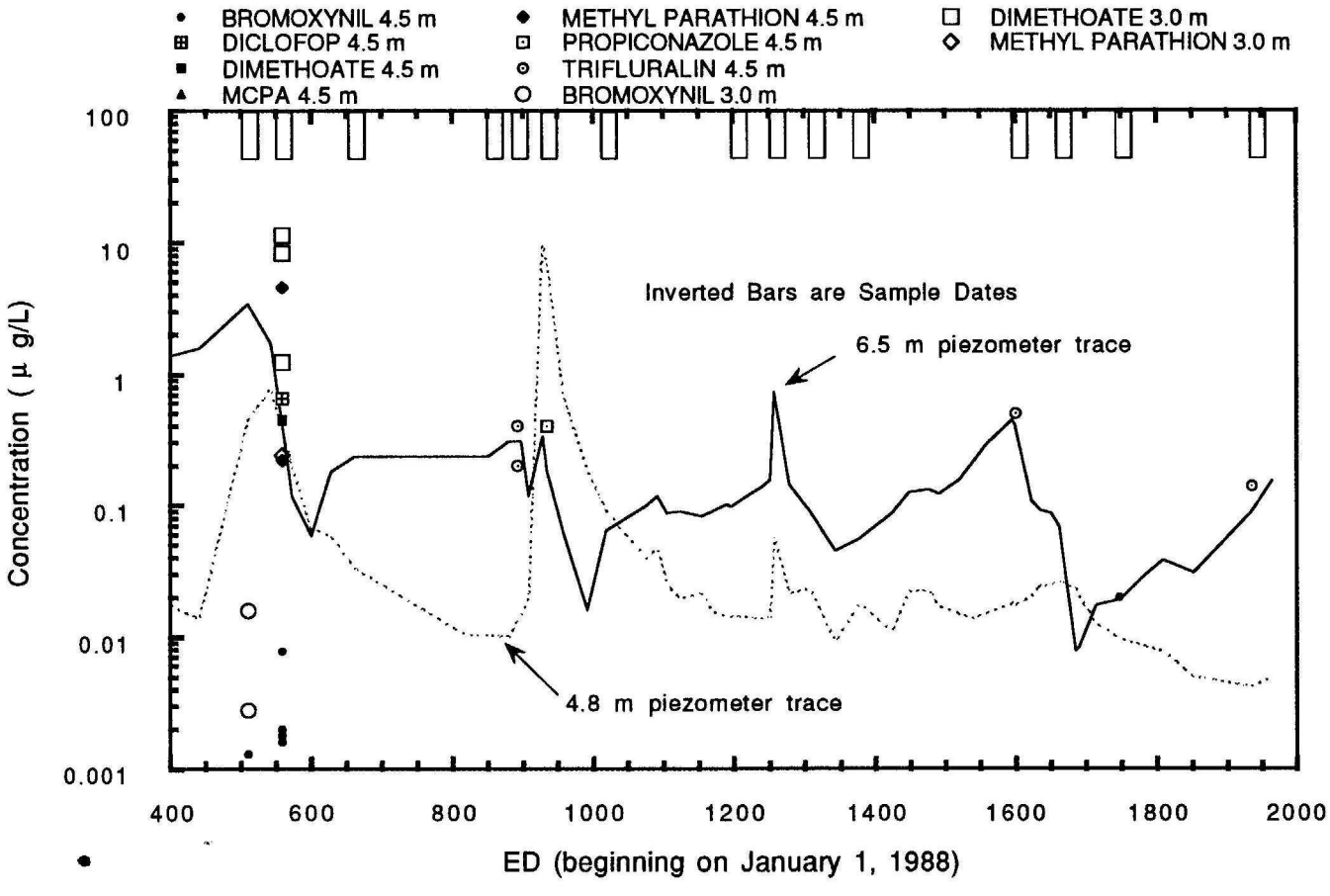

Figure 5. Pesticide detections in the vadose zone as a function of experiment day (ED) beginning on January 1 1988. Also included is a dimensionless piezometer trace for 4.5-m and 6.8-m piezometers, to indicate relative changes in piezometric levels over time.

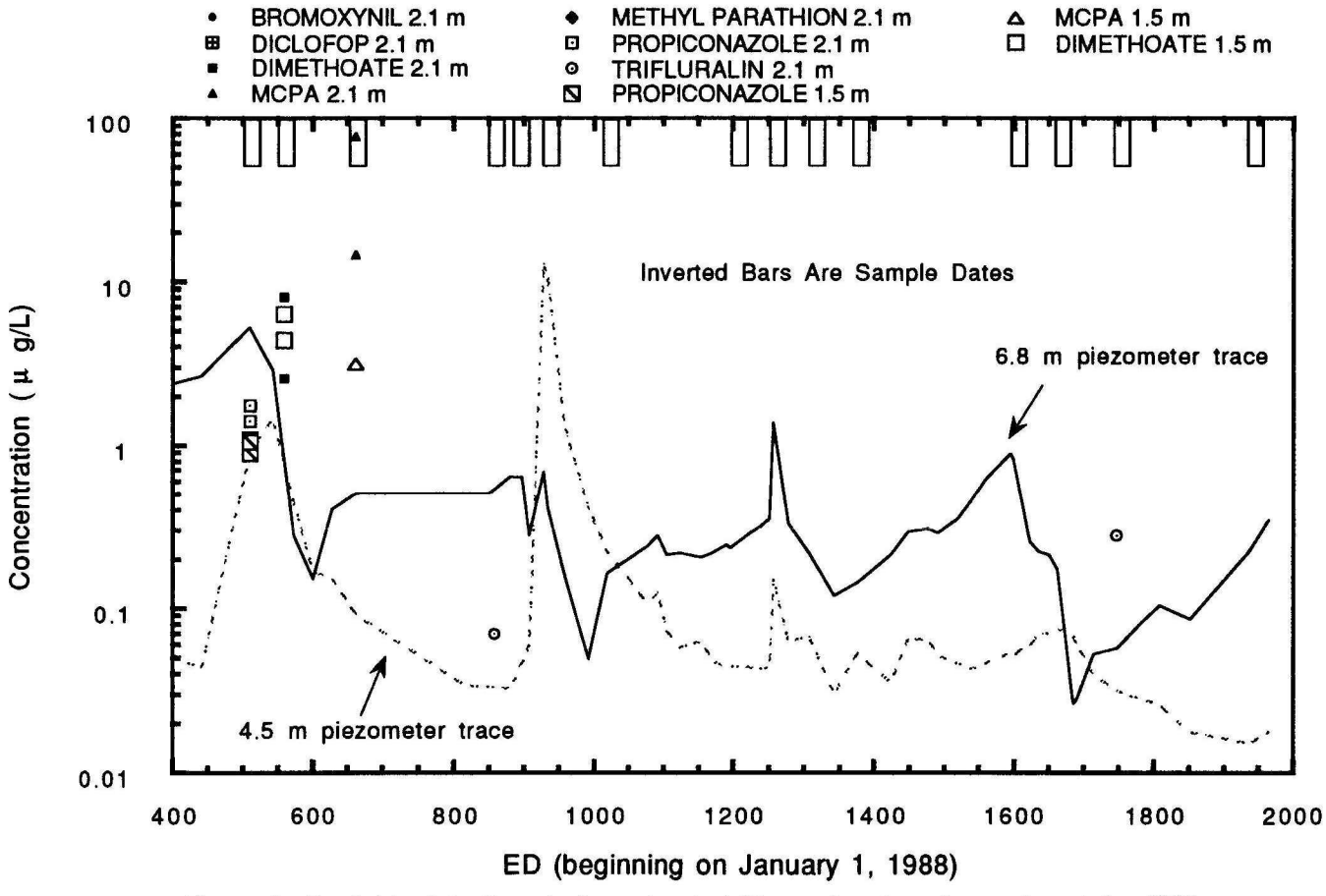

Figure 6. Pesticide detections in the saturated till as a function of experiment day (ED) beginning on January 1, 1988. Also included is a sensitized dimensionless trace for the 4.5-m and 6.8-m piezometers, to indicate relative changes in piezometric level over time.

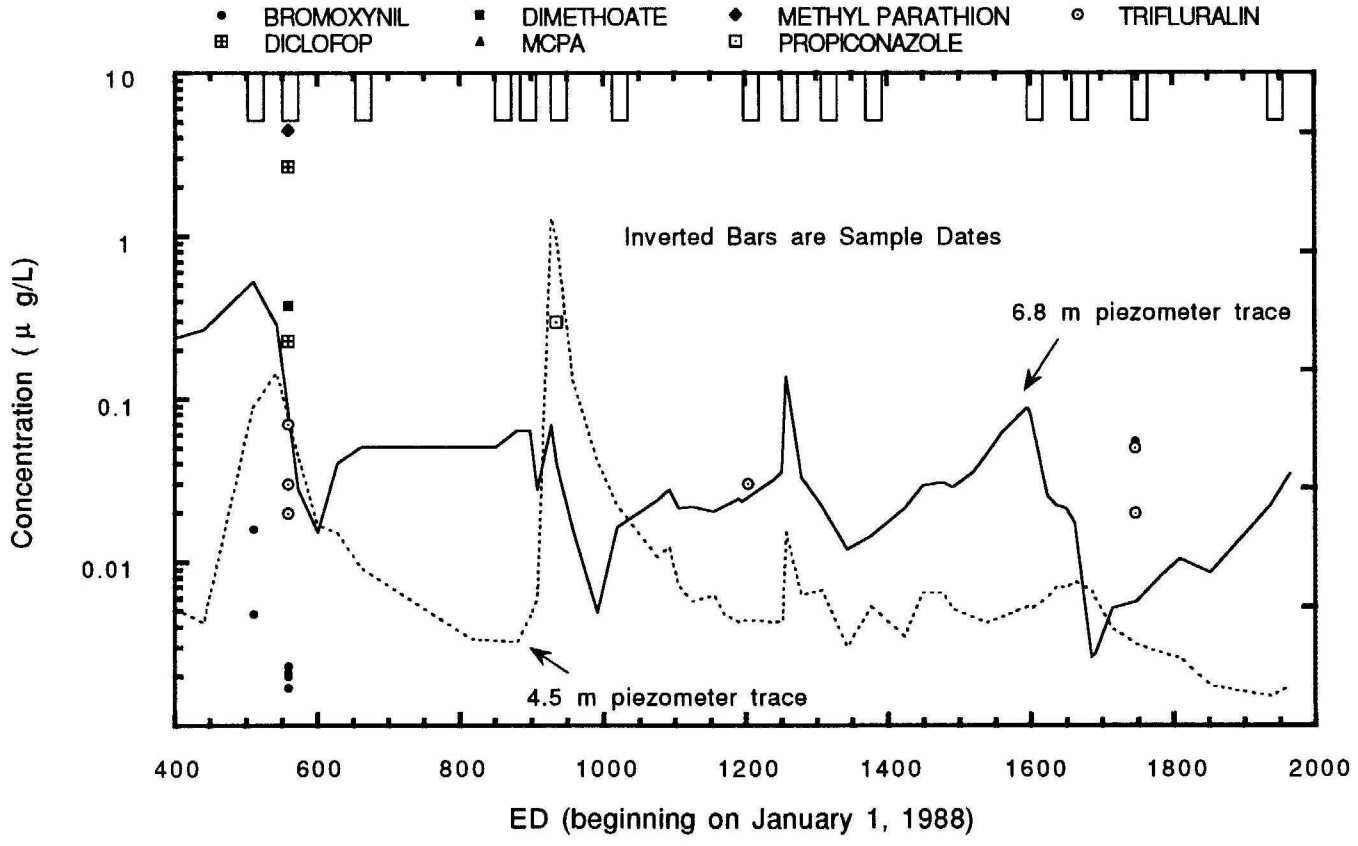

Figure 7. Pesticide detections in the Carrington aquifer as a function of experiment day (ED) beginning on January 1, 1988. Also included is a dimensionless piezometric trace for the 4.5-m and 6.8-m piezometers, to indicate relative changes in piezometric level over time.

There were three brief periods of pesticide detection in the Carrington aquifer and in the saturated till. For three sampling dates in 1988 using micro-extraction procedures alone, no detections were made in any of the vadose samplers or in the till or aquifer wells. The first major detection period was in early summer 1989 (ED 500 to 575). The second was in early summer 1990 (ED 850 to 950). The third detection period was in October of 1992 (ED 1750). While some detections occurred at other times, they were sporadic and usually without replication within the samplers on site.

In most cases pesticide detections corresponded to major periods of water flux at all levels. Several pesticides were detected at all sampling levels during some periods of rising water table in the saturated till. Most pesticide detections were made in early summer (mid June to mid July), during the period of maximum recharge to the water table, combined with the drawdown of the Carrington aquifer from pumping for irrigation. Detection times for pesticides corresponded closely with periods of bromide and chloride tracer and nitrate peaks as shown and discussed in Schuh et al. (1994a). Major groups of pesticide detections corresponded to major peaks of bromide at the same depths. Sporadic and nonreplicated detections of pesticides frequently corresponded to sporadic and nonreplicated detections of tracers.

Only one of the five years sampled, 1989, exhibited a substantial number of detections that were repeated between depths, sites, and pesticide species. For all other years, detections were more sparsely replicated between wells, depths, and pesticide species. The 1989 flush of detections was likely caused by the drought of 1988. Carrington was very dry in 1988 with about one half of the normal precipitation (Schuh et al. 1994a). There were no detections of applied pesticides during 1988 at any of the sampled levels (Appendix C), although use of micro-extraction procedures for wells had larger minimum detection levels then those applied in later years. The apparent flush of pesticides in the year following a drought year, and the lack of similar occurrences in subsequent years under the same chemical rotation, indicates that an unusually high retention of pesticides in the soil from the previous year likely resulted from dry conditions.

The hydrologic conditions providing the mechanism for pesticide movement in 1989 were already described by Schuh et al. (1994a). Briefly, immediately following the application of herbicides and tracers in 1989, a substantial precipitation event occurred. This resulted in movement of bromide tracer to virtually all sample wells, beginning immediately after the rainfall event, peaking in late July, and tapering off in October. It was concluded that bromide moved through a coupled mechanism of preferential flow which occurred during the rainstorm and carried small amounts of water and tracer deeper in the soil and vadose profile. There they combined with a more advanced bulk volume of water still moving to the water table from spring recharge. Bromide movement to the aquifer was

enhanced by pumping of the aquifer, and the subsequent enhancement of water movement from the saturated till to the aquifer. The same mechanism is offered for the movement of pesticides in 1989.

The spatial distribution of recharge on the Carrington site was shown (Schuh et al. 1993a, Schuh et al. 1993b) to be highly variable, and dominated by the slight (less than 3 cm) differences in elevation caused by microtopography. During rainfall events, slight differences in elevation were shown to determine the difference between locations of substantial drainage from the root zone (active sites) and sites of virtually no drainage from the root zone (inactive sites). These mechanisms have been summarized in the section REVIEW OF WATER, TRACER, AND NITRATE MOVEMENT ON THE CARRINGTON RECHARGE SITE in this report.

If we consider any replication of any pesticide (more than one detection of any pesticides on site), then for the three years (12 sample periods) after 1989, only one replicated pesticide detection occurred at the 6.8-m (22-ft.) level (Figure 7). One replicated pesticide detection occurred in the saturated till (Figure 6), and no replicated detections occurred in the vadose zone (Figure 5). Except for 1989, all pesticide detections were sporadic. This is consistent with site recharge hydrology, which is highly spatially variable.

The proportion of samples in which at least one pesticide was detected were 10 percent from 1988 through 1993 for the Carrington aquifer. If 1988 (drought year) and 1989 (year following drought year) are excluded, 6 % of samples had detections from 1990 through spring 1993. In the saturated till, about 13 percent of samples had at least one pesticide detection. If 1988 and 1989 are excluded, about 17% had at least one detection. These values compare with 6% (1988), 11% (1989), 6% (1990), 7% (1991), and 20% (1992) on susceptible unconfined aquifers in South Dakota (10 % overall) over the same time period. This also compares with detection percentages of 3% for 1992 and 18% for 1993 in a North Dakota survey.

ANALYSIS OF SPECIFIC PESTICIDES

In this section we will examine the detections of each of the applied pesticides, and evaluate the impact of their use on the Carrington RECHARGE site.

Bromoxynil

Bromoxynil was applied to the experimental plot in 1988 and 1991. Bromoxynil was not analyzed in 1988 because all lab measurements were made using micro-extraction procedures and micro-extraction methods for bromoxynil had not yet been locally adopted. For all years following 1988, macro-extraction lab procedures were used for all Carrington aquifer wells, and for the west replicate wells. Data for bromoxynil are in Appendix Table B.1. Detections are illustrated on Figures 5, 6, and 7. In 1989 analytical procedures allowed detection to 0.0025 µg/L using macro-extraction procedures. For 1990 through 1993 laboratory MDL for bromoxynil was higher (0.01 µg/L) because of changes in laboratory instrumentation described under METHODS. Micro extraction procedures were used from 1989 through 1993 on vadose samplers, and on north, east, and south replicates of the shallow till wells.

In 1989 there were two detections of bromoxynil above lab MDL in the Carrington aquifer in the first sampling (ED 511, May 26). One of the two replicate detections was above the later (0.01 mg/L) MDL used for 1990 through 1993. Validity of field detections was supported by the following additional evidence. (i) Laboratory distilled water QC blanks for 1989 indicated no detections of bromoxynil. (ii) While distilled water wash procedures were used, tests of the field cleaning procedures used, reviewed previously in this report and reported in detail by Schuh et al. (1993), indicate that bromoxynil is effectively removed by a single water wash, and that field procedures consisting of multiple washes and up to 30 bails from the well should effectively remove bromoxynil. (iii) Moreover, even if this were not accepted, the largest bromoxynil detection (0.16 µg/L) was in the first sampled well (so there could be no bailer carryover from another well). The second detection was in the third well in the sampling order. Because the second well in the sampling order was a nondetect, carryover to the third well is also ruled out. (iv) Further supporting evidence of field validity is in detections at similar concentrations in the 3.0 m (10 ft.) saturated till well which were sampled using a different bailer, and in further detections at both levels on the following sample date (ED 559). Thus, there is replication within depth, between depths, and between dates. As of ED 511 bromide tracer had not yet been applied.

On ED 559 (July 13) there were four additional apparent detections of bromoxynil at concentrations between 0.0017 and 0.0024 µg/L in the Carrington aquifer well. <u>These apparent detections are below the laboratory MDL (at 95% confidence) and thus must be held in lower confidence than detections measured on the previous date.</u> However, as on the previous sample

date, there were no "apparent" detections in laboratory deionized water blanks. There were corresponding detections (largest concentration was 0.0078 µg/L) and apparent (below lab MDL) detections of bromoxynil in the overlying saturated till. There were also bromoxynil detections above MDL in the previous sampling time, as discussed above.

In addition, there are three other factors of substantial supporting evidence. First, hydrologic conditions, as indicated by piezometric traces for the saturated till and the Carrington aquifer indicate that the samples on ED 559 corresponded closely to the period of peak recharge to the saturated till, and also to the time of pressure drawdown in the Carrington aquifer from irrigation pumping, which increased water movement from the saturated till to the aquifer. Second, measurements of bromide tracer indicated that bromide concentrations increased up to, and peaked on the same sampling date (ED 559) in all sampled Carrington aquifer wells. Bromide movement was discussed thoroughly in Schuh et al. (1994a), and demonstrated that high solubility chemical species were capable of rapid movement to the aquifer.

The third factor is that several other pesticides were detected in the Carrington aquifer and in the saturated till on this date. These included diclofop, dimethoate, trifluralin, and methyl parathion. This sampling date was unique in the five year experiment with respect to the multiple detections. Hydrologic causes, explained in Schuh et al. (1994a) included substantial spring infiltration; a large rain soon after pesticide and tracer application; concentrated movement of water from the surface through runoff to microtopographic low areas; and aquifer drawdown from pumping. In addition, 1989 followed after a drought year (1988) which likely inhibited breakdown of chemicals applied in the previous year.

Nothing similar to the 1989 event occurred during the remaining three years of the experiment. There was only one additional event in which bromoxynil was detected. This occurred on ED 1746 (October 12, 1992). The detected bromoxynil concentration was well above lab MDL. There were no detections in lab deionized water blanks. Bromoxynil was also detected in one saturated till well. Trifluralin was also detected in the two replicate wells of the Carrington aquifer on the same sample date. Samples were taken using dedicated disposeable PTFE (teflon) bailers for each well. Field distilled water blanks taken on site indicated no detections.

Overall, bromoxynil was detected (above lab MDL) in the Carrington aquifer on two of fifteen sample dates over five years. On the first of those dates, there were two replicate detections in the Carrington aquifer. On the other there were no replicates. There were less reliable "qualitative" detections indicated on one other sample date. Thus, detections in the Carrington aquifer must be considered as both temporally and spatially sporadic. There is no indication of increasing levels of bromoxynil in the Carrington aquifer.

In the saturated till the pattern of detections was very similar to that of the Carrington aquifer. On ED 511 there were two detections of bromoxynil in the 3.0-m (10-ft.) saturated till well. One of the detections was above the later (1990 through 1993) lab MDL of 0.01 µg/L. There was one apparent, or possible detection in the 4.5-m (15 ft.) saturated till well on ED 511. Supporting evidence is the same as for the Carrington aquifer samples discussed above. On ED 559 there was one detection above MDL in the 4.5-m (15-ft.) well. There were also three additional apparent detections of lesser confidence. In the saturated till, as in the Carrington aquifer ED 559 was a date on which multiple pesticide detections were made. On ED 559 bromide tracer peaks were observed in the saturated till wells. There was one additional detection of bromoxynil on ED 1746 (October 12, 1992) corresponding to a single detection in the Carrington aquifer. There were no detections of bromoxynil in the vadose zone, but MDLs were substantially higher for vadose zone samples because of limited sample size and use of micro-extraction procedures.

From the standpoint of field transport of pesticides, these data indicate that transport of bromoxynil in water on a coarse loamy till soil, having a water table at about 3.6 to 4.2 m (12 to 14 ft.) below land surface, under sub-humid to semi-arid dryland farming conditions does occur. However, that occurence is usually sporadic. The data indicate that under certain extreme combinations of conditions, flux of pesticides to all levels within the till and in the surface of the aquifer, can occur relatively rapidly after application. Those conditions, represented by only one event in this five year experiment, included a drought year which inhibited pesticide breakdown, followed by a year with some substantial rainfall events early in the crop season. Mechanisms included combined early preferential flow of water and solute (likely through surface cracks or other macropores, or through concentrated infiltration in field micro depressions) mixing of preferential flow with deeper moving water still approaching the water table from spring recharge events, and drawdown of till water into the aquifer in response to irrigation pumping. However, all evidence indicates that under most normal circumstances bromoxynil movement to the water table is sporadic, that concentrations are extremely low (approaching MDL), and that times of movement are brief.

From a toxicological standpoint there have been no EPA maximum contaminant levels or lifetime health advisory levels established for bromoxynil. However, detection levels of bromoxynil made in this experiment are all extremely low, even when viewed against contaminants with relatively high levels of toxicity. The use of bromoxynil at labeled rates in a dryland crop rotation under agronomic practices common to North Dakota, and for soil, water table, and aquifer conditions similar to those tested in this experiment, is likely to be of little toxicological concern under current standards.

Diclofop

Diclofop was applied in 1988 and in 1991. Data for diclofop after 1989 are in Appendix Table B.2. Detections are illustrated on Figures 5, 6, and 7. Unlike bromoxynil, three sample sets for diclofop were taken in the vadose zone, the saturated till wells, and in the Carrington aquifer during the drought year of 1988. All samples were determined using micro-extraction procedures. Laboratory MDL ranged from 1 to 3.2 µg/L. No detections of diclofop were made in 1988.

After 1988 more sensitive macro-extraction procedures were used for the 6.8-m (22-ft.) wells, and whenever possible for the till wells. The only detections of diclofop were made in mid July (ED 559) of 1989, the year after the first application. On this date, no detections were made in the vadose zone. However, MDL for the micro-extraction procedures was relatively high (Table B.2). There were two detections in the Carrington aquifer at 6.8 m (22 ft.), and one in the saturated till at 4.5 m (15 ft.). These detections corresponded to the single period of nearly all applied pesticides during the five year experiment. They also corresponded to peak movement of a bromide tracer, and to the largest single defined recharge event of the five-year period of experiment. Finally, conditions of this event were those of a substantial recharge event following a year of drought, which caused minimal movement and degradation of pesticides from the previous year. Conditions of this event have been described previously by Schuh et al. (1994a), and have been explained in the previous discussion of bromoxynil. After the 1989 detection, there were no further detections of diclofop at any level of the till or in the aquifer for the remainder of the experiment.

Quality assurance, other than on-site depth replication provided in all of the sample years, indicated that spurious detections caused by inadequate field decontamination and environmental detritus were very unlikely. Tests of field cleaning procedures used during 1989 indicated that a multiple water-wash regime was adequate to remove all traces of diclofop below the 0.1 µg/L detection level applied in this experiment (Schuh et al. 1993). In addition to multiple distilled water washes, as many as 30 bailer volumes were extracted from the wells of the Carrington site, which would provide considerable additional cleaning. None of the field blanks used in 1990 through 1993 on the reported site, or on a neighboring site (sampled in 1992-1993) were found to have detections of diclofop. This included both bailer checks and open bottle tests left to trap wind-blown detritus during sample periods. Field blank results are summarized on the tables in Appendix B. Moreover, the only detection event corresponded to the substantial hydrologic, tracer, and pesticide evidence of water and contaminant movement.

From a toxicological standpoint, the EPA has not set an MCL or a lifetime health advisory level for diclofop. However, detections were extremely sporadic, were provided with only limited total ground-water replication (three out of 12 well samples on one sample date), and were detected on only one sample date in five years. The hydrologic conditions described for the period of movement

(following a drought in application year) were of an uncommon nature. It is concluded that diclofop does move to nearly all of the sampled depths of the Carrington site under certain conditions. However, that movement is limited to a few highly active field micro-sites and to conditions that are not frequent in North Dakota climate and agricultural practice. The use of diclofop at labeled rates in a dryland crop rotation under agronomic practices common to North Dakota is thus considered to be of small toxicological concern under field conditions described in this experiment, and under current toxicological standards.

Dimethoate

Dimethoate was applied to the experiment site in June of 1988 and in June of 1991. Detections of dimethoate were similar to diclofop. Data for dimethoate are in Appendix Table B.3. Detections are illustrated on Figures 5, 6, and 7. Dimethoate was sampled and tested using micro-extraction procedures on May 13, 1988. There were no background detections in any of the wells or the vadose samples. Dimethoate was not analyzed in the remaining 1988 samples.

In 1989 dimethoate was detected at all levels of the vadose zone, in the saturated till, and in the Carrington aquifer in mid July (ED 559). Dimethoate detections decreased in concentration and in frequency with depth. There were two detections out of three lysimeters sampled just below the root zone (1.5 m [5 ft.], Figure 5), and two detections out of four lysimeters sampled in the deeper vadose zone (2.1 m [7 ft.], Figure 5). Vadose zone concentrations varied from 2 to 8 µg/L (Table B.3). There were three detections out of four replicates in the shallow till wells (3.1 m [10 ft.], Figure 6). Concentrations were similar to the vadose samples and ranged from 1 to 12 µg/L. There were only two detections out of four replicate wells in the deeper (4.5 m [15 ft.]) till wells (Figure 6), and concentrations were about 0.45 µg/L. In the top of the Carrington aquifer (6.8 m [22 ft.], Figure 7) there was one dimethoate detection out of four depth-replicate samples, and the concentration level was 0.38 µg/L. .

After 1989, there were no detections of dimethoate at any level in the vadose zone or ground water during twelve sampling events, despite reapplication of dimethoate in 1991. The combination of climatologic, agronomic, and hydrologic events leading to the dimethoate detections in July of 1989 have already been discussed in the sections on hydrology and on tracer movement (Schuh et al. 1994a). Complementary movement and detections of other pesticides and their relationship to hydrologic and tracer evidence have also been discussed for diclofop and bromoxynil.

Reliability of reported detections is supported by direct investigations of field decontamination procedures (Schuh et al. 1993c). After applying water spiked with dimethoate to a bailer, multiple water washes resulted in cleaning of dimethoate to concentrations below 0.002 µg/L (MDL for the Carrington experiment were 0.2 µg/L). While there was some difficulty in getting

adequate analyte recovery in the bailer test, general results for pesticides indicated that those having octanol-water partition coefficients (K_{ow}) less than 2,000 were adequately cleaned by multiple distilled water washes alone. K_{ow} for dimethoate is five (Table 3).

In addition, dimethoate detections are replicated within depth, between depths, and between pesticides; and detections correspond to well documented tracer movement and recharge to the water table. Although dimethoate was applied again in 1991, none of the field blanks (bailer checks, and open bottle tests for wind blown detritus) resulted in detection of dimethoate during any of the subsequent sampling dates in 1990, 1991, 1992, and the spring of 1993.

From a toxicological standpoint, there is no EPA MCL established for dimethoate. LHA for dimethoate has been set at 1 µg/L. Vadose samples on the single detection date all exceeded the LHA. However, we do not drink vadose water, and there is significant decontamination potential in the vadose zone. The surface of the water table also indicated dimethoate concentrations above LHA. However, all detections of dimethoate in the deeper till water and in the Carrington aquifer were in concentrations below LHA. Dimethoate detections occurred on only one out of fifteen sample dates over five years, and evidence indicates that the single date of detection resulted from a relatively rare combination of events. The use of dimethoate at labeled rates in a dryland crop rotation under agronomic practices common to North Dakota is likely to be of minor toxicological concern under field conditions described in this experiment.

MCPA

MCPA was applied with bromoxynil in 1988 and 1991. Micro-extraction samples indicated that there were no detections of MCPA in 1988. In the fall of 1989 there were three detections of MCPA in the vadose zone. One occurred in the shallow vadose lysimeter (1.5 m [5 ft.]), and two occurred in the deeper (2.1-m [7-ft.]) vadose zone lysimeter. There was insufficient sample to test the shallow till wells (3.0 m [10 ft.]) for MCPA in 1989. Following 1989 there were no further detections of MCPA in the vadose zone. There were no detections of MCPA in the saturated till or the Carrington aquifer during the entire experiment. MDL for MCPA was higher than for other target species, however, and this may have influenced the number of detections in relation to other species.

Experiments with field decontamination procedures (Schuh et al. 1993c) indicated that a single water wash procedure alone achieved complete cleaning of MCPA to levels below 2 µg/L (with no additional apparent detections noted below 2 µg/L). Field cleaning procedures are thus considered to be more than adequate for MCPA in this experiment.

From a toxicological standpoint, there is no EPA MCL for MCPA. There is, however, an EPA lifetime health advisory concentration of 11 µg/L. Two of the vadose samples detected were above

11 µg/L. However, vadose water is not used for human, livestock, or wildlife consumption. There were no detections of MCPA in saturated ground water.

Methyl Parathion

Methyl parathion was applied to sunflowers in August of 1989 and in August of 1992. Methyl parathion was not tested in 1988. For spring 1989 through spring 1993 there was only one detection of methyl parathion on July 13 1989 (Appendix Table B.5, and Figures 5, 6, and 7). Two detections were made in both the till wells (two detections) and one detection in the Carrington aquifer. The time of detection corresponded to peak periods of drainage and recharge to the saturated till and Carrington aquifer, and to a period of maximum bromide tracer detection at all depths. Hydrology and tracer movement have been discussed previously in separate sections and in relation to previously discussed pesticides. After 1989 there were no further detections.

There is a problem with the detections of methyl parathion in 1989, in that they precede the date of application. Investigations of field decontamination procedures (Schuh et al. 1993) indicated that for four bailers soaked in a spiked solution of methyl parathion at two different concentrations (20 and 2 µg/L, two replicates each) all were cleaned to below 0.01 µg/L with a single distilled water wash. With multiple distilled water washes there were no "possible" trace detections noted. For the detection levels noted, between well cross transfer of contaminants caused by inadequate field decontamination procedures is not considered to be a likely problem. Of all of the additional field blanks tested for methyl parathion in 1990 through the spring of 1993, including both bailer wash blanks and open bottle tests for wind-blown detritus, none indicated presence of methyl parathion as a spurious contaminant (Appendix B).

We suspect that the detections made in July of 1989 likely represent a true field presence, but this is difficult to confirm without a known source. Some insight into the possible source is offered by an event in 1992 in which a spray plane sprayed the sunflower field with ethyl parathion on August 7, without contract or permission. Later the field was sprayed with methyl parathion as planned (on August 21). According to the Carrington Experiment Station Superintendent, similar events in which aerial sprayers had "done the station a favor" by using their extra spray on station crops, or where fields were mistakenly identified, had occurred in the past with sufficient frequency to cause the station to purchase an elevated sprayer of its own to minimize such errors. We consider unauthorized spraying to be the most plausible explanation for the early detection in 1989.

From a toxicological standpoint, methyl parathion has no EPA MCL. However, there is an LHA of 2 µg/L. The one detection in the Carrington aquifer in 1989 was above the LHA. However, this occurrence was not repeated within the four depth replicates on the detection date, and no further detections occurred in the Carrington aquifer from 1990 through the spring of 1993. There was one

detection of methyl parathion in the saturated till at above LHA in 1989. But although there were three replicates of detections (out of eight till samples, shallow and deep) there were no replicates above LHA. Following 1989 there were no additional detections in the saturated till. An additional interpretive problem arises from the unknown conditions of unauthorized spraying, since there was no assurance of application at a labeled rate or of proper application.

The single time of detection in ground water occurred with the single combination of events (a drought year, followed by a year of substantial concentrated rains and recharge early in the crop season) in which other pesticides moved to ground water. The event was not repeated in a full five years of testing. Further questions of the rates and conditions of application in relation to the sample date in which detections were made, caste further doubt on the validity of field comparison of these data. Clearly, if methyl parathion had not been applied until August 9 as planned, it could not have reached ground water in the preceding July. The single detection event in this experiment thus cannot be considered as representative of labeled use conditions.

Propiconazole

Propiconazole was applied in 1988 and in 1991. There were no detections of propiconazole at any level during the drought year of 1988. In 1989 there were repeated detections of propiconazole in the vadose lysimiters at both 1.5 m (5 ft.) (three detections out of three samples, about 1 µg/L) and 2.1 m (7 m) (two detections out of three samples, about 1.5 µg/L) on one sample date (ED 511 5/25/89) as shown on Appendix Table B.6. The time of vadose-zone detections corresponded to a period of recharge to the water table, and also to other detections of herbicides applied in 1988. The bromide tracer had not yet been applied. The hydrologic conditions for this recharge event were discussed previously in the sections on hydrology and tracer movement (Schuh et al. 1994a), and in previous descriptions of pesticide movement. Following 1989 there were no detections of propiconazole in the vadose zone.

In the saturated till and in the Carrington aquifer there were no detections of propiconazole in 1989. However, on July 23 of 1990 there was one detection each in the saturated till and in the Carrington aquifer (Figures 6 and 7, and Appendix Table B.6). From fall 1990 through spring 1993 there were no further detections of propiconazole at any level, vadose or saturated.

The authors believe that the propiconazole data are reliable indicators of field phenomena, and not spurious indicators of inadvertent procedural contamination. There are several reasons for this confidence. (1) During the course of the experiment there were no detections of propiconazole in bailer wash blanks or in open bottle blanks used to assess the potential for wind-blown contamination. An open bottle field DW blank on July 23, 1990 when the deep detections were made, indicated no contamination. (2) An independent experiment on effectiveness of cleaning

procedures used during the early part of this experiment (Schuh et al. 1993) indicated that propiconazole was effectively cleaned from a PVC bailer to well below the MDL applied in this experiment by a single distilled water wash. Multiple distilled water washes alone cleaned propiconazole from the bailer to concentrations at least one order of magnitude less than the MDL applied in the experiment, with no observed spikes that might indicate "qualitative" or possible presence of the analyte. Thus, decontamination procedures used should have been more than adequate.

In addition, (3) both detections made in 1990 were in the west wells. Since the west wells were always sampled first, and since separate bailers were used for each well set (saturated till and Carrington aquifer), both samples were taken using lab cleaned bailers, without opportunity for cross contamination from other wells. Finally, (4) propiconazole detections conform to periods of known recharge, tracer movement, and movement of other pesticides.

From a toxicological standpoint the EPA has established no MCL or LHA for propiconazole. Vadose detections constitute no threat to human health. There was only one detection date for ground water in five years, and on that date only one out of four replicates in the Carrington aquifer indicated a detection, and only one out of four replicates in the saturated till indicated a detection. Detections were therefore sporadic, ephemeral, and non replicated. A contaminant problem affecting human health using labeled rates and practices described for this experiment would seem to be unlikely for climatic and hydrologic conditions described in this experiment.

Trifluralin

Over five years of sampling, there were three times in which low levels of trifluralin were detected in the wells at the top of the Carrington aquifer. Two of the three sample times were those in which other pesticides were detected. Detections were also replicated between wells in two of the three sample times. The first detection date was ED 559 (July 13 1989). Trifluralin was detected in three of four Carrington aquifer wells. These data might be questioned on the basis of field decontamination of the bailer using multiple water washes alone between wells. Tests of bailer wash procedures following bailer contact with water having concentrations of 5 to 20 µg/L trifluralin have indicated that use of multiple distilled water washes followed by fifteen or more bailings of the well have resulted in trifluralin concentrations below 0.01 µg/L in four different well tests. All of the reported detections on ED 559 were above 0.01 µg/L (0.02 to 0.08 µg/L). However, this is still calling it a bit tight. For compounds like trifluralin, having high octanol/water partition coefficients, solvent wash decontamination should really be used, and our initial quality assurance was not fully adequate. The intrinsic value of these data is questionable.

On the basis of additional complementary evidence, however, we believe that these detections are likely valid field detections. Complementary evidence includes, 1. One of the detections is in the west well, which is the first well sampled. Possible inadequate field decontamination would not apply to this sample. 2. Another detection was in the east well. This well was sampled following the south well, and there were no detections in the south well. Thus, carryover contamination on the bailer to the east sample is unlikely. At least two of the three replicates were likely to be free from contamination caused by inadequate field decontamination. 3. Bailer cleaning tests began with initially high (4 to 20 µg/L) concentrations of trifluralin. The concentration of trifluralin in the east well was only 0.07 µg/L. Thus, multiple distilled water wash and bailing procedures would likely have cleaned the bailer well below the 0.03 µg/L level detected in the north well. Other circumstantial evidence includes the detection of a number of other applied chemicals in the Carrington aquifer well on this date, a peak of bromide tracer concentration (applied at the same time as trifluralin) in the Carrington aquifer well samples on this date, and hydrologic evidence of both drainage to the water table in the till, and drawdown from the till to the aquifer caused by pumping during the sample period. There were no trifluralin detections in the vadose zone or in the saturated till wells on ED 559.

The second trifluralin detection in the Carrington aquifer occurred on ED 1204 (April 19, 1991). There were no replications within the Carrington aquifer well set, between depths, or even with other chemicals or tracers on this date. The last detections occurred on ED 1747 (October 12 1992). Two replicate detections were found. All wells were bailed using dedicated polyethylene bailers that were left in the well between sampling periods, and all wells were sampled using dedicated disposable PTFE (teflon) bailers. Field distilled water blanks also indicated no detections of trifluralin. Field quality assurance and intrinsic values of this data is considered to be good. Complementary evidence can be found in one detection of trifluralin in a vadose zone sample on ED 1747, In detection of bromoxynil in one of the samples containing trifluralin on ED 1747, and in one detection of bromoxynil in the saturated till on ED 1747.

There were no trifluralin detections in the saturated till in 1989. There were three detections (two were identical) of trifluralin in the saturated till wells on ED 893 (July 21) 1990. These detections corresponded to a period of rising piezometric head in the saturated till. The intrinsic value of these samples might be questioned on the basis of water cleaning procedures. Complementary evidence supporting validity includes sampling order and levels of cleaning tested for water wash procedures on trifluralin. Detections were in west, north, and east samples. The west well was sampled first, so that the problem of transference between wells due to inadequate field decontamination is not applicable. Moreover, the east well was sampled after the south well in which there was no detection. Thus, cross contamination to the east well is unlikely. In addition, detection levels in the saturated till

wells are more than an order of magnitude higher than the residual detection levels indicated for use of multiple distilled water wash of bailers and multiple bailings of the well (Schuh et al. 1993c). Additional detections of trifluralin were on ED 1600 (May 18 1992) and ED 1936 (April 19, 1993). The last two detections were not replicated within the well set or between well sets. However, both samples were taken using a dedicated disposable PTFE bailer, and intrinsic value of the sample is considered to be good. It would appear that as with other pesticides and tracers, trifluralin movement is both spatially and temporally sporadic.

In the vadose zone, there were only two detections of trifluralin. The first occurred on May 8, 1990 (ED 858). It was not replicated within or between well sets, nor were there any other pesticide detections on this date. The second detection occurred on ED 1747 (October 12 1992), on the same date as two detections in the Carrington aquifer.

In general, the quality assurance of field detections of trifluralin varies over the experiment. Intrinsic values of earlier samples are questionable. However, there is substantial supporting evidence that indicates that the detections are likely real. Quality assurance and intrinsic value of later detections (1992 and 1993) is good. While individual detections might be questioned, it seems to be reasonably certain that some movement of trifluralin to all levels, vadose zone, saturated till, and Carrington aquifer did, in fact, occur. As with other pesticides, detections were few (three of fifteen sample days for 1989 through 1993) and both temporally and spatially sporadic.

These findings are consistent with those of Bischoff (1991), who found that trifluralin was the most frequently detected pesticide in ground water samples taken in South Dakota under soil, water table, and climatic conditions similar to those in this experiment. Bischoff (1991) also reported that trifluralin was one of the most commonly detected pesticides in soil samples taken as deep as 15 feet (4.5 m) on a Poinsett silt loam in South Dakota. The soil and water-table conditions of the South Dakota experiment were similar to those of the Carrington experiment. Also, detected concentrations (0.5 µg/L, and 0.28 µg/L respectively) in the saturated till and in the vadose zone at 2.1 m (7 ft.) in 1992 were similar to those (0.5 to 0.7 µg/L) predicted by Knighton (1990) for trifluralin at the 2.0-m (7-ft.) depth on a sandy soil 200 days after application, under conditions of transient darcian flow, using the LEACHM model (Wagonet and Hutson 1987).

Trifluralin movement, on the Carrington site, is not dependent on piston darcian flow alone. Rather, hydrologic and tracer evidence indicates that solute moves under a complex regime of piston flow, concentrated flow consisting of darcian flow through microtopographically determined active sites, preferential flow through macropores, reflux of preferentially recharged water that has reached the water table and then moved upward under capillary pressure into the vadose and soil profiles of neighboring (non recharge) sites, redrainage of reflux waters, and drawdown of the vadose and

saturated till waters to the Carrington aquifer under pressure gradients induced by pumping of the aquifer.

From a toxicological standpoint, as of November 1991 trifluralin was listed for regulation, but had no assigned MCL. The LHA for trifluralin was 5 μg/L. None of the detections reached the LHA, and almost all were near the lower detection limit with a concentration of about 0.4% of the LHA. There was no evidence during the course of the five year RECHARGE experiment of increasing levels of trifluralin at any sampled depth. Sparse detection levels were well below those of toxicological concern at all depths. Contamination of the Carrington aquifer with trifluralin to levels of toxicological concern under conditions of labeled use does not appear to be a likely problem under the climate, practices, and conditions of this experiment.

Summary

There were several detections of pesticides at all levels, including the vadose zone, saturated till, and Carrington aquifer, over the course of the five-year experiment. During this period there were only two times at which a substantial number of replicated detections were made, and in which multiple pesticide species were detected. These were in July of 1989 and July of 1990. Of these, 1989 had the largest number of detections. While both main detection periods occurred during times of major recharge events, and while both corresponded to evidence of tracer movement, only the 1989 set of detections exhibited a truly widespread range of pesticide detections. We believe that this was caused by an uncommon combination of events, including a drought year which inhibited the breakdown and movement of pesticides in 1988, followed by substantial rainfall and recharge in June of the following year. These conditions were not repeated within the five year period. If 1989 were removed from the analysis, overall detections would appear to be temporally and spatially sporadic, and usually non replicated or poorly replicated at all depths. While sporadic, pesticide detections generally do correspond to hydrologic evidence of water movement and to tracer peaks and spikes.

While some pesticide detections may be spurious, we believe that most of the data presented accurately reflects a field situation; that is, a highly complex and variable set of hydrologic events and mechanisms which move solute to the water table in localized pulses. The results of these pulses only become significant if individual pulses and events are sufficiently numerous, frequent, and high in contaminant concentration to effect large volumes of water in saturated storage, which serves as the final integrator. During the course of this experiment there were almost no single pulses or events in the saturated zone carrying pesticides with concentrations at levels of toxicological concern. There was also no evidence of "buildup" of any of the contaminants in the saturated till or in the aquifer over the five year period.

Implications of these findings for regulatory and compliance programs are that discrete samples on individual wells at single times are of little regulatory value because of the large variability of surface infiltration. Sudden and ephemeral appearances and disappearances of pesticides can occur during and following storm events, and these appearances are often spatially isolated, even within a few feet. Stress must be placed on trends, and on spatial replication of data in order to properly interpret the significance of any single or isolated detections.

INTERPRETING EXPERIMENT RESULTS IN A LARGER AREA CONTEXT

In order to understand the significance of site hydrology, tracer movement, and pesticide detections it is necessary to examine the relationship of the Carrington Experiment site to the surrounding area. The hydrology of the Carrington site, and its relationship to surrounding area hydrology, was discussed in detail by Schuh et al. (1994a). The results of that report are summarized briefly here.

First, recharge to the Carrington aquifer on the experiment site is likely above average. The experiment site is considered to be at least a moderately active recharge area. Average measured site recharge of about 40% of average annual precipitation is well above the 2.5 to 10 % of annual precipitation measured by Rehm et al. (1982) for a fine-textured North Dakota upland site. However, the sites measured by Rehm were of finer materials than the coarse-loamy soil materials measured on the Carrington Site.

Second, the experiment site was located in an area topographic low, and in a flow-through zone to the drainageway 176 m (600 ft.) east of the site which is a tributary of Scott Slough (Figure 3). Because of the levelness of the land surface, water travel for runoff is slow, allowing for enhanced recharge through local sites occupying microtopographic low elevations. Surficial features indicate that local recharge to the Carrington aquifer is likely above average for the aquifer as a whole.

Third, the thickness of the saturated till overlying the Carrington aquifer, is thinner (about 6.8 m or 22 ft.) on the experiment site than for most other areas of the aquifer. The average overall thickness of the till is about 12 m (40 ft.), and the overlying till thickness reaches more than 18 m (16 feet) over parts of the aquifer. Thus, impedance to recharge for the Carrington aquifer is lower on the Carrington site than for the aquifer in general. This too would enhance the role of the experimental site as a recharge area.

Finally, the experiment site is located within the cone of pressure drawdown caused by pumping of the aquifer for irrigation. It has been demonstrated that the drop in aquifer pressure caused by pumping contributes to an increase in recharge by a factor as large as four during the main recharge period in summer. Thus, local water use contributes to the local tendency toward greater recharge.

Because the experiment site is a local recharge area, the risk of contamination is likely higher on the measured site than for most of the area overlying the aquifer. Pesticide detections in the Carrington aquifer measured in this experiment are thus likely more frequent than average for the area. This interpretation does not exclude the likelihood that there are other sites, such as seasonal potholes, which are still more prone to contaminant movement.

While thicker saturated till would offer further protection to the Carrington aquifer, there is still concern over movement of contaminants to the saturated till, since domestic and livestock supply wells are sometimes placed in the saturated till zone. Water table depth between 3 and 4 m (10 and 13 ft.) below land surface is fairly common for the area, so that contaminants moving to the saturated till beneath the site would probably be fairly representative of the larger area. Increased movement of contaminants caused by capillary movement of water upward into the soil zone during recharge events, followed by redrainage when the aquifer is pumped, would likely have a high contamination potential at the 3-m (10 ft.) level, and would become a more serious problem with shallower depths to water.

The height of effective capillary upflow was between 1.5 and 2.0 m (5 to 7 ft.), so that capillary waters moving upward from a water table at about 2.0 to 2.5 m (7 to 8 ft.) would be expected to reach to the soil zone. However, at such a shallow depth a larger portion of upfluent waters would be expected to evaporate, and would not be available for reflux to the water table under the influence of pumping. The closer to the surface capillary waters reach during interactive flow, the more likely they are to dissolve contaminants and move them downward. Conversely, as the water table moves beyond 4 m (13 ft.) from land surface, and as capillary upflux fails to reach the root zone entirely, the likelihood of secondary contaminant movement in interactive waters from the water table decreases greatly. The gradually falling water table over the period of the experiment may have been an additional significant factor in decreasing pesticide detections following 1989.

Area Pesticide Detections

The Carrington aquifer water was sampled several times at two additional sites during each year of the experiment to see whether significant contamination was entering or leaving the general area of the experiment site, and to assess the contamination status of the aquifer itself. As explained previously, initial detections of alachlor and trifluralin beneath the experiment site were made in the fall of 1987 (but not in the spring of 1988). Early ground-water detections may have been caused by contamination during drilling of sample wells. The alachlor may have originated from application on a neighboring field to the west, which was in irrigated corn.

Two additional sets of wells were sampled for a general pesticide screening at location T 147N R 66W S 31ABA, located about 110 m (400 ft.) northwest of the experiment site and at location T 147N R 66W 31AAD located about 370 m (1232 ft.) southeast of the experiment site. The general direction of flow for the Carrington aquifer is from northwest to southeast (Figure 43 of Schuh et al. 1994b), and an approximate flow velocity would be about 40 feet per year. The ABA well was located in a road ditch (Figure 43 of Schuh et al. 1994a). Fields in all directions from the sample well were farmed using crop rotations common to the area. Till thickness was 8.4 m (28 ft.), and the well screen

in the Carrington aquifer was placed from 10 to 12 m (34 to 39 ft.) below land surface. The top of the well screen was thus about 1.8 m (6 ft.) below the surface of the Carrington aquifer. The AAD site was located in the drainageway leading to Scott slough. Till depth was 9.3 m (31 ft.). The screened interval of the well was placed at 18 to 19.5 m (60 to 65 ft.), about 18 m (30 ft.) below the top of the aquifer. The pesticide screening applied to these wells was intended to be general in nature, and to reflect the overall pesticide use in the area rather than simply on the plot itself. Analytes measured that were included in the experiment included diclofop, methyl parathion, and trifluralin. Sampling methods used were the same as those used on the experiment site. All laboratory work for the general area samples was done by the North Dakota State Health Department Laboratory.

Samples taken in 1987 and 1988 have already been discussed. Sampling was resumed in the fall of 1989 and continued through the spring of 1993. In October of 1989 a water sample was taken from the ABA well (Table 4) and an additional sample was taken from the south replicate of the Carrington aquifer wells on the experimental plot. There were no detections in either sample. Trifluralin had been detected in the south replicate of the experiment samples taken on the same date. However, the detected amount was below the detection level reported for the general area samples taken by the Health Department Laboratory (0.055 µg/L) for that sample set.

In 1990 samples were taken from the ABA and AAD wells, and also from the west replicate of the experiment site in May, July, and October (Table 5). There were no detections of any of the pesticides analyzed. In 1991 samples were taken from the ABA and AAD wells in May, August, and October (Table 6). There were no detections in either of the wells. Samples were also taken from the ABA and AAD wells in May and October of 1992 and in April of 1993 (Table 7). Results indicated no detections of pesticides for those sample times.

Results of water samples taken outside the experimental site support previous discussion indicating that detections underlying the experiment site were site specific. For very dilute concentrations of pesticides reaching ground water infrequently, and at sporadic and limited recharge "action" sites, concentrations would quickly dilute to negligible levels. Except for an initial detection of alachlor on the experiment site from a sample taken in 1987, there were no indications that pesticides were moving from or to the site, and there were no indications of accumulations of pesticide in Carrington aquifer near the experiment site during the five year experiment. The single alachlor detection was not repeated or verified in later sampling.

Hydrologic evidence indicates that the experiment site was located in a relatively high recharge area, and supporting area data indicates no detections of pesticide beyond the site area, it is concluded that while dilute quantities of pesticides do move to the Carrington aquifer and to the saturated till under certain conditions, the accumulation of detectable quantities of pesticides in

Table 4. 1989 pesticide detections in area wells.

Number following < is lab MDL.

Well Number	Analyte	10-26-89 µg/kg
E3	alachlor	< 0.45
	atrazine	< 3.8
	cyanazine	< 0.5
	dicamba	< 1.1
	diclofop	< 0.6
	fenvalerate	< 1.1
	MCPA	< 2.2
	metrabuzine	< 0.11
	metalachlor	< 0.78
	parathion -ethyl	< 0.17
	parathion-methyl	< 0.11
	picloram	< 1.12
	simazine	< 4.6
	triallate	< 0.09
	trifluralin	< 0.055
	2,4-D	< 2.25
147-66-31 ABA1	alachlor	< 0.45
	atrazine	< 3.8
	cyanazine	< 0.5
	dicamba	< 1.1
	diclofop	< 0.6
	fenvalerate	< 1.1
	MCPA	< 2.2
	metrabuzine	< 0.11
	metalachlor	< 0.78
	parathion -ethyl	< 0.17
	parathion-methyl	< 0.11
	picloram	< 1.12
	simazine	< 4.6
	triallate	< 0.09
	trifluralin	< 0.055
	2,4-D	< 2.25

Table 5a. 1990 pesticide detections in area wells (Continued on next page). Number following < is lab MDL.

Well Number	Analyte	5-9-90 µg/kg	7-23-90 µg/kg	10-15-90 µg/kg
147-66-31 ABA3	alachlor	< 0.45	< 0.4	< 0.22
	atrazine	< 3.8	< 3.5	< 5
	cyanazine	< 0.5	< 0.4	< 0.8
	dicamba	< 1.1	< 1	< 1
	diclofop	< 0.6	< 0.5	< 1
	fenvalerate	< 1.1	< 1	< 2
	MCPA	< 2.2	< 2	< 2
	metrabuzine	< 0.11	< 0.1	< 0.2
	metalachlor	< 0.78	< 0.7	< 1.4
	parathion -ethyl	< 0.17	< 0.15	< 0.3
	parathion-methyl	< 0.11	< 0.1	< 0.2
	picloram	< 1.12	< 0.08	< 1
	simazine	< 4.6	< 4.2	< 8.4
	triallate	< 0.09	< 0.08	< 0.16
	trifluralin	< 0.055	< 2	< 0.1
	2,4-D	< 2.25		< 2
147-66-31AAD3	alachlor	< 0.45	< 0.4	< 0.22
	atrazine	< 3.8	< 3.5	< 5
	cyanazine	< 0.5	< 0.4	< 0.8
	dicamba	< 1.1	< 1	< 1
	diclofop	< 0.6	< 0.5	< 1
	fenvalerate	< 1.1	< 1	< 2
	MCPA	< 2.2	< 2	< 2
	metrabuzine	< 0.11	< 0.1	< 0.2
	metalachlor	< 0.78	< 0.7	< 1.4
	parathion -ethyl	< 0.17	< 0.15	< 0.3
	parathion-methyl	< 0.11	< 0.1	< 0.2
	picloram	< 1.12	< 0.08	< 1
	simazine	< 4.6	< 4.2	< 8.4
	triallate	< 0.09	< 0.08	< 0.16
	trifluralin	< 0.055	< 2	< 0.1
	2,4-D	< 2.25		< 2

Table 5b. (Continued) 1990 pesticide detections in area wells .

Well Number	Analyte	5-9-90 µg/kg	7-23-90 µg/kg	10-15-90 µg/kg
W3	alachlor	< 0.45	< 0.4	< 0.22
	atrazine	< 3.8	< 3.5	< 5
	cyanazine	< 0.5	< 0.4	< 0.8
	dicamba	< 1.1	< 1	< 1
	diclofop	< 0.6	< 0.5	< 1
	fenvalerate	< 1.1	< 1	< 2
	MCPA	< 2.2	< 2	< 2
	metrabuzine	< 0.11	< 0.1	< 0.2
	metalachlor	< 0.78	< 0.7	< 1.4
	parathion -ethyl	< 0.17	< 0.15	< 0.3
	parathion-methyl	< 0.11	< 0.1	< 0.2
	picloram	< 1.12	< 0.08	< 1
	simazine	< 4.6	< 4.2	< 8.4
	triallate	< 0.09	< 0.08	< 0.16
	trifluralin	< 0.055	< 2	< 0.1
	2,4-D	< 2.25		< 2

Table 6. 1991 pesticide detections in area wells. Number following < is lab MDL.

Well Number	Analyte	5-2-91 µg/kg	8-6-91 µg/kg	10-7-91 µg/kg
147-66-31 ABA2	alachlor	NS	< 0.9	< 0.11
	atrazine	NS	< 7.7	< 2.5
	cyanazine	NS	< 1	< 0.4
	dicamba	NS	< 1	NS
	diclofop	NS	< 1.2	< 0.5
	fenvalerate	NS	< 2.2	< 1
	malathion	NS	< 0.5	< 0.2
	MCPA	NS	< 2	< 2
	metalachlor	NS	<1.56	< 0.7
	metrabuzine	NS	< 0.22	< 0.1
	parathion -ethyl	NS	< 0.34	< 0.15
	parathion-methyl	NS	< 0.22	< 0.1
	picloram	NS	< 1	NS
	simazine	NS	< 9.3	< 4.2
	triallate	NS	< 0.18	< 0.08
	trifluralin	NS	< 0.11	< 0.05
	2,4-D	NS	< 2	NS
147-66-31AAD1	alachlor	< 0.11	< .45	< 0.11
	atrazine	< 2.5	< 3.8	< 2.5
	cyanazine	< 0.4	< 0.5	< 0.4
	dicamba	< 1	NS	NS
	diclofop	< 0.5	< 0.6	< 0.5
	fenvalerate	< 1	< 1.1	< 1
	malathion	< 0.2	< 0.25	< 0.2
	MCPA	< 2	NS	< 2
	metalachlor	< 0.7	< 0.78	< 0.7
	metrabuzine	< 0.1	< 0.11	< 0.1
	parathion -ethyl	< 0.15	< 0.17	< 0.15
	parathion-methyl	< 0.1	< 0.11	< 0.1
	picloram	< 1	NS	NS
	simazine	< 4.2	< 4.6	< 4.2
	triallate	< 0.08	< 0.09	< 0.08
	trifluralin	< 0.05	< 0.055	< 0.05
	2,4-D	< 2	NS	NS

Table 7. 1992 and spring 1993 pesticide detections in area wells. Number following < is lab MDL.

Well Number	Analyte	5-20-92	10-23-92 *	4-22-93
		µg/kg	µg/kg	µg/kg
147-66-31 ABA2	alachlor	< 0.04	< 0.04	< 0.04
	atrazine	< .25	< .25	< .25
	cyanazine	< 0.02	< 0.02	NS
	dicamba	< 1	< 1	< 1
	diclofop	< 0.05	< 0.05	< 0.05
	fenvalerate	< 0.1	< 0.1	< 0.1
	malathion	< 0.02	< 0.02	< 0.04
	MCPA	NS	NS	NS
	metalachlor	< 0.01	< 0.01	< 0.01
	metribuzine	< 0.01	< 0.01	< 0.01
	parathion -ethyl	< 0.015	< 0.015	< 0.015
	parathion-methyl	< 0.01	< 0.01	< 0.01
	picloram	< 1	< 1	< 1
	simazine	< 0.45	< 0.45	< 0.45
	triallate	< 0.01	< 0.01	< 0.01
	trifluralin	< 0.005	< 0.005	< 0.005
	2,4-D	< 2	< 2	< 2
147-66-31AAD1	alachlor	< 0.04	< 0.04	< 0.04
	atrazine	< .25	< .25	< .25
	cyanazine	< 0.02	< 0.02	NS
	dicamba	< 1	< 1	< 1
	diclofop	< 0.05	< 0.05	< 0.05
	fenvalerate	< 0.1	< 0.1	< 0.1
	malathion	< 0.02	< 0.02	< 0.02
	MCPA	NS	NS	NS
	metalachlor	< 0.01	< 0.01	< 0.01
	metrabuzine	< 0.01	< 0.01	< 0.01
	parathion -ethyl	< 0.015	< 0.015	< 0.015
	parathion-methyl	< 0.01	< 0.01	< 0.01
	picloram	< 1	< 1	< 1
	simazine	< 0.45	< 0.45	< 0.45
	triallate	< 0.01	< 0.01	< 0.01
	trifluralin	< 0.005	< 0.005	< 0.005
	2,4-D	< 2	< 2	< 2

* 10-23-92 data exceded holding time

ground water, caused by labeled non point application of pesticides in normal rain-fed agricultural use, is not occurring in the vicinity of the Carrington Research Extension Center. Because the experimental site is indicated to be more vulnerable than other areas overlying the Carrington aquifer, accumulations of pesticides in detectable concentrations are not likely to occur in the Carrington aquifer, or in other similar confined aquifers in East Central North Dakota. However, it is possible that a shallower water table (less than 3 m from the surface) would significantly increase the potential for pesticide contamination of water in the saturated glacial till.

Impact of Agricultural Management

Aside from the option of less pesticide use, it appears that the primary impact of agricultural management on pesticide movement is related to the prevention of surface runoff, and minimizing the concentration of rain water in microtopographic low areas. Hydrologic analysis indicates that on the Carrington site, activity of surface water in dissolving and carrying solute is increased by multiple passes through the soil and vadose zone, resulting from surface concentration of water. As described by Schuh et al. (1993a,b) and Schuh et al. (1994a), water from precipitation first moves across the soil surface to microtopographic areas of low elevation, providing a mechanism for entrainment of pesticides at the soil surface.

Second, concentrations of water in microtopographic low positions of high activity move water more quickly and in greater quantities to the water table, providing an increased likelihood of dissolution of pesticides from the soil profile in microtopographic low areas. Water recharged to the water table redistributes laterally to other ground-water positions, and moves upward into the soil and vadose profiles under capillary actions. Movement of upfluent capillary water into the root zone offers another mechanism for moving pesticide, when upfluent waters reach contaminant laden layers of the soil or vadose zone. It also offers an opportunity for deposition of contaminants already introduced to the water table at higher profile positions. Finally, pumping of the aquifer provides the mechanism for drawdown of both water and contaminants.

The multiple paths of activity described above are attenuated by preventing surface redistribution of water. Hypothetically, under conditions of perfectly homogeneous piston flow, all of the above described mechanisms are diminished and potential movement for a given contaminant is limited to local direct vertical flow. Homogeneous infiltration and drainage eliminates contaminant entrainment potential from overland flow, highly concentrated local recharge, lateral redistribution at the water table from localized recharge, and upflux into neighboring soil and vadose zones. Capillary drawdown effect from pumping of the aquifer would also remain effective under conditions of quasi-piston flow described above.

It is hypothesized that the goal in minimizing contaminant movement to the water table would be to approximate as close as possible, conditions of homogeneous piston flow. To approach

homogeneous drainage, it would be desirable to localize infiltration in the immediate are of precipitation contact with the land surface. Essentially the problem is one of preventing runoff. Because this is identical to the strategy for preventing erosion, remedial practices would be expected to be much the same. Practices promoting this goal would include tillage practices promoting random roughness, crop residue cover, dense crop stem-soil contact configurations, and dense crop canopies to prevent slaking of the surface soil which would inhibit local infiltration and help form runoff channels to nearby microtopographic positions of low elevation. Counter to this practice, one would expect that low-pressure irrigation practices employing non distributed spray mechanisms, such as low pressure "bubble" nozzles, would tend to enhance surface movement and concentrated deep flow of irrigation waters and soil contaminants on some soils.

One problem with agronomic practices preventing runoff and promoting localized infiltration is that they also tend to help form macropores. Minimum and no-till practices promoting more substantial residue cover, and additional pesticides used for weed and insect control under minimum till conditions also tend to promote macropores through enhancement of faunal activity near the surface. Because insect burrowing and plant root effects are not large more than a meter beneath the surface (for most crop and animal species), and because dry conditions in the root zone would tend to absorb water moving through macropores before it reaches great depths, pesticide movement through such channels might be expected to be highly sporadic and local. However, water and solute movement through macropores does occur. For example, trifluralin detections in October of 1992 corresponded not to a single recharge event, as defined by substantial bulk flow to the water table or to the Carrington aquifer, but rather to a concentration of rainfall events. The presence of chloride tracers with the trifluralin, and the absence of evidence of substantial bulk flow of water support the belief that limited and sporadic movement of pesticides through macropores occurred at this time.

There is a dilemma, then, in delineating practices least prone to carrying pesticides to ground water. On one hand practices used to eliminate runoff and concentration of water in microtopographic low areas should decrease pesticide contamination. On the other hand, practices promoting this goal tend to also promote macropores which might enhance other means of flux to the water table. It would seem likely that for the conditions of this experiment, a loamy soil having a water table 2.5 to 4 m (7 to 13 ft.) beneath land surface, practices promoting localized infiltration would likely have the greatest net benefit, while for a shallower water table (much nearer the soil zone) macropore conduits would be more likely to provide a direct conduit to the water table itself, and net benefits of minimum tillage practices may not be so great. Quantitative benefits for use of practices promoting localized infiltration on pesticide use needs to be further assessed for different water table depths.

A second practice that would promote homogeneous drainage and also limit drainage to the water table is the use of early, broadcast or narrow-row seeded crops. Such crops would inhibit

localized runoff thorough soil-surface coverage. They would also tend to inhibit water movement to the water table through early use of water. Slow moving spring recharge waters would thus be partially intercepted by the crop, and precipitation during May and June, which was influential in carrying pesticides during this experiment, would be less likely to reach the water table because of crop use, or drier soil conditions resulting from crop use.

Use of small grain production for prevention of ground water contamination, is nothing more than a contaminant corollary of the common water use logic for planting small grains on the Northern Great Plains. Early root extraction of water enables efficient use of soil water for grain production. Because of less drainage from the root zone, less contaminant movement would also be expected to result. This logic seems to be born out by the evidence of the Carrington experiment. There was virtually no drainage, and no ground-water contamination under wheat in 1988. Of course 1988 was also a drought year. However, the other year with least vadose detections, and least overall detections of pesticide in ground-water contaminants was 1991, which was also in wheat.

In 1992 an experiment was initiated on the Carrington Station to examine the relation between cropping practices, recharge, and the movement of nitrates and pesticides to the aquifer. This experiment compares the effect of biological management (no additives that are not from a plant or animal source), integrated management (applying chemicals and fertilizers only as needed), and conventional agricultural production practices. Under biological management, fertility is maintained with manure, interseeding with green manure crops, and other methods. Early results (after two years) indicate that there were no verifiable detections of pesticides in the Carrington aquifer under any of the treatments, and that there was no significant difference in the amount of nitrates reaching the water table and the aquifer. Timing of movement, however, did differ between treatments (Schuh et al. 1994c). Since many factors influencing soil tilth and roughness act slowly over time, there remains the possibility of long-term effect due to management.

In summary, it is almost a trivial observation that practices that minimize recharge itself, should also minimize contaminant movement. These practices, in turn, are usually those that minimize runoff and erosion and maximize crop water use. Slow moving spring recharge waters (on glacial tills) and spring rains are best intercepted and used by crops, such as small grains, having early root and canopy formation. Additional benefits of such crops include better retention of precipitation at the point of surface contact, and minimization of multiple opportunities for solution and movement of pesticide to the water table which results from overland flow and concentration of pesticides in microtopographic low positions on the landscape.

In general, there seems to be a tradeoff between practices which would maximize localized surface retention through residue management, but which would also likely enhance the presence of macropores through enhancement of soil faunal habitat. It is likely that for the conditions of this

experiment (ei. water table at 2.5 to 4 m [7 to 13 ft.] below land surface) inhibition of surface water runoff and concentration would serve best to minimize pesticide movement to the water table. However, it is also possible that as the water table becomes shallower, the effects of direct movement through macropores could become more important. It is likely that brief and sporadic low concentration spikes of pesticide will occur from time to time under either regime. Further assessment of the advantages and disadvantages of each regime, and of the relationship of these practices to water table depth needs to be conducted.

Interpretation of Pesticide Detections in Water Samples

One problem of particular concern is the interpretation of pesticide detections in water samples from wells used to determine compliance with clean-water regulations. Pesticide detections in this experiment were seasonal (mainly in mid-summer), were related to specific hydrologic and climatic events, and were generally sporadic, spatially limited, and ephemeral in nature. If the regulatory problem is properly defined as one of protection of the ground-water supply for human consumption and other uses, then the relationship between specific detections and the long-term total concentration or accumulation of pesticides in the water supply must be carefully considered. Although spot detections of pesticides did occur in this experiment, there was no evidence of a long-term or wide-spread retention or buildup of any pesticide in the Carrington aquifer or in the saturated till. This observation is supported by samples both on and off site, and by the fact that many of the pesticides used in this experiment have been used in the agricultural area overlying the Carrington aquifer for many years.

The difficulty of interpreting single and isolated pesticide detections in water samples is further illustrated by the fact that in most cases detections were not replicated in samples from wells at the same approximate depth within a few meters from the initial detection. We believe that the results of this experiment confirm the importance of basing regulatory actions on sampling plans and regulatory interpretations that pay careful attention to the specific agronomic, climatic and hydrologic circumstances, and that the limitations of temporally and spatially limited data, or "snap shots" as they are sometimes called, be carefully considered. Special attention should be given to replication of detections in both time and space, and to interpretation of the trends and frequencies of pesticide pulses that reach the aquifer. While it is clear that many pesticides will reach ground water at shallow to moderate depths under certain limited and specified conditions; rare, sporadic, and dilute detections certainly do not warrant the degree of concern appropriate for aquifers where widespread, repeated, or consistent buildup of pesticides in quantities approaching indices of toxicological risk are noted.

CONCLUSIONS

On an experimental site farmed under a wheat-sunflower-soybean rotation from spring 1988 through spring 1993, several pesticides were detected in the vadose zone beneath the root zone (1.5 and 3.1 m [5 and 7 ft.]), in the saturated till (3.1 and 4.5 m [10 and 15 ft.]), and at the top (just below the till boundary) of a confined aquifer (the Carrington aquifer) at 6.8 m (22 ft.). In 1988 (a drought year) there were no detections at any level. However, lab detection levels for all pesticides were higher than in later years because of micro-extraction laboratory methods. There were multiple detections of pesticides at all sampled depths in the summer of 1989, the year following the drought. These detections were attributed to the combined effect of pesticide carryover from the drought year, and a substantial rainfall within a few days of application of pesticides. All detections were at levels below current health limits (MCL and HAL). Some detections were orders of magnitude below levels of health concern.

Following 1989, there were isolated pesticide detections in 1990 and in 1992. However, with the exception of conditions in 1989, few of the detections were replicated between wells, between depths, or between applied chemicals. Pesticide detections generally corresponded well to periods of documented recharge to the water table, and documented drawdown to the Carrington aquifer through pumping of irrigation wells. They also corresponded well with periods of peak detections of bromide, fluoride, and chloride tracers applied during the course of the experiment. Detections, however, were sporadic, and spatially and temporally discontinuous.

Patterns of pesticide detections correspond well with the fundamental mechanisms for solute movement described previously (Schuh et al. 1994a) for the Carrington site. These mechanisms are: (1) Infiltration and drainage is dominated by microtopography of the Carrington site. Water "runs off" from mictrotopographic high to microtopographic low plot areas, and drains through the root zone to the aquifer through these selective "active" sites. Differences in elevation determining the difference between active and inactive surface infiltration and recharge sites can be less than 2 cm. (2) Water draining to the phreatic surface on active sites redistributes laterally to positions underlying sites of lesser activity. The result is that water moves upward into the upper vadose and soil zones under capillary action from the water table. (3) Pumping of the aquifer causes pressure drawdown of the aquifer, and increases the gradient drawing water from the overlying till. The resulting receding water table also causes capillary drawdown from the upper vadose zone and from the lower soil zone. Each of these movements provides a mechanism for dissolution, concentration, and movement of solute.

Characteristics of pesticide detections in this experiment are consistent with the pattern of intermittent spikes measured for tracers. Conclusions of previous hydrology and tracer experiments (Schuh and Klinkebiel 1994, Schuh et al. 1994a) indicated that during the first year of application,

some solute moves to ground water through a coupled process of preferential flow which carries solute quickly to a level below the root zone, and bulk flow in which solute deposited below the root zone dilutes and moves slowly to the water table and there redistributes. However, during the first year most solute moves to a level just below the root zone and tends to remain there for succeeding years. In later years, occasional fluxes of localized recharge can carry solute to the water table in intermittent and spatially sporadic "spikes", which are usually of short duration and have little lasting effect on long-term levels in ground water. In fact, water samples taken from wells in road ditches and drainageways several hundred feet from the experiment field did not indicate any pesticide detections between 1988 and 1993.

The percent of samples having at least one pesticide detection on the Carrington site was similar in this experiment to large-scale ground-water sample surveys in both North Dakota and South Dakota (in the range of 3 to 20% depending on year and conditions). The common lack of temporal and spatial replication of detections is a matter of serious concern for the design of sample plans in regulatory programs. These results indicate that much of what is detected may not be related to a long-term contamination trends in some aquifers, and that considerable attention must be given to temporal and spatial replication of samples to adequately discern the actual contaminant status of the ground-water resource.

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APPENDIX A

Table A.1. Drill log for test hole at T147N, R66W, section 31, AAB.

Depth Interval (m)	Thickness (m)	Description
0.00 to 0.30	0.30	Topsoil
0.30 to 3.96	3.66	Clay; dark yellowish brown, 30%, w/silt, sand&gravel (oxidized, silty-sandy till); low plasticity.
3.96 to 6.40	2.44	Clay; olive black, 35%, with silt, sand & gravel, (till); moderately plastic.
6.40 to 12.80	6.40	Sand; coarse grained, moderately well sorted, subrounded; quartz, w/secomtant shale, carbonate, & dark silicate grains; some lignite.
12.80 to 26.52	13.71	Sand & gravel; 20% gravel, subangular to subrounded; quartze, shale, abundant lignite; medium sant to pebbles of gravel; primarily very coarse granules of gravel; by 80' most gravel is tertiary to cretaceous local bedrock material, including Pierre shale.
26.52 to 36.58	10.06	Shale/Clay; olive black clay to moderately indurated shale bedrock (Pierre Shale)

APPENDIX B: PESTICIDE DATA

APPENDIX B.1 BROMOXYNIL CONCENTRATIONS

Table B.1.a. **Spring 1988 to Fall 1988 water Bromoxynil concentrations measured at Carrington ND.**

There were no bromoxynil determinations made in 1988. Micro-extraction procedures were still in development.

Table B.1.b. **Spring 1989 to Fall 1989 water Bromoxynil concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.5	N	-	.1250	NS	NS	-	.025
1.5	E	-	.1250	NS	NS	-	.025
1.5	W	-	.1250	NS	NS	NS	.025
2.1	N	-	.1250	NS	NS	-	.025
2.1	E	-	.1250	NS	NS	NS	.025
2.1	W	-	.1250	NS	NS	NS	*W&E
3.0-3.2	N	-	.0025	NS	NS	NS	ND
3.0-3.2	E	**.0028**	.0025	NS	NS	NS	ND
3.0-3.2	S	-	.0025	NS	NS	NS	ND
3.0-3.2	W	**.0159**	.0025	NS	NS	NS	ND
4.3-4.6	N	-	.0025	*.0016*	.0025	-	.005
4.3-4.6	E	-	.0025	**.0078**	.0025	-	.005
4.3-4.6	S	-	.0025	*.0018*	.0025	-	.005
4.3-4.6	W	*.0013* -	.0025	.0020	.0025	-	.005
6.7-7.0	N	-	.0025	*00023*	.0025	-	.005
6.7-7.0	E	**.0048**	.0025	*.0017*	.0025	-	.005
6.7-7.0	S	-	.0025	*.0021*	.0025	-	.005
6.7-7.0	W	*.00159*	.0025	*.0020*	.0025	-	.005

Table B.1.c. **Spring 1990 to Fall 1990 water Bromoxynil concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.5	N	-	.50	-	.50	-		NS	
1.5	E	-	.50	-	.50	-	.50	NS	
1.5	W	-	.50	-	.50	-	.50	NS	
2.1	N	-	.57	-	2.86	-	.50	NS	
2.1	E	NS		-	.50	-	.50	NS	
2.1	W	-	.57	-	.53	-	.50	NS	
3.0-3.2	N	NS		NS		-	.01	NS	
3.0-3.2	E	NS		NS		-	.50	NS	
3.0-3.2	S	NS		NS		-	.01	NS	
3.0-3.2	W	NS		NS		-	.01	NS	
4.3-4.6	N	-	.50	-	.50	-	.01	-	.01
4.3-4.6	E	-	.50	-	.50	-		-	.01
4.3-4.6	S	-	.50	-	.50	-	.01	-	.01
4.3-4.6	W	-	.01	-	.01	-	.01	-	.01
6.7-7.0	N	-	.01	-	.01	-	.01	-	.01
6.7-7.0	E	-	.01	-	.01	-	.01	-	.01
6.7-7.0	S	-	.01	-	.01	-	.01	-	.01
6.7-7.0	W	-	.01	-	.01	-	.01	-	.01
FB		NS		-	.01	NS		NS	

Table B.1.d. **Spring 1991 to Fall 1991 water Bromoxynil concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.5	N	-	.05	-	.05	-	.05	-	.05
1.5	E	-	.05	-	.05	-	.05	-	.05
1.5	W	-	.05	-	.05	-	.05	-	.1
2.1	N	NS		-	.05	-	.05	-	.05
2.1	E	-	.05	-	.05	-	.05	-	.05
2.1	W	-	.05	-	.05	-	.1	-	.05
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.3-4.6	N	-	.05	-	.05	.07	.05	-	.05
4.3-4.6	E	-	.05	-	.05	-	.05	-	.05
4.3-4.6	S	-	.05	-	.05	-	.05	-	.05
4.3-4.6	W	-	.01	-	.01	-	.01	-	.01
6.7-7.0	N	-	.01	-	.01	-	.01	-	.01
6.7-7.0	E	-	.01	-	.01	-	.01	.02 D*	.01
6.7-7.0	S	-	.01	-	.01	-	.01	-	.01
6.7-7.0	W	-	.01	-	.01	-	.01	-	.01
FB 4.3-4.6		-	.01	.02 D*	.01	-	.01	-	.01
FB 6.7-7.0		-	.01	-	.01	-	.01	-	.01
FB OPEN		-	.01	NS		NS		NS	

Table B.1.e. **Spring 1992 to Spring 1993 water Bromoxynil concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	4-21-93 µg/L	MDL µg/L
1.5	N	-	.05	-	.05	-**	.05	NS	.05
1.5	E	-	.05	-	.05	-**	.05	NS	.05
1.5	W	-	.05	-	.05	-**	.05	NS	.05
2.1	N	-*	.05	-	.05	-**	.05	-***	.05
2.1	E	-*	.05	-	.05	-**	.05	-***	.05
2.1	W	-	.05	-	.05	-**	.1	-***	.1
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.3-4.6	N	-	.05	-	.05	-	.05	-	.05
4.3-4.6	E	-	.05	-	.05	-	.05	-	.05
4.3-4.6	S	-	.05	-	.05	-	.05	-	.05
4.3-4.6	W	-	.01	-	.01	0.02	.01	-	.01
6.7-7.0	N	-	.01	-	.01	NS		-	
6.7-7.0	E	-	.01	-	.01	-	.01	-	.01
6.7-7.0	S	-	.01	-	.01	0.05	.01	-	.01
6.7-7.0	W	-	.01	-	.01	-	.01	-	.01
FB 4.3-4.6		NS		NS		-	.01	NS	.01
FB 6.7-7.0		-	.01	-	.01	-	.01	-	.01
FB OPEN		NS		-	.01	NS		NS	

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined
*** All 1.52 and 2.13 vadose samples combined by depth.

APPENDIX B.2 DICLOFOP CONCENTRATIONS

Table B.2.a. **Spring 1988 to Fall 1988 water Diclofop concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank. (Continued next page).**

Depth m	Site	5-11-88 µg/L	MDL µg/L	6-2-88 µg/L	MDL µg/L	7-20-88 µg/L	MDL µg/L
.30	N	NS		NS		NS	
.30	E	-	5.5	NS		NS	
.30	W	-	5.5	NS		NS	
.5	N	-	5.5	NS		NS	
.5	E	-	5.5	NS		NS	
.5	W	-	5.5	NS		NS	
.9	N	NS		NS		NS	
.9	E	-	5.5	-	5.5	NS	
.9	W	NS		-	5.5	NS	
1.5	N	NS		NS		NS	
1.5	E	NS		-	5.5	-	2
1.5	N	NS		NS		NS	
2.1	E	NS		NS		NS	
3.2-3.5	N	NS		NS		NS	
3.2-3.5	E	NS		NS		NS	
3.2-3.5	S	NS		NS		NS	
3.2-3.5	W	NS		NS		NS	
4.3-4.6	N	NS		-	5.5	-	2
4.3-4.6	E	NS		-	5.5	-	2
4.3-4.6	S	NS		-	5.5	-	2
4.3-4.6	W	NS		-	5.5	-	2
6.7-7.0	N	NS		-	5.5	-	2
6.7-7.0	E	NS		-	5.5	-	2
6.7-7.0	S	NS		-	5.5	-	2
6.7-7.0	W	NS		-	5.5	-	2

Table B.2.a. Continued) Spring 1988 to Fall 1988 water Diclofop concentrations measured at Carrington ND.

Depth m	Site	9-27-88 µg/L	MDL µg/L	10-27-88 µg/L	MDL µg/L
.30	N	NS		NS	
.30	E	NS		NS	
.30	W	NS		NS	
.5	N	NS		NS	
.5	E	NS		NS	
.5	W	NS		NS	
.9	N	NS		NS	
.9	E	-	3.2	NS	
.9	W	NS		NS	
1.5	N	NS		NS	
1.5	E	-	3.2	NS	
1.5	W	NS		NS	
2.1	E	-	3.2	-	3.2
3.2-3.5	N	NS		NS	
3.2-3.5	E	NS		NS	
3.2-3.5	S	NS		NS	
3.2-3.5	W	NS		NS	
4.3-4.6	N	-	3.2	-	1
4.3-4.6	E	-	3.2	-	1
4.3-4.6	S	-	3.2	-	1
4.3-4.6	W	-	3.2	-	1
6.7-7.0	N	-	3.2	NS	
6.7-7.0	E	-	3.2	-	1
6.7-7.0	S	-	3.2	NS	
6.7-7.0	W	-	3.2	NS	

Table B.2.b. Spring 1989 to Fall 1989 water Diclofop concentrations measured at Carrington, ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.

Depth m	Site	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.5	N	-	2	-	2	-	.20
1.5	E	-	2	-	2	-	.20
1.5	W	-	2	-	2	-	.20
2.1	N	-	2	-	2	-	.20
2.1	E	-	2	-	2	-*	.20
2.1	W	-	2	-	2	-*	ND
3.2-3.5	N	-	.25	-	2	NS	ND
3.2-3.5	E	-	.25	-	2	NS	ND
3.2-3.5	S	-	.25	-	2	NS	ND
3.2-3.5	W	-	.25	-	2	NS	ND
4.3-4.6	N	-	.25	-	.10	-	.04
4.3-4.6	E	-	.25	-	.10	-	.04
4.3-4.6	S	-	.25	0.66	.10	-	.04
4.3-4.6	W	-	.25	-	.10	-	.04
		-					
6.7-7.0	N	-	.25	-	.10	-	.04
6.7-7.0	E	-	.25	-	.10	-	.04
6.7-7.0	S	-	.25	0.23	.10	-	.04
6.7-7.0	W	-	.25	2.68	.10	-	.04

* E and W samples for 2.13 m combined

Table B.2.c. **Spring 1990 to Fall 1990 water Diclofop concentrations measured at Carrington, ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* Indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.5	N	-	.50	-	.50	-	.50	-	.50
1.5	E	-	.50	-	.50	-	.50	NS	
1.5	W	-	.50	-	.50	-	.50	NS	
2.1	N	-	.50	-	.50	-	.50	-	.50
2.1	E	NS	.50	-	.50	-	.50	NS	
2.1	W	-	.50	-	.50	-	.50	NS	
3.2-3.5	N	NS		NS		-	.10	NS	
3.2-3.5	E	NS		NS		-	.50	NS	
3.2-3.5	S	NS		NS		-	.10	-*	.50
3.2-3.5	W	NS		NS		-	.10	-*	.50
4.3-4.6	N	-	.50	-	.50	-	.10	-	.10
4.3-4.6	E	-	.50	-	.50	-	.10	-	.10
4.3-4.6	S	-	.50	-	.50	-	.10	-	.10
4.3-4.6	W	-	.10	-	.10	-	.10	-	.10
6.7-7.0	N	-	.10	-	.10	-	.10	-	.10
6.7-7.0	E	-	.10	-	.10	-	.10	-	.10
6.7-7.0	S	-	.10	-	.10	-	.10	0.1 D*	.10
6.7-7.0	W	-	.10	-	.10	-	.10	-	.10
FB OPEN		-	.10	-	.10				

* combined samples

Table B.2.d. **Spring 1991 to Fall 1991 water Diclofop concentrations measured at Carrington, ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* Indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.5	N	-	.50	-	.50	-	.50	-	.50
1.5	E	-	.50	-	.50	-	.50	-	.50
1.5	W	-	.50	-	.50	-	.50	-	1
2.1	N	NS		-	.50	-	.50	-	.50
2.1	E	-	.50	-	.50	-	.50	-	.50
2.1	W	-	.50	-	.50	-	1	-	.50
3.2-3.5	N	NS		NS		NS		NS	
3.2-3.5	E	NS		NS		NS		NS	
3.2-3.5	S	NS		NS		NS		NS	
3.2-3.5	W	NS		NS		NS		NS	
4.3-4.6	N	-	.50	-	.50	-	.50	-	.50
4.3-4.6	E	-	.50	-	.50	-	.50	-	.50
4.3-4.6	S	-	.50	-	.50	-	.50	-	.50
4.3-4.6	W	-	.10	-	.10	-	.10	-	.10
6.7-7.0	N	-	.10	-	.10	-	.10	-	.10
6.7-7.0	E	-	.10	-	.10	-	.10	-	.10
6.7-7.0	S	-	.10	-	.10	-	.10	-	.10
6.7-7.0	W	-	.10	-	.10	-	.10	-	.10
FB 4.3-4.6		-	.10	-	.10	-	.10	-	.10
FB 6.7-7.0		-	.10	-	.10	-	.10	-	.10
FB OPEN		-	.10	NS		NS		NS	

Table B.2.e. **Spring 1992 to Spring 1993 water Diclofop concentrations measured at Carrington, ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	4-21-93 µg/L	MDL µg/L
1.5	N	-	.5	-	.5	-**	.5	NS	.5
1.5	E	-	.5	-	.5	-**	.5	NS	.5
1.5	W	-	.5	-	.5	-**	.5	NS	.5
2.1	N	-*	.5	-	.5	-**	.5	-**	.5
2.1	E	-*	.5	-	.5	-**	.5	-**	.5
2.1	W	-	.5	-	.5	-**	.5	-**	.5
3.2-3.5	N	NS		NS		NS		NS	
3.2-3.5	E	NS		NS		NS		NS	
3.2-3.5	S	NS		NS		NS		NS	
3.2-3.5	W	NS		NS		NS		NS	
4.3-4.6	N	-	.5	-	.5	-	.5	-	.5
4.3-4.6	E	-	.5	-	.5	-	.5	-	.5
4.3-4.6	S	-	.5	-	.5	-	.5	-	.5
4.3-4.6	W	-	.10	-	.10	-	.10	-	.10
6.7-7.0	N	-	.10	-	.10	-	.10	-	.10
6.7-7.0	E	-	.10	-	.10	-	.10	-	.10
6.7-7.0	S	-	.10	-	.10	-	.10	-	.10
6.7-7.0	W	-	.10	-	.10	-	.10	-	.10
FB 4.3-4.6		NS		NS		-	.10	NS	
FB 6.7-7.0		-	.10	-	.10	-	.10	-	.10
FB OPEN		NS		-	.10			NS	

* combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined
*** All 1.52 and 2.13 vadose samples combined by depth.

APPENDIX B.3 DIMETHOATE CONCENTRATIONS

Table B.3.a. **Spring 1988 to Fall 1988 water Dimethoate concentrations measured at Carrington ND.**

There were no dimethoate determinations made in 1988. Micro-extraction procedures were still in development.

Table B.3.b. **Spring 1989 to to Fall 1989 water Dimethoate concentrations measured at Carrington ND. (-) is nondetect. NS indicates no sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.5	N	-	2	-	.4	-	1
1.5	E	-	2	4.38	.4	-	1
1.5	W	-	2	6.34	.4	-	1
2.1	N	-	2	2.57	.4	-	1
2.1	E	-	2	-	.4	-*	1
2.1	W	-	2	8.05	.4	-*	*E&W
3.2-3.5	N	-	1	1.24	.4	NS	ND
3.2-3.5	E	-	1	11.47	.4	NS	ND
3.2-3.5	S	-	1	-	.4	NS	ND
3.2-3.5	W	-	1	8.35	.4	NS	ND
4.3-4.6	N	-	1	-	.2	-	.10
4.3-4.6	E	-	1	0.44	.2	-	.10
4.3-4.6	S	-	1	0.45	.2	-	.10
4.3-4.6	W	-	1	-	.2	-	.10
		-					
6.7-7.0	N	-	1	-	.2	-	.10
6.7-7.0	E	-	1	-	.2	-	.10
6.7-7.0	S	-	1	-	.2	-	.10
6.7-7.0	W	-	1	0.38	.2	-	.10

* E and W samples for 2.13 m combined

Table B.3.c. **Spring 1990 to Fall 1990 water Dimethoate concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.5	N	-	.90	-	.90	-	.90	-	.90
1.5	E	-	.90	-	.90	-	.90	NS	
1.5	W	-	.90	-	.90	-	.90	NS	
2.1	N	-	.90	-	.90	-	.90	-	.90
2.1	E	NS		-	.90	-	.90	NS	
2.1	W	-	.90	-	.90	-	.90	NS	
3.2-3.5	N	NS		NS		-	.20	NS	
3.2-3.5	E	NS		NS		-	.90	NS	
3.2-3.5	S	NS		NS		-	.20	-*	.90
3.2-3.5	W	NS		NS		-	.20	-*	.90
4.3-4.6	N	-	.90	-	.90	-	.20	-	.20
4.3-4.6	E	-	.90	-	.90	-	.20	-	.20
4.3-4.6	S	-	.90	-	.90	-	.20	-	.20
4.3-4.6	W	-	.18	-	.20	-	.20	-	.20
6.7-7.0	N	-	.18	-	.20	-	.20	-	.20
6.7-7.0	E	-	.18	-	.20	-	.20	-	.20
6.7-7.0	S	-	.18	-	.20	-	.20	-	.20
6.7-7.0	W	-	.18	-	.20	-	.20	-	.20
FB (OPEN)		-	.18	-	.90				

Table B.3.d. **Spring 1991 to Fall 1991 water Dimethoate concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.5	N	-	.9	NS		-	.9	-	.9
1.5	E	-	.9	NS		-	.9	-	.9
1.5	W	-	.9	NS		-	.9	-	2
2.1	N	NS		NS		-	.9	-	.9
2.1	E	-	.9	NS		-	.9	-	.9
2.1	W	-	.9	NS		-	2	-	.9
3.2-3.5	N	NS		NS		NS		NS	
3.2-3.5	E	NS		NS		NS		NS	
3.2-3.5	S	NS		NS		NS		NS	
3.2-3.5	W	NS		NS		NS		NS	
4.3-4.6	N	-	.9	NS		-	.9	-	.9
4.3-4.6	E	-	.9	NS		-	.9	-	.9
4.3-4.6	S	-	.9	NS		-	.9	-	.9
4.3-4.6	W	-	.18	-	.18	-	.2	-	.2
6.7-7.0	N	-	.18	-	.18	-	.2	-	.2
6.7-7.0	E	-	.18	-	.18	-	.2	-	.2
6.7-7.0	S	-	.18	-	.18	-	.2	-	.2
6.7-7.0	W	-	.18	-	.18	-	.2	-	.2
FB 4.3-4.6		-	.18	-	.18	-	.2	-	.2
FB 6.7-7.0		-	.18	-	.18	-	.2	-	.2
FB OPEN		-	.18	NS		NS		NS	

Table B.3.e. **Spring 1992 through spring 1993 water Dimethoate concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* Indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	4-21-93 µg/L	MDL µg/L
1.5	N	-	1	-	1	-**	1	NS	1
1.5	E	-	1	-	1	-**	1	NS	1
1.5	W	-	1	-	1	-**	1	NS	1
2.1	N	-*	1	-	1	-**	1	-**	1
2.1	E	-*	1	-	1	-**	1	-**	1
2.1	W	-	1	-	1	-**	1	-**	1
3.2-3.5	N	NS		NS		NS		NS	
3.2-3.5	E	NS		NS		NS		NS	
3.2-3.5	S	NS		NS		NS		NS	
3.2-3.5	W	NS		NS		NS		NS	
4.3-4.6	N	-	1	-	1	-	1	-	1
4.3-4.6	E	-	1	-	1	-	1	-	1
4.3-4.6	S	-	1	-	1	-	1	-	1
4.3-4.6	W	-	.2	-	.2	-	.2	-	.2
6.7-7.0	N	-	.2	-	.2	-	.2	-	.2
6.7-7.0	E	-	.2	-	.2	-	.2	-	.2
6.7-7.0	S	-	.2	-	.2	-	.2	-	.2
6.7-7.0	W	-	.2	-	.2	-	.2	-	.2
FB 4.3-4.6		NS		NS		-	.2	NS	.2
FB 6.7-7.0		-	.2	-	.2	-	.2	-	.2
FB OPEN		NS		-	.2			NS	

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined
*** All 1.52 and 2.13 vadose samples combined by depth. es combined by depth.

APPENDIX B.4 MCPA CONCENTRATIONS

Table B.4.a. **Spring 1988 to Fall 1988 water MCPA concentrations measured at Carrington ND (Continued next page).**

Depth m	Site	5-11-88 µg/L	MDL µg/L	6-2-88 µg/L	MDL µg/L	7-20-88 µg/L	MDL µg/L
.30	N	NS		NS		NS	
.30	E	-	4	NS		NS	
.30	W	-	4	NS		NS	
.5	N	-	4	NS		NS	
.5	E	-	4	NS		NS	
.5	W	-	4	NS		NS	
.9	N	NS		NS		NS	
.9	E	NS		NS		NS	
.9	W	NS		NS		NS	
1.5	N	NS					
1.5	E	NS		NS		NS	
1.5	W	NS		NS		NS	
2.1	E	NS		NS		NS	
3.2-3.5	N	NS		NS		NS	
3.2-3.5	E	NS		NS		NS	
3.2-3.5	S	NS		NS		NS	
3.2-3.5	W	NS		NS		NS	
4.3-4.6	N	NS		-	2.5	-	4
4.3-4.6	E	NS		-	2.5	-	4
4.3-4.6	S	NS		-	2.5	-	4
4.3-4.6	W	NS		-	2.5	-	4
6.7-7.0	N	NS		-	2.5	-	4
6.7-7.0	E	NS		-	2.5	-	4
6.7-7.0	S	NS		-	2.5	-	4
6.7-7.0	W	NS		-	2.5	-	4

Table B.4.a. **(Continued) Spring 1988 to Fall 1988 water MCPA concentrations measured at Carrington ND.**

Depth m	Site	9-27-88 µg/L	MDL µg/L	10-27-88 µg/L	MDL µg/L
.30	N	NS		NS	
.30	E	NS		NS	
.30	W	NS		NS	
.5	N	NS		NS	
.5	E	NS		NS	
.5	W	NS		NS	
.9	N	NS		NS	
.9	E	NS		NS	
.9	W	NS		NS	
1.5	N	NS		NS	
1.5	E	NS		NS	
1.5	W	NS		NS	
2.1	E	NS		NS	
3.2-3.5	N	NS		NS	
3.2-3.5	E	NS		NS	
3.2-3.5	S	NS		NS	
3.2-3.5	W	NS		NS	
4.3-4.6	N	-	4	-	2
4.3-4.6	E	-	4	-	2
4.3-4.6	S	-	4	-	2
4.3-4.6	W	-	4	-	2
6.7-7.0	N	NS		NS	
6.7-7.0	E	NS		-	2
6.7-7.0	S	NS		NS	
6.7-7.0	W	NS		NS	

Table B.4.b. **Spring 1989 to Fall 1989 water MCPA concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.52	N	-	75	NS	NS	3.15	3.0
1.52	E	-	75	NS	NS	BDL	3.0
1.52	W	-	75	NS	NS	NS	3.0
2.13	N	-	75	NS	NS	77.32	3.0
2.13	E	-	75	NS	NS	14.67*	3.0
2.13	W	-	75	NS	NS	*	3.0
3.0-3.2	N	-	6.3	NS	NS	NS	ND
3.0-3.2	E	-	6.3	NS	NS	NS	ND
3.0-3.2	S	-	6.3	NS	NS	NS	ND
3.0-3.2	W	-	6.3	NS	NS	NS	ND
4.5-4.9	N	-	6.3	-	6.3	-	25
4.5-4.9	E	-	6.3	-	6.3	-	25
4.5-4.9	S	-	6.3	-	6.3	-	25
4.5-4.9	W	-	6.3	-	6.3	-	25
6.1-6.4	N	-	6.3	-	6.3	-	25
6.1-6.4	E	-	6.3	-	6.3	-	25
6.1-6.4	S	-	6.3	-	6.3	-	25
6.1-6.4	W	-	6.3	-	6.3	-	25

* E and W samples for 2.13 m combined

Table B.4.c. **Spring 1990 to Fall 1990 water MCPA concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.52	N	-	210	-	210	-		NS	
1.52	E	-	210	-	210	-	210	NS	
1.52	W	-	210	-	210	-	210	NS	
2.13	N	-	310	-	210	-	210	NS	
2.13	E	NS		-	210	-	210	NS	
2.13	W	-	240	-	210	-	210	NS	
3.0-3.2	N	NS		NS		-	210	NS	
3.0-3.2	E	NS		NS		-	40	NS	
3.0-3.2	S	NS		NS		-	40	NS	
3.0-3.2	W	NS		NS		-	40	NS	
4.5-4.9	N	-	210	-	210	-	40	-	40
4.5-4.9	E	-	210	-	210	NS		-	40
4.5-4.9	S	-	210	-	210	-	40	-	40
4.5-4.9	W	-	41	-	41	-	40	-	40
6.1-6.4	N	-	40	-	41	-	40	-	40
6.1-6.4	E	-	40	-	41	-	40	-	40
6.1-6.4	S	-	40	-	41	-	40	-	40
6.1-6.4	W	-	40	-	41	-	40	-	40
FB		-	210	-	41				

Table B.4.d. **Spring 1991 to Fall 1991 water MCPA concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL.* Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.52	N	-	200	NS		-	200	-	200
1.52	E	-	200	NS		-	200	-	200
1.52	W	-	200	NS		-	200	-	400
2.13	N	NS		NS		-	200	-	200
2.13	E	-	200	NS		-	200	-	200
2.13	W	-	200	NS		-	400	-	1
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	200	NS		-	200	-	200
4.5-4.9	E	-	200	NS		-	200	-	200
4.5-4.9	S	-	200	NS		-	200	-	200
4.5-4.9	W	-	40	-	40	-	40	-	40
6.1-6.4	N	-	40	-	40	-	40	-	40
6.1-6.4	E	-	40	-	40	-	40	-	40
6.1-6.4	S	-	40	-	40	-	40	-	40
6.1-6.4	W	-	40	-	40	-	40	-	40
FB 4.5-4.9		-	40	-	40	-	40	-	40
FB 6.1-6.4		-	40	NS		NS		NS	
FB OPEN									

Table B.4.e. **Spring 1992 to Spring 1993 water MCPA concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	4-21-93 µg/L	MDL µg/L
25	N	-	25	-	25	-**	25	NS	
25	E	-	25	-	25	-**	25	NS	
25	W	-	25	-	25	-**	25	NS	
25	N	-*	25	-	25	-**	25	-**	25
25	E	-*	25	-	25	-**	25	-**	25
25	W	-	25	-	25	-**	25	-**	25
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	25	-	25	-	25	-	25
4.5-4.9	E	-	25	-	25	-	25	-	25
4.5-4.9	S	-	25	-	25	-	25	-	25
4.5-4.9	W	-	5	-	5	-	5	-	5
6.1-6.4	N	-	5	-	5	NS	5	6.9	5
6.1-6.4	E	-	5	-	5	-	5	-	5
6.1-6.4	S	-	5	-	5	-	5	-	5
6.1-6.4	W	-	5	-	5	-	5	-	5
FB 4.5-4.9		NS		NS		-	5	NS	
FB 6.1-6.4		-	5	-	5	-	5	-	5
FB OPEN		NS		-	5			NS	

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined
*** All 1.52 and 2.13 vadose samples combined by depths combined by depth.

APPENDIX B.5 METHYL PARATHION CONCENTRATIONS

Table B.5.a. Spring 1988 to Fall 1988 water Methyl Parathion concentrations measured at Carrington ND.

There were no methyl parathion determinations made in 1988.

Table B.5.b. **Spring 1989 to Fall 1989 water Methyl Parathion concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.52	N	-	.30	-	.10		.10
1.52	E	-	.30	-	.10		.10
1.52	W	-	.30	-	.10		.10
2.13	N	-	.30	-	.10		.10
2.13	E	-	.30	-	.10	-*	.10
2.13	W	-	.30	-	.10	-*	*E&W
3.0-3.2	N	-	.20	0.24	.04	NS	ND
3.0-3.2	E	-	.20	-	.04	NS	ND
3.0-3.2	S	-	.20	-	.04	NS	ND
3.0-3.2	W	-	.20	-	.10	NS	ND
4.5-4.9	N	-	.20	-	.04	-	.02
4.5-4.9	E	-	.20	0.22	.04	-	.02
4.5-4.9	S	-	.20	4.59	.04	-	.02
4.5-4.9	W	-	.20	-	.04	-	.02
6.1-6.4	N	-	.20	-	.04	-	.02
6.1-6.4	E	-	.20	-	.04	-	.02
6.1-6.4	S	-	.20	-	.04	-	.02
6.1-6.4	W	-	.20	4.48	.04	-	.02

* E and W samples for 2.13 m combined

Table B.5.c. **Spring 1990 to Fall 1990 water Methyl Parathion concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.52	N	-	.20	-	.20	-	.15	-	.20
1.52	E	-	.20	-	.20	-	.15	NS	
1.52	W	-	.20	-	.20	-	.15	NS	
2.13	N	-	.20	-	.20	-	.15	-	.20
2.13	E	NS		-	.20	-	.15	NS	
2.13	W	-	.20	-	.20	.20 D*	.15	NS	
3.0-3.2	N	NS		NS		-	.03	NS	
3.0-3.2	E	NS		NS		-	.15	NS	
3.0-3.2	S	NS		NS		-	.03	-*	.20
3.0-3.2	W	NS		NS		-	.03	-*	.20
4.5-4.9	N	-	.03	-	.03	-	.03	-	.03
4.5-4.9	E	-	.03	-	.03	-	.03	-	.03
4.5-4.9	S	-	.03	-	.03	-	.03	-	.03
4.5-4.9	W	-	.03	-	.03	-	.03	-	.03
6.1-6.4	N	-	.03	-	.03	-	.03	-	.03
6.1-6.4	E	-	.03	-	.03	-	.03	-	.03
6.1-6.4	S	-	.03	-	.03	-	.03	-	.03
6.1-6.4	W	-	.03	-	.03	-	.03	-	.03
FB		-	.2	-	.03				

* combined samples

Table B.5.d. **Spring 1991 to Fall 1991 water Methyl Parathion concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.52	N	-	.15	-	.15	-	.2	-	.2
1.52	E	-	.15	-	.15	-	.2	-	.2
1.52	W	-	.15	-	.15	-	.2	-	.4
2.13	N	NS		-	.15	-	.2	-	.2
2.13	E	-	.15	-	.15	-	.2	-	.2
2.13	W	-	.15	-	.15	-	.4	-	.2
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	.15	-	.15	-	.2	-	.2
4.5-4.9	E	-	.15	-	.15	-	.2	-	.2
4.5-4.9	S	-	.15	-	.15	-	.2	-	.2
4.5-4.9	W	-	.03	-	.03	-	.03	-	.03
6.1-6.4	N	-	.03	-	.03	-	.03	-	.03
6.1-6.4	E	-	.03	-	.03	-	.03	-	.03
6.1-6.4	S	-	.03	-	.03	-	.03	-	.03
6.1-6.4	W	-	.03	-	.03	-	.03	-	.03
FB 4.5-4.9		-	.03	-	.03	-	.03	-	.03
FB 6.1-6.4		-	.03	-	.03	-	.03	-	.03
FB OPEN		-	.03	NS		NS		NS	

Table B.5.e. **Spring 1992 to Spring 1993 water Methyl Parathion concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	4-21-93 µg/L	MDL µg/L
25	N	-	.2	-	.2	-**	.2	-	.2
25	E	-	.2	-	.2	-**	.2	***	.2
25	W	-	.2	-	.2	-**	.2	***	.2
25	N	-*	.2	-	.2	-**	.2	-	.2
25	E	-*	.2	-	.2	-**	.2	***	.2
25	W	-	.2	-	.2	-**	.2	***	.2
3.0-3.2	N	NS		NS		NS		NS	NS
3.0-3.2	E	NS		NS		NS		NS	NS
3.0-3.2	S	NS		NS		NS		NS	NS
3.0-3.2	W	NS		NS		NS		NS	NS
4.5-4.9	N	-	.2	-	.2	-	.2	-	.2
4.5-4.9	E	-	.2	-	.2	-	.2	-	.2
4.5-4.9	S	-	.2	-	.2	-	.2	-	.2
4.5-4.9	W	-	0.03	-	0.03	-	0.03	-	.03
6.1-6.4	N	-	0.03	-	0.03	-	0.03	-	.03
6.1-6.4	E	-	0.03	-	0.03	-	0.03	-	.03
6.1-6.4	S	-	0.03	-	0.03	-	0.03	-	.03
6.1-6.4	W	-	0.03	-	0.03	-	0.03	-	.03
FB 4.5-4.9		NS		NS		-	0.03	NS	
FB 6.1-6.4		-	0.03	-	0.03	-	0.03	-	.03
FB OPEN		NS		-	0.03			NS	

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined
*** All 1.5 m samples combined, and all 2.1 m samples combined

APPENDIX B.6 PROPICONAZOLE CONCENTRATIONS

Table B.6.a. Spring 1988 to Fall 1988 water Propiconazole concentrations measured at Carrington ND (Continued next page).

Depth m	Site	5-11-88 µg/L	MDL µg/L	6-2-88 µg/L	MDL µg/L	7-20-88 µg/L	MDL µg/L
.30	N	NS		NS		NS	
.30	E	-	20	NS		NS	
.30	W	-	20	NS		NS	
.5	N	-	20	NS		NS	
.5	E	-	20	NS		NS	
.5	W	-	20	NS		NS	
.9	N	NS		NS		NS	
.9	E	-	20	-	15	NS	
.9	W	NS		-	38	NS	
1.5	N	NS		NS		NS	
1.5	E	NS		-	15	-	15
1.5	W	NS		-	15	NS	
2.1	E	NS		NS		NS	
3.2-3.5	N	NS		NS		NS	
3.2-3.5	E	NS		NS		NS	
3.2-3.5	S	NS		NS		NS	
3.2-3.5	W	NS		NS		NS	
4.3-4.6	N	NS		-	20	-	15
4.3-4.6	E	NS		-	20	-	15
4.3-4.6	S	NS		-	20	-	15
4.3-4.6	W	NS		-	20	-	15
6.7-7.0	N	NS		-	20	-	15
6.7-7.0	E	NS		-	20	-	15
6.7-7.0	S	NS		-	20	-	15
6.7-7.0	W	NS		-	20	-	15

Table B.6.a. (Continued) Spring 1988 to Fall 1988 water Propiconazole concentrations measured at Carrington ND.

Depth m	Site µg/L	9-27-88 µg/L	MDL µg/L	10-27-88 µg/L	MDL µg/L
.30	N	NS		NS	
.30	E	NS		NS	
.30	W	NS		NS	
.5	N	NS		NS	
.5	E	NS		NS	
.5	W	NS		NS	
.9	N	NS		NS	
.9	E	-	5.65	NS	
.9	W	NS		NS	
1.5	N	NS		NS	
1.5	E	-	5.65	NS	
1.5	W	NS		NS	
2.1	E	-	5.65	-	5.65
3.2-3.5	N	NS		NS	
3.2-3.5	E	NS		NS	
3.2-3.5	S	NS		NS	
3.2-3.5	W	NS		NS	
4.3-4.6	N	-	5.65	-	.5
4.3-4.6	E	-	5.65	-	.5
4.3-4.6	S	-	5.65	-	.5
4.3-4.6	W	-	5.65	-	.5
6.7-7.0	N	-	5.65	NS	
6.7-7.0	E	-	5.65	-	.5
6.7-7.0	S	-	5.65	NS	
6.7-7.0	W	-	5.65	NS	

Table B.6.b. Spring 1989 to Fall 1989 water Propiconazole concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D[a] indicates that target analyte was detected in lab deionized water blank.

Depth m	Site µg/L	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.52	N	0.89	.25	-	2.0	-	.20
1.52	E	1.08	.25	-	2.0	-	.20
1.52	W	1.05	.25	-	2.0	-	.20
2.13	N	1.76	.25	-	2.0	-	.20
2.13	E	1.41	.25	-	2.0	-	.20
2.13	W	-	.25	-	2.0	NS	ND
3.0-3.2	N	-	.05	-	2.0	NS	ND
3.0-3.2	E	-	.05	-	2.0	NS	ND
3.0-3.2	S	-	.05	-	2.0	NS	ND
3.0-3.2	W	-	.05	-	2.0	NS	ND
4.5-4.9	N	-	.05	-	.05	-	.04
4.5-4.9	E	-	.05	-	.05	-	.04
4.5-4.9	S	-	.05	-	.05	-	.04
4.5-4.9	W	-	.05	-	.05	-	.04
6.1-6.4	N	-	.05	-	.05	-	.04
6.1-6.4	E	-	.05	-	.05	-	.04
6.1-6.4	S	-	.05	-	.05	-	.04
6.1-6.4	W	-	.05	-	.05	-	.04

Table B.6.c. **Spring 1990 to Fall 1990 water Propiconazole concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.52	N	-	.80	-	1	-	1	-	1
1.52	E	-	.80	-	1	-	1	NS	
1.52	W	-	.80	-	1	-	1	NS	
2.13	N	-	.80	-	1	-	1	-	1
2.13	E	NS		-	1	-	1	NS	
2.13	W	-	.80	-	1	-	1	NS	
3.0-3.2	N	NS		NS		-	1	NS	
3.0-3.2	E	NS		NS		-	1	NS	
3.0-3.2	S	NS		NS		-	1	-*	1
3.0-3.2	W	NS		NS		-	1	-*	1
4.5-4.9	N	-	.80	-	1	-	.20	-	.20
4.5-4.9	E	-	.80	-	1	-	1	-	.20
4.5-4.9	S	-	.80	-	1	-	.20	-	.20
4.5-4.9	W	-	.20	-	.20	.40	.20	-	.20
6.1-6.4	N	-	.20	-	.20	-	.20	-	.20
6.1-6.4	E	-	.20	-	.20	-	.20	-	.20
6.1-6.4	S	-	.20	-	.20	-	.20	-	.20
6.1-6.4	W	-	.20	-	.20	.30	.20	-	.20
FB		-	.80	-	.20				

* combined samples

Table B.6.d. **Spring 1991 to Fall 1991 water Propiconazole concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.52	N	-	1	-	1	-	1	-	1
1.52	E	-	1	-	1	-	1	-	1
1.52	W	-	1	-	1	-	1	-	2
1	N	NS		-	1	-	1	-	1
1	E	-	1	-	1	-	1	-	1
1	W	-	1	-	1	-	2	-	1
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	1	-	1	-	1	-	1
4.5-4.9	E	-	1	-	1	-	1	-	1
4.5-4.9	S	-	1	-	1	-	1	-	1
4.5-4.9	W	-	.20	-	.20	-	.20	-	.20
6.1-6.4	N	-	.20	-	.20	-	.20	-	.20
6.1-6.4	E	-	.20	-	.20	-	.20	-	.20
6.1-6.4	S	-	.20	-	.20	-	.20	-	.20
6.1-6.4	W	-	.20	-	.20	-	.20	-	.20
FB 4.5-4.9		-	.20	-	.20	-	.20	-	.20
FB 6.1-6.4		-	.20	-	.20	-	.20	-	.20
FB OPEN		-	.20	NS		NS		NS	

Table B.6.e. **Spring 1992 to Spring 1993 water Propiconazole concentrations measured at Carrington, ND.**

Depth m	Site µg/L	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L
25	N	-	.2	-	.2	-**	.2	-**	1
25	E	-	.2	-	.2	-**	.2	-**	1
25	W	-	.2	-	.2	-**	.2	-**	1
25	N	-*	.2	-	.2	-**	.2	-**	1
25	E	-*	.2	-	.2	-**	.2	-**	1
25	W	-	.2	-	.2	-**	.2	-**	1
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	.2	-	.2	-	.2	-	1
4.5-4.9	E	-	.2	-	.2	-	.2	-	1
4.5-4.9	S	-	.2	-	.2	-	.2	-	1
4.5-4.9	W	-	.03	-	.03	-	.03	-	.2
6.1-6.4	N	-	.03	-	.03	-	.03	-	.2
6.1-6.4	E	-	.03	-	.03	-	.03	-	.2
6.1-6.4	S	-	.03	-	.03	-	.03	-	.2
6.1-6.4	W	-	.03	-	.03	-	.03	-	.2
FB 4.5-4.9		NS		NS		-	.03	-	.2
FB 6.1-6.4		-	.03	-	.03	-	.03	-	.2
FB OPEN		NS		-	.03				

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined

APPENDIX B.7 TRIFLURALIN CONCENTRATIONS

Table B.7.a. **Spring 1988 to Fall 1988 water Trifluralin concentrations measured at Carrington ND.**

There were no trifluralin determinations made in 1988.

Table B.7.b. **Spring 1989 to Fall 1989 water Trifluralin concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	5-25-89 µg/L	MDL µg/L	7-13-89 µg/L	MDL µg/L	10-15-89 µg/L	MDL µg/L
1.52	N	-	.15	-	.10	-	.10
1.52	E	-	.15	-	.10	-	.10
1.52	W	-	.15	-	.10	-	.10
2.13	N	-	.15	-	.10	-	.10
2.13	E	-	.15	-	.10	-	.10
2.13	W	-	.15	-	.10	Combine	*E&W
3.0-3.2	N	-	.10	-	.10	NS	ND
3.0-3.2	E	-	.10	-	.10	NS	ND
3.0-3.2	S	-	.10	-	.10	NS	ND
3.0-3.2	W	-	.10	-	.10	NS	ND
4.5-4.9	N	-	.01	-	.02	-	.01
4.5-4.9	E	-	.01	-	.02	-	.01
4.5-4.9	S	-	.01	-	.02	-	.01
4.5-4.9	W	-	.01	-	.02	-	.01
6.1-6.4	N	-	.01	**0.03**	.02	**0.02**	.01
6.1-6.4	E	-	.01	-	.02	**0.03**	.01
6.1-6.4	S	-	.01	-	.02	**0.07**	.01
6.1-6.4	W	-	.01	-	.02	-	.01

Table B.7.c. **Spring 1990 to Fall 1990 water Trifluralin concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	5-08-90 µg/L	MDL µg/L	6-11-90 µg/L	MDL µg/L	7-23-90 µg/L	MDL µg/L	10-16-90 µg/L	MDL µg/L
1.52	N	-	.10	-	.10	-	.10	-	.10
1.52	E	-	.10	-	.10	-	.10	NS	
1.52	W	-	.10	-	.10	-	.10	NS	
2.13	N	-	.10	-	.10	-	.10	-	.10
2.13	E	NS		-	.10	-	.10	NS	
2.13	W	*.07*	.10	-	.10	-	.10	NS	
3.0-3.2	N	NS		NS		-	.10	NS	
3.0-3.2	E	NS		NS		-	.10	NS	
3.0-3.2	S	NS		NS		-	.10	-*	.10
3.0-3.2	W	NS		NS		-	.10	-*	.10
4.5-4.9	N	-	.10	.20	.10	-	.02	-	.02
4.5-4.9	E	-	.10	.20	.10	-	.02	-	.02
4.5-4.9	S	-	.10	.40	.10	-	.02	-	.02
4.5-4.9	W	-	.02	-	.02	-	.02	-	.02
6.1-6.4	N	-	.02	-	.02	-	.02	-	.02
6.1-6.4	E	-	.02	-	.02	-	.02	-	.02
6.1-6.4	S	-	.02	-	.02	-	.02	-	.02
6.1-6.4	W	-	.02	-	.02	-	.02	-	.02
FB		-	.10	-	.20				

* combined samples

Table B.7.d. **Spring 1991 to Fall 1991 water Trifluralin concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site	4-17-91 µg/L	MDL µg/L	6-11-91 µg/L	MDL µg/L	8-5-91 µg/L	MDL µg/L	10-8-91 µg/L	MDL µg/L
1.52	N	-	.10	-	.10	-	.10	-	.10
1.52	E	-	.10	-	.10	-	.10	-	.10
1.52	W	-	.10	-	.10	-	.10	-	.20
.10	N	NS		-	.10	-	.10	-	.10
.10	E	-	.10	-	.10	-	.10	-	.10
.10	W	-	.10	-	.10	-	.20	-	.10
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	.10	-	.10	-	.10	-	.10
4.5-4.9	E	-	.10	-	.10	-	.10	-	.10
4.5-4.9	S	-	.10	-	.10	-	.10	-	.10
4.5-4.9	W	-	.02	-	.02	-	.02	-	.02
6.1-6.4	N	.03	.02	-	.02	-	.02	-	.02
6.1-6.4	E	-	.02	-	.02	-	.02	-	.02
6.1-6.4	S	-	.02	-	.02	-	.02	-	.02
6.1-6.4	W	-	.02	-	.02	-	.02	-	.02
FB 4.5-4.9		-	.02	-	.02	-	.02	-	.02
FB 6.1-6.4		-	.02	-	.02	-	.02	-	.02
FB OPEN		-	.02	NS		NS		NS	

Table B.7.e. **Spring 1992 to Fall 1992 water Trifluralin concentrations measured at Carrington ND. (-) is nondetect. NS indicatesno sample taken. *Italicized data are below reported laboratory MDL*. Probability of true detection is below 95%. D* indicates that target analyte was detected in lab deionized water blank.**

Depth m	Site µg/L	5-18-92 µg/L	MDL µg/L	7-20-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L	10-12-92 µg/L	MDL µg/L
25	N	-	.1	-	.1	.28** D*	.1	-**	.1
25	E	-	.1	-	.1	-**	.1	**	.1
25	W	-	.1	-	.1	-**	.1	**	.1
25	N	-*	.1	-	.1	.28** D*	.1	-**	.1
25	E	-*	.1	-	.1	-**	.1	**	.1
25	W	-	.1	-	.1	-**	.1	**	.1
3.0-3.2	N	NS		NS		NS		NS	
3.0-3.2	E	NS		NS		NS		NS	
3.0-3.2	S	NS		NS		NS		NS	
3.0-3.2	W	NS		NS		NS		NS	
4.5-4.9	N	-	.1	-	.1	.28 D*	.1	-	.1
4.5-4.9	E	-	.1	-	.1	-	.1	-	.1
4.5-4.9	S	.5	.1	-	.1	-	.1	-	.1
4.5-4.9	W	-	.02	-	.02	-	.02	-	.02
6.1-6.4	N	-	.02	-	.02	-	.02	-	.02
6.1-6.4	E	-	.02	-	.02	0.02	.02	-	.02
6.1-6.4	S	-	.02	-	.02	-	.02	-	.02
6.1-6.4	W	-	.02	-	.02	0.05	.02	-	.02
FB 4.5-4.9		NS		NS		-	.02	NS	
FB 6.1-6.4		-	0.02	-	.02	-	.02	-	.02
FB OPEN		NS		-	.02			NS	

* Combined N and E 2.13 m vadose samples
** All 1.52 and 2.13 m vadose samples combined

APPENDIX C: EVALUATION OF LABORATORY QUALITY CONTROL

APPENDIX C
SCREENING PROCEDURE FOR EVALUATION OF LABORATORY QUALITY CONTROL

MEMORANDUM

TOPIC: Evaluation of Effect of Laboratory Quality Control Procedures on Reliability of Project Data for SWC Projects 1845, 1845-1, 1690-1, 950, and 1856, from 1989 through 1993.

TO: Milton Lindvig

FROM: William Schuh

Date: December 21, 1993

From 1989 to 1993 several projects involving water samples for pesticides in ground water and soil have been implemented by the North Dakota State Water Commission. For many projects Minnesota Valley Testing Inc. (MVTL) of New Ulm, Minnesota has provided the service of laboratory analysis. During that period a number of changes have occurred in laboratory procedures, both in analytical practices and in sample handling and receiving practices. Some practice changes observed have included increased stress on sample custody protocol and the provision of forms to assist laboratory users; the provision of laboratory cleaned bottles and coolers (free of charge) to help assure sample cleanliness; change in gas chromatograph (from a Hewlett Packard 5890 to a Hewlett Packard 5840A from 1990 on), and corresponding changes in chromatographic columns; and the adoption of the practice of checking field sample detections on a second chromatographic column (from 1991 on). Such procedural changes can cause some complications in the assessment of comparative data from year to year through changing detection levels, etc. However, it must be recognized that procedural changes are necessary for improvement and upgrading of methods, and are, in that respect inevitable.

The use of a confirmation column for all field sample detections has been an important procedural improvement for insuring against the possibility spurious detections caused by different compounds having similar chromatographic signatures on a given instrument and column. While not having run the second column in the early years (1989 and 1990) allows the possibility of mistaken identity of compounds detected and is in this respect regrettable, the adoption of the confirmation column in 1991 has provided a remedy and an upgrade in the certainty of the identity of detections, and is a procedural improvement.

However one major concern has arisen from the detection of target compounds in laboratory quality control (QC) distilled water blanks run with water samples, and in soil blanks used for soil analysis. The purpose of this report is to evaluate the effect of those QC sample detections on reliability and intrinsic value of lab results from samples sent to MVTL by the North Dakota State Water Commission between 1988 and 1993, to adopt procedures for "filtering" the value of those data for use in project assessment, and to develop some procedural recommendations that will assist in improving the certainty and intrinsic value of laboratory data contracted by the SWC to MVTL and to other laboratories.

Distilled Water QC blank detections: Problem Definition

The running of a distilled water (DW) QC blank with each sample run has been practiced routinely by MVTL on all samples sent since 1988. Earlier practice was to adjust the calibration for field samples by subtracting the value of the DW blank. Current practice does not subtract DW blank detections in interpretation of field sample data.

For some of the sample runs, target analytes have been detected in QC-DW spikes. From speaking with chemists it is my understanding that the presence of low level apparent detections can result from various causes. These include the characteristic background noise of the equipment used, the possible interference of laboratory compounds or contaminants that may have a similar chromatographic signature, and also the possible presence of the target analyte from laboratory contamination. It is apparently common for organic analytic laboratories to have low levels of organic interferences from extraction and cleaning procedures, and if sufficiently low and consistent in presence these detections are sometimes treated as "background noise" and simply subtracted from the total. Because of the need for calibration of analytical equipment, target analyte samples are also present in the laboratory and with improper handling or cleaning of glassware can cause contamination of both blanks and field samples.

A characteristic of background noise is its consistency. By definition systematic error must be systematic (or predictable) rather than random or sporadic. Systematic error, because of its predictability, can be effectively dealt with through calibration. However, if blank detections are caused by laboratory contamination with a target analyte, the question of the timing and source of contamination arises. **The presence of a target analyte in a DW blank does not necessarily mean that the field samples have become adulterated. However, neither does it succeed in demonstrating that they have not, and the assurance that reported field detections are not**

laboratory artifacts is an important part of the reason for laboratory QC procedures.

Unless the source of the contaminant in the DW blank can be identified, the possibility of introduction of the target analyte into field samples cannot be completely ruled out. QC blanks are run through the same extraction processes as field samples, and there is always the possibility of extraction with contaminated solvents, or of introduction of contaminants through improperly cleaned glassware. Unless the source of detections in QC blanks can be identified, there is no certainty that detections in field samples have not resulted from contamination during the extraction and preparation process.

The occurrence, distribution, and quantitative variability of laboratory QC detections over the examined period indicates that QC detections cannot be dealt with as systematic error. Occurrences are sporadic. Different target analytes are detected in QC water samples at different times and in different quantities. There are differences between years as well. The frequency of detections was least in 1989 (with no blank detections). In 1990 and 1992 blank detections were similar. But in 1991 the number of detections was almost double. While there were no detections in water blanks in 1989, there were detections in soil blanks. **Because of these inconsistencies, the possibility of laboratory contamination of samples cannot be ruled out in most cases. It therefore becomes necessary to develop a logic "filter" for further assessment and evaluation of the validity of the field data. In the next section the proposed filter will be described. It will then be applied to each of the individual data sets for the five years of analysis.**

Soil blank detections: Problem Definition

With each set of soil samples analyzed for pesticides, a blank soil sample is run for quality control. In order to be assured that contamination of field soil samples has not occurred in the laboratory, the laboratory blank soil sample should be treated in the same manner as the field soil sample at all steps of the extraction and analytical process, and it should be initially free from all contaminants and remain so throughout the analysis. Soil blank sources free from target contaminants can be assured by baking soil at high temperatures in a muffle furnace, and by initially sampling and testing the soil source before using it for analysis of blanks.

If a contaminant is found in a soil blank, this does not mean that the field samples are necessarily contaminated in the lab. However, neither is there assurance that they are not, and this assurance is vital for interpretation of field sample data.

EVALUATION OF ASSURANCE THAT FIELD SAMPLES HAVE NOT BEEN CONTAMINATED IN THE LABORATORY, BASED ON LABORATORY QUALITY CONTROL BLANKS

To assess the assurance that submitted samples have not been contaminated with target species in the laboratory, it is necessary to evaluate detections made in field samples in comparison with laboratory distilled water QC blanks and field blanks. A systematic procedure, or logic filter for screening detection validity based on lab QC information is developed for water samples (LFW) and for soil samples (LFS).

Interpretive Filter for Assessing the Accuracy of Field Detections in Water Samples

While there are some questions of the validity of some of the field data, it would be unfortunate to indiscriminately discard data that is valid, and ignore conclusions that can be validly drawn from the data. The following logical screening principles are proposed for application to all of the SWC data.

LFW(1). The possibility of laboratory contamination of samples affects only type 1 errors (false detections) and does not substantially influence type 2 errors (false non detections). If QC blanks for a given set of field samples indicate the presence of a given target analyte, and if the field samples do not indicate the presence of that target analyte, then the validity of the indicated non detect is not impaired.

A possible exception is where a large detection in a field blank is treated as systematic error and subtracted from the calibration for field detections. If this is practiced, the effect is to raise the MDL by the amount of the field blank. For example, if a given analyte has a detected presence of quantity X in a field blank, if the presence is due to laboratory contamination that occurs in the blank alone but not in the other samples, and if the quantity X is subtracted from detections in the other samples, assuming falsely that they are similarly "systematically contaminated", then the result would be to cause a non detection at level (MDL + X). If the amount of the blank detection is small, this problem is insignificant. For the purpose of our experiment, which is more concerned with qualitative presence than quantitation at levels far below those of toxicological concern, even a doubling of the MDL would not be of great concern. For example, the changing of the MDL from 0.1 µg/L to 0.2 µg/L is well within the variance of MDL from common procedures alone over the time of the experiment, and would not greatly affect the interpretation of results.

Applying LFW(1), all non detects will be considered unimpaired by blank detections as long as blank detections are small (we arbitrarily set the boundary of X < MDL based on our own experiment objectives). If blank detections are above MDL, and if blanks are used to adjust calibration, the non detection is still accepted but it will be noted that the true MDL may be higher than indicated by as much as the blank indicated quantity.

LFW(2). The primary concern arising from detection of target analyte in DW blanks is that of type 1 errors (false detections). From QC blank summaries three possibilities can be considered which can be used to evaluate the risk of type 2 errors. These are (a) no detections in lab QC blanks; (b) detections in lab QC blanks which are confirmed by a second chromatographic column; (c) detections in lab QC blanks which are not confirmed by a second chromatographic column. The proposed logical filter for each of these possibilities is as follows.

LFW(2a) If there are no QC blank detections, there is assurance (never certainty) that field sample detections are not lab artifacts. However, some consideration must be given to the breadth of interpretation of this rule. One might apply it very broadly, and state that the presence of any given analyte in a QC blank is an indicator that any or all of the target analytes found in field samples are at risk. In applying this, a detection of any species in any quantity would invalidate all species for the samples set.

I believe that this application is too broad and would invalidate much good data. I consider it much more likely that bench contaminants at any given time are specific and not general in nature, and that questions of validity should be confined to target analyte species specifically found in blank samples. If accompanying blanks are found to be clear of any target analyte species, and if other indicators (such as field DW blanks) are found to be clear of that target species, then field detections should be considered free of laboratory or field bias. This does not remove all question (there is always room for some skepticism). But assurance of sample accuracy should be reasonably assured by this filter.

Thus, in applying **LFW(2a), all specific target analytes found to be present in field samples but absent from analysis of laboratory blanks in a given sample set will be considered to be reasonably assured of validity.**

LFW(2b) In some, but not all of the samples, detections of target analytes in lab blanks are checked using a confirmation column. Where field sample detections are assured

using a confirmation column, and where lab blanks are also assured using a confirmation column, there are two possibilities. (i) The confirmation column may affirm the initial detection in the field blank, or (ii) the confirmation column may not confirm the initial detection in the field blank. I believe that confirmation of a field sample detection, accompanied by lack of confirmation of the laboratory QC blank, should result in the acceptance of the field sample. Conversely, if the QC blank detection is confirmed, there still remains the possibility that the detection level will be far below that of routine laboratory MDL and of the field target species. While it might be argued that in such cases acceptance of the field data should still be considered. I would prefer not to accept the detection, based on the possibility that once certain contamination is present in a sample set quantitative uniformity is not assured. There may be more contamination of one sample than another. If the disparity is large enough this is not likely. But in this case I would prefer to take the additional assurance eliminating all field data for a given analyte accompanying a QC sample having a confirmed detection, regardless of quantity in the blank.

In applying LFW(2b), if a confirmation column is applied to both field and laboratory QC data, and if the QC detection is confirmed in any quantity by the second column, then the field data will be rejected as unreliable. Conversely, if the field data is confirmed on a second chromatographic column, and the lab QC detection is disconfirmed, the field data will be accepted as having reasonable assurance of validity.

LFW(2c) In many samples, specific target species detected on the first chromatographic column were not run on a second column. In 1991 and 1992 there were ten cases where detected analytes in DW blanks were checked. Only two of these were confirmed. The other eight were disconfirmed on the second column. Thus, in most cases where there were apparent detections in the DW blank on the first column, the detections were not likely caused by laboratory contamination. Unfortunately, the 20% confirmed detections on the second column still leave us with lack of adequate assurance of non contamination where QC blanks are not analyzed for confirmation. As a general procedure, I would suggest considering non confirmed first detections in DW blanks as indications of contamination, and would discard all field sample detections of the analyte found in the blank for the sample set in which detections were made. In some cases, however, if field sample detection levels are large, and if the blank detection is sufficiently low (at least one order of magnitude below the laboratory MDL) the field detections might be retained. The latter is a special case.

In applying LFW(2c), where pesticides are found in lab DW blanks, and where no confirmation column is used, then results of the first column alone will be considered as evidence of possible laboratory contamination and corresponding detections of the target analyte in field samples will be discarded. An exception will be where large, and/or replicated detections are made in the field samples, and where the level of detection in the DW blank is far below MDL.

LFW(3) Non detections of a target analyte in field DW water blanks submitted with samples is not sufficient assurance to offset concerns raised by large concentrations of target analyte in a lab QC blank. If the plausibility of lab contamination is indicated, it is always possible that sporadic contamination of other samples could have occurred. The fact that one sample has not been contaminated does not prove that another has not.

In applying LFW(3), where lab blanks have indicated possible lab contamination, lack of contaminants in field blanks will not be considered sufficient evidence of assured lab cleanliness to offset the concerns raised by the lab blank. Field blanks will be considered as supporting evidence only.

Interpretive Filter for Assessing the Accuracy of Field Detections in Soil Samples

For soil samples, acceptance of field sample pesticide detections will be based on levels of detections in the laboratory soil blank and will parallel those of the water samples above.

LFS(1) Detections in soil blanks normally indicate risk of false detections only. If there are detections of a target analyte in the soil blank, but none in the field sample, the field sample results will be accepted.

LFS(2)

LFS(2a) If there are no detections in the soil blank, the field samples are considered to be reasonably assured of absence of laboratory contamination.

LFS(2b) If there are detections in the soil blank and if a confirmation column is used for second determination, acceptance of field data will depend on the confirmation column. (i) If the soil blank detection is confirmed, corresponding field

sample results will be discarded. (ii) if the soil blank detection is disconfirmed (while the field sample detection is confirmed), then field sample results will be accepted.

LFS(2c) If there is no confirmation column, then a soil blank detection of a target analyte will be considered as sufficient indication of risk to discard field soil sample results for the same target analyte. An exception is where the soil blank detection is very low in relation to MDL (> one order of magnitude below MDL) or the field sample results.

LFS(3) Lack of detection in a field soil blank (if submitted) will not be considered sufficient evidence of laboratory cleanliness to offset concerns raised by detections in soil blanks.

PROJECT DATA EVALUATION

Project 1845 Carrington Recharge

A. Water Samples

1. 1989

WO /1989/21-808
WO/1989/21-835
WO/1989/21-1090
WO/1989/21-3283

There were no DW blank detections in 1989. All field detections are accepted.

2. 1990

* Sample set 5/10 WO/1990/21-0755

microextractions - there were no base neutral or acid extraction detections in DW blanks. All microextraction data are accepted.

macroextractions - there were no base neutral extractions. Bromoxynil was detected in the DW blank in one of two sample runs (see summary on table 1). Detection level was approximately 3 times the MDL. No confirmation column was run on the blank detection. There were no detections in field samples. Lab calibration for field data was not adjusted for the field detection. Because there were no field detections of bromoxynil, all macroextraction laboratory results are accepted as valid.

* Sample set 6/23 WO/1993/21-0930

microextractions - methyl parathion was detected in the laboratory DW blank. Detection level was about half of MDL. No confirmation column was run. Since there were no methyl-parathion detections in field samples, LFW(1) is applied and all data are accepted. See summary on table 1.

macroextractions - bromoxynil was detected at about 16 times the lab MDL in DW blanks. MCPA was also detected at about one fourth of the lab MDL. Although there were no confirmation columns, the large detection levels may indicate laboratory contamination. Calibration for field samples was not altered for the laboratory blank. Since there were no field detections of bromoxynil or MCPA, according to LFW(1) there is no effect of DW blank detections on field analysis. All data are accepted, including replicated trifluralin detections (three detections). See summary on table 1.

* Sample set 7/25 WO/21-1185

microextractions - methyl parathion was detected in a field blank at almost double MDL. There was one field detection at MDL (below the level of the DW blank). No confirmation column was run on the blank. Lab contamination is considered possible. According to LFW(2c) all microextraction data for methyl parathion id discarded. All other microextraction data is retained.

macroexraction - diclofop (at about 3 times MDL) and MCPA (at about one quarter of MDL) were both detected in lab DW blanks. There were no confirmation columns run. Although there is not adequate assurance that laboratory contamination with MCPA and diclofop did not occur, there were no detections in field samples. There were, however, detections of propiconazole in field samples, for which there were no detections in lab DW blanks. According to LFW(1) all data are accepted.

* Sample set 10/18 WO/1990/21-1685

microextractions - diclofop was detected about one fifth MDL in the lab blank. There was no confirmation column. There were no field detections. According to LFW (1) all data are accepted. See table 1 summary.

macroextraction - bromoxynil was detected in the lab DW blank at about three times the lab MDL, but there were no field detections. Diclofop was detected in the DW blank about MDL, and there was one field detection. All data are accepted except field diclofop detections, which are rejected according to LFW (2c). See table 1 summary.

1991

Sample set 4/19 WO/1991/21-588

microextractions - there were no detections in DW blanks and none in field samples. All data area accepted. See table 1 summary.

macroextraction - diclofop and propiconazole were detected at about double lab MDL. However, there were no field detections of these species. There was one field detection of trifluralin, but trifluralin was not detected in any of the lab blanks. All data is accepted. See table 1 summary.

Sample set 6/13 WO/1991/21-944

microextractions - in DW blanks there were detections of dimethoate near lab MDL, and detections of MCPA and trifluralin at about one fourth lab MDL. Because of low spike recoveries dimethoate and MCPA were not reported by the laboratory. There were no trifluralin data, so according to LFW (1) all data are accepted as reported. See table 1 summary.

macroextraction -bromoxynil was detected in DW blank at about seven times the lab MDL, and MCPA was detected at about half lab MDL. However, there were field detections of neither. According to LFW (1) all data are accepted.

Sample set 8/07 WO/1991/21-1216

microextractions -there were confirmed detections of bromoxynil in DW blanks. MCPA detections in the blanks were non confirmed. However there were no detections in field samples. According to LFW (1) all data are accepted.

macroextraction - there detections of nearly every target analyte in DW blank. No confirmation test was made on any of the target analytes. Only bromoxynil was detected in field samples. According to LFW(2b) bromoxynil field detections are discarded. All other data are accepted according to LFW (1).

Sample set 10/10 WO/1991/21-1583

microextractions -bromoxynil, dimethoate, and propiconazole were detected in DW blank on the first column. Only bromoxynil was tested on a second column. The first detection was not confirmed. There were no detections in field samples. According to LFW(2b) and LFW(1) field data are accepted.

macroextraction - there were no detections in the DW blank on the first test. However, bromoxynil was detected in the confirmation column. There was one field detection of bromoxynil at concentration equal to the lab confirmation. This is a special case. Because of the similarity of concentration with the confirmation column the field detection of bromoxynil is discarded. All other data are accepted according to LFW(1).

1992

Sample set 5/18 WO/1992/21-0461

microextraction -diclofop, methyl parathion, and trifluralin were all detected in field blanks. However, they were not confirmed on the second column. A confirmed detection of trifluralin occurred in one field sample. The trifluralin detection is accepted according to LFW(2b) and LFW(2c). Diclofop and methyl parathion field detections are accepted according to LFW(2c). All other data are accepted according to LFW(1).

macroextraction - only propiconazole was detected in the DW blank. There was no attempt at confirmation. However, there were no field detections. Propiconazole is accepted according to LFW(2c) and LFW(1). All other data are accepted according to LFW(1).

Sample set 7/20 WO/1992/21-0637

microextraction -there were no detections in lab blanks, and there were no detections in field samples. All data are accepted according to LFW(1).

macroextraction - only trifluralin was detected in a field blank. The detection was disconfirmed on a second column. Also there were no field detections. All field data are accepted according to LFW(1) and LFW(2b).

Sample set 10/15 WO/1992/21-0957

microextraction - MCPA and trifluralin were detected in the lab blank. Trifluralin was confirmed on a second column. No confirmation run was made with MCPA. Trifluralin was detected in field data. MCPA was not detected in field data. All data is accepted according to LFW(1) and LFW(2c) except the trifluralin detection, which is discarded according to LFW(2b).

macroextraction - There were no detections in field blanks or in field samples. All data are accepted according to LFW(1).

1993

Sample set 4/21/93 WO/1993/21-0688

microextraction - There were no detections in laboratory blanks or in field samples. All data are accepted according to LFW(1).

macroextraction - bromoxynil and MCPA were detected in laboratory blanks. No confirmation procedures were performed on blanks. Bromoxynil was not detected in field samples (all data accepted according to LFW(1). MCPA was detected in the field data. MCPA field detection is discarded according to LFW(2c).

B. Soil Samples:

Three replicate soil samples were taken before the field application of trifluralin (6/3/89) and after completion of the experiment (6/24/93). Results of both samplings indicated similar and plausible trifluralin distributions with depth. However, both sample

sets also were accompanied by relatively large indications of trifluralin in the laboratory blank. The 6/3/89 soil blank data was very close to the laboratory MDL, and also larger than some of the indicated field data. Similarly, the 6/24/93 data indicated soil blank concentrations that are five times the MDL, half as large as the largest field detections, and twice as large as the smaller field detections.

It is difficult to understand why such large soil blank concentrations could occur from soil samples free from contamination. Under such conditions, there is no assurance that the field data has not been contaminated in the laboratory, and the soil data must be discarded. The only alternative would be if the laboratory could provide clear evidence that the QC detections in the laboratory were systematic, erroneous, or in some other manner unrelated to laboratory procedures.

APPENDIX C. SCREEN OF CARRINGTON RECHARGE PROJECT DATA BASED ON LAB QUALITY CONTROL

Table C.1. Results of water chemistry from the Carrington Recharge Project (SWC#1845) data screened for laboratory quality control , based on detections of target analytes in distilled water blanks. (C-NC) designates confirmation or non confirmation (respectively) for detections of target analytes in distilled water blanks using a second chromatographic column. Corrective measures described are based on procedures (labeled LFW) which are numbered and described in the accompanying report.

Recieved Data	Procedure macro/micro	Detections in Lab DW Blanks	Lab DW Concentration ug/L	MDL	Second Column for Blanks? yes-no / C-NC	Field Detections ? yes-no	Field Detection Concentration ug/L	Corrective Measures
1989								
5/31	micro	none						LFW(2a) All field data accepted
	macro	none						LFW(2a) All field data accepted
6/06	micro	none						LFW(2a) All field data accepted
	macro	none						LFW(2a) All field data accepted
7/15	micro	none						LFW(2a) All field data accepted
	macro	none						LFW(2a) All field data accepted
10/26	micro	none						LFW(2a) All field data accepted
	macro	none						LFW(2a) All field data accepted
1990								
5/10	micro	none						LFW(2a) All field data accepted
	macro	bromoxynil (1 of two sets run)	0.031	0.01	no	no		LF (1). All field data accepted*
6/13	micro	methyl parathion	0.0501	0.2	no	no		LF(1). All field data accepted*
	macro	bromoxynil	0.162	0.01	no	no		LF(1). All field data accepted*
		MCPA	11.025	41	no	no		LF(1). All field data accepted*
7/25	micro	methyl parathion	0.348	0.2	no	yes	0.2	LF (2c). methyl parathion field detections discarded
	macro	diclofop	0.902	0.2	no	no		LF(1). All field data accepted*
		MCPA	5.904	41	no	no		LF(1). All field data accepted*
10/18	micro	diclofop	0.091	0.5	no	no		LF(1). All field data accepted*
	macro	bromoxynil	0.026	0.01	no	no		LF(1). All field data accepted*
		diclofop	0.091	0.1	no	yes	0.1	LF (2c). diclofop field detections discarded

* DW blank detection was not subtracted in calibration of field data

† DW blank detection was subtracted in calibration of field data measurements

Table C.1. (continued). Results of water chemistry from the Carrington Recharge Project (SWC#1845) data screened for laboratory quality control , based on detections of target analytes in distilled water blanks. (C-NC) designates confirmation or non confirmation (respectively) for detections of target analytes in distilled water blanks using a second chromatographic column. Corrective measures described are based on procedures (labeled LFW) which are numbered and described in the accompanying report.

Recieved Data	Procedure macro/micro	Detections in Lab DW Blanks	Lab DW Concentration ug/L	MDL	Second Column for Blanks? yes-no / C-NC	Field Detections ? yes-no	Field Detection Concentration ug/L	Corrective Measures
1991								
4/19	micro	none						All data accepted
	macro	diclofop	0.278	0.2	no	no		LFW(1). All field data accepted †
		propiconazole	0.171	0.1	no	no		LFW(1). All field data accepted†
6/13	micro	dimethoate	0.752	0.90	no	no		None reported by lab due to low spike recoveries
		MCPA	49.14	200	no	no		None reported by lab due to low spike recoveries
		trifluralin	0.025	0.10	no	no		LFW(1). All field data accepted †
	macro	bromoxynil	0.066	0.01	no	no		LFW(1). All field data accepted†
		MCPA	23.92	40	no	no		LFW(1). All field data accepted†
8/07	micro	bromoxynil	0.028/0.022	0.05	yes/C	no		LFW(1). All data accepted†
		MCPA	122/ND	200	yes/NC	no		LFW(1) and LFW(2b) all data is accepted.†
	macro	bromoxynil	0.01	0.01	no	yes	0.07	LFW(2b) bromoxynil field detection discarded
		diclofop	0.303	0.1	no	no		LFW(1). All field data accepted †
		dimethoate	0.062	0.2	no	no		LFW(1). All field data accepted†
		MCPA	10.7	40	no	no		LFW(1). All field data accepted †
		methyl parathion	0.075	0.03	no	no		LFW(1). All field data accepted†
		propiconazole	0.075	0.2	no	no		LFW(1). All field data accepted †
		trifluralin	0.062	0.02	no	no		LFW(1). All field data accepted†
10/10	micro	bromoxynil	0.164/ND	0.05	yes/NC	no		LFW(1) and LFW(2b) all field data is accepted.†
		dimethoate	0.682	0.9	no	no		LFW(1). All field data accepted †
		propiconazole	0.592	1	no	no		LFW(1). All field data accepted†
	macro	bromoxynil	ND/0.02	0.01	yes/?	yes	0.02	Special case/ non detect on first column, detection on second column. Bromoxynil field detection is discarded based on similarity of concentration to the confirmation column measurement for the DW blank to the measured field concentration.
		trifluralin	0.013	0.02	no	no		LFW(1). All field data accepted†
1992								
5/18	micro	diclofop	0.32	0.5	yes/NC	no		LFW(1) and LFW(2b). All data accepted*
		methyl parathion	0.02	0.20	yes/NC	no		LFW(1), LFW(2b), and LFW(2c). All data accepted*
		trifluralin	0.02	0.10	yes/NC	yes	0.5	LFW(2b), and LFW(2c). All data accepted
	macro	propiconazole	0.20	1.00	yes/NC	no		LFW(1). All field data accepted.*
7/20	micro	none				no		LFW(1). All field data accepted.*
	macro	trifluralin	0.015	0.02	yes/NC	no		LFW(1) and LFW(2b). All data accepted.*
10/12	micro	MCPA	21.5	25	no			
		trifluralin	1.26/1.46	0.1	yes/C	yes	0.28/0.28	LFW(2b) trifluralin field detections discarded
	macro	none						LFW(1) and LFW(2b) all field data is accepted.*
1993								
4/23	micro	none						All data accepted
	macro	bromoxynil	0.005	0.05	no	no		LFW(1) and LFW(2c) allfield data is accepted.*
		MCPA	0.771	5.00	no		6.90	LFW(2c) MCPA field detection discarded

* DW blank detection was not subtracted in calibration of field data

† DW blank detection was subtracted in calibration of field data measurements

Table C.2. Results of soil pesticide alalysis from the Carrington Recharge Project (SWC#1845) data screened for laboratory quality control , based on detections of target analytes in soil blanks.

Recieved Data	Soil Depth (cm)	Horizon	Detections in Soil Samples ug/L	Soil Blank Concentration ug/L	MDL	Corrective Measures
6/3/89	0-20	A	3.04/10.58/5.69	4.06	5.60	Soil Blank > Some Field Samples No assurance of non contamination in the laboratory/ data rejected
	20-60	B	3.68/11.00/10.81	4.06	5.60	same
	>60	C	10.72/2.67/ND	4.06	5.60	same
6/24/93	0-20	A	41/37/51	26	5.00	Soil Blank > Some Field Samples Soil Blank > MDL No assurance of non contamination in the laboratory/ data rejected
	20-60	B	13/12/12	26	5.00	same
	>60	C	12/12/11	26	5.00	same

* DW blank detection was not subtracted in calibration of field data

† DW blank detection was subtracted in calibration of field data measurements