GROUND-WATER AND SURFACE-WATER QUALITY, HERBICIDE TRANSPORT, AND IRRIGATION PRACTICES: GREENFIELDS BENCH AQUIFER, TETON COUNTY, MONTANA

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ABSTRACT

The Greenfields Bench, located in west-central Montana (figure 1), is a series of gravel terraces that support a shallow aquifer that serves as the sole source of drinking water for three public water supplies and more than 400 private wells. The farming practices on the Bench include irrigation of malting barley and the yearly application of herbicides for the control of weeds. The most commonly used herbicide (imazamethabenz-methyl, U.S. trade name Assert®) has been found in the ground water on the Bench. In addition to Assert and its acid metabolite, eight other pesticides have been detected in wells serving the Town of Fairfield, the Tri-County Water District, and in numerous private wells. The Montana Water Quality Standards have not been exceeded for any of the pesticides. However, the variety of pesticides found and the frequency of pesticide detections in area wells was indicative of aquifer vulnerability and elucidated the need for additional data collection to better understand the hydrogeological processes and to develop appropriate management strategies.

The detection of Assert in the public water supply for the Town of Fairfield prompted an expanded ground-water sampling effort across the entire Bench that consisted of quarterly sampling of 16 domestic wells from the spring of 1998 through the summer of 1999. The purpose of the expanded sampling effort was to, 1) determine whether Montana Water Quality Standards were being exceeded in private water supplies or in the other two public water supplies on the Bench, and, 2) characterize the magnitude and extent of Assert contamination in ground water and in ground-water discharge to surface-water bodies.

Results from 91 ground-water samples show that Assert (or its metabolite) concentrations in domestic wells range from 0.2 to 5.0 µg/L (Table A-9). The Montana Water Quality Standard for Assert is 400 µg/L.

Ground water on the Greenfields Bench discharges to surface water via drains, springs, and seeps. Water-quality samples were collected from various ground-water discharge sites to assist in the development of total maximum daily loads for the receiving streams and to assess surface-water quality for human health and ecological impacts. Data indicate that Assert concentrations remain essentially unchanged through the flow system as ground water discharges to the streams. Concentrations of Assert in surface water ranged from 0.2 to 1.5 µg/L (37 samples).

Using 20 observation wells, an experimental study was conducted in 2000 and 2001 to evaluate the influence of flood- and sprinkler-irrigation on the transport (leaching) of the herbicide Assert from the organic soil zone to the saturated zone. The objective of the study was to characterize the transport of Assert and its acid metabolite to the ground water under three irrigation methods: flood, wheel-line sprinkler, and center-pivot sprinkler. Results indicate that four factors appear to control Assert concentrations in ground water: 1) hydraulic-loading characteristics of the irrigation method, 2) Assert persistence in soil, 3) hydraulic characteristics of the aquifer, and 4) adsorption/desorption of Assert onto clay particles and organic matter.

The Montana Department of Agriculture (MDA) has established its first Specific Pesticide Management Plan (SMP) on the Greenfields Bench because of the high frequency of pesticide detections in ground water, the large number of different kinds of pesticides found in ground water, and the aquifer-wide extent of pesticide occurrence. The Greenfields Bench SMP, adopted as a rule in 2001, outlines voluntary management strategies for Assert-use that are focused on protecting the water resources of the area.
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Montana Department of Environmental Quality, Montana Department of Natural Resources and Conservation, and BASF, formerly American Cyanamid provided funding for the projects. The U.S. Bureau of Reclamation provided funding for herbicide analyses of canal water samples as well as in-kind service in well installation for the Field Study.

Fred Schmidt with the Montana Bureau of Mines and Geology (MBMG) installed observation wells. Laszlo Torma and Heidi Hickes of the Montana Department of Agriculture Analytical Laboratory provided technical assistance and analytical data.

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INTRODUCTION

Three public water supplies and more than 400 private residences obtain their drinking water from the Greenfields Bench aquifer, a topographically isolated bench of Cretaceous age overlain by a veneer (4-50 ft. thick) of gravel deposits. The aquifer receives about 70% of its recharge from on-farm irrigation, leaking irrigation canals and ponded tailwater (Osborne 1983). Water levels undergo dramatic seasonal fluctuations that correspond to surficial irrigation water application, demonstrating the direct hydraulic connection between surface water (irrigation canals and other watercourses) and ground water.

The herbicide Assert was first detected in ground water on the eastern edge of the Greenfields Bench (figure1) during routine monitoring conducted by the Montana Department of Agriculture (MDA) in 1996. Sampling efforts were expanded to other areas on the Bench to provide an initial assessment of Assert occurrence in ground water. At the same time, the Town of Fairfield, located on the Greenfields Bench was one of four Montana Bureau of Mines and Geology (MBMG) demonstration sites for source-water protection area boundary delineation (Miller, 1998). To fully characterize source-water quality, pesticide-analytes were included in the ground-water sampling strategy. Public wells and numerous private wells were sampled for pesticides in May and July of 1996. Assert, Assert metabolite, picloram, prometon, and clopyraid were detected in four of the town’s wells and in numerous private wells in the surrounding area.

Further data-collection efforts were necessary to characterize pesticide transport mechanisms and to describe the surface and subsurface flow system. The detection of pesticide residues in ground water, coupled with the vulnerability of the aquifer, activated the Montana Agricultural Chemical Ground Water Protection Act of 1991 (80-15-212, MCA). The Act necessitates the formulation of a pesticide Specific Management Plan under these conditions.

The water-resource investigations were sponsored by the Teton County Conservation District, and were funded by the Montana Department of Environmental Quality and the Montana Department of Natural Resources and Conservation. These programs provided the resources to characterize the magnitude and extent of pesticide occurrence in the ground water on the Greenfields Bench, evaluate pesticide discharges to surface water draining the Bench, and to investigate the relative significance of sprinkler and flood irrigation in the process of pesticide fate and transport. To date, the pesticide concentrations in ground water are below Montana Water Quality Standards, so there are no demonstrated health implications for Bench residents.

PURPOSE AND SCOPE

The first section of this report discusses geologic controls on ground-water flow, ground-water/surface-water interaction, and water quality. Drains, springs and seeps carry discharged ground water to surface-water bodies that are included on the Montana 303 (D) list as “water bodies in need of Total Maximum Daily Load Development.” Water-quality data were collected to characterize surface-water quality and inorganic-constituent loading rates on those water bodies receiving discharged ground water from the Bench.

The second section of this report describes the results of an experimental study of herbicide (Assert) transport under three irrigation methods.

This report summarizes the data collection efforts funded by three grants that were sponsored by the Teton County Conservation District: 1) DEQ Contract 270068, “Pesticides in Ground Water on the Greenfields Bench,” 2) DEQ Contract 280099, “Initial Development of TMDL Contaminant Allocation and Management Practices to Prevent Agricultural Contamination in the Sun River Drainage, Greenfields Bench, Montana,” and, 3) DNRC Contract RRG-00-1100, “Irrigation Methods and Pesticide Transport to Ground Water: Greenfields Bench, Teton County, Montana.”
METHODS

Hydrogeology was characterized from existing data and from data collected during this project which included water-level measurements, aquifer-test data, and water-quality analyses from domestic wells and observation wells. Water-level data was gathered from 86 domestic wells. Inorganic water-quality samples were collected from 16 domestic wells. Static water levels were measured and nitrate samples were collected at the same time that Assert samples were collected. Nitrate is reported as nitrate as nitrogen in milligrams per liter (mg/L) and Assert and the Assert acid metabolite (Assert/met), are reported as micrograms per liter (µg/L). The analytical limit of quantitation (LOQ) for Assert was 0.2 µg/L. Samples containing less than 0.2 µg/L Assert are reported as 0.00 µg/L for use in statistical summaries.

Flow-measurement and water-quality sampling of selected drains, seeps, and springs were performed to assess the affect of ground-water discharge on surface-water quality.

In an experimental field study, the fate and transport of Assert was evaluated under three irrigation methods: flood irrigation, wheel-line sprinkling, and center pivot sprinkling. Using soil sample analyses and ground-water data collected from 20 observation wells, recharge and mass-flux calculations were performed on two field-scale study plots. The methods used in the experimental field study are discussed in more detail in the second section of this report.

GEOGRAPHIC SETTING

The Greenfields Bench, also known as the Fairfield Bench or the “Bench,” is located about 30 miles northwest of the City of Great Falls and encompasses about 83,000 acres in southern Teton and northern Cascade counties. The Bench is located on the semi-arid high plains of Montana and is typified by a dry continental climate. The mean annual precipitation for the years from 1960 through 2000 is 12.35 inches (figure 2A), but has wide, monthly and annual fluctuations. Mean monthly temperatures vary from about 23 to 66 degree Fahrenheit (figure 2B). Estimates of the mean evapotranspiration rate range from 35 to 40 inches per year (SCS, 1974; Osborne, 1983.)

The Bench is a topographically isolated prairie plateau reaching an altitude of more than 4000 feet. Bordered to the south by the Sun River, to the north and east by Muddy Creek and to the west by Freezeout Lake, the Bench has more than 300 feet of local relief (figure 3). The gravel-covered bedrock remains as upland terraces because the adjacent bedrock, unprotected by the gravel veneer, is more easily eroded. The Greenfields Bench aquifer is composed of the gravel deposits that overly the bedrock.

The Town of Fairfield is located on the western portion of the Greenfields Bench. Fairfield has about 665 residents and about 45 businesses, including gas stations, hardware stores, restaurants, and a 9-hole golf course with clubhouse. The Town uses seven public water supply wells to withdraw water from the Greenfields Bench aquifer, the only source of domestic water on the Bench.

Two other public water supplies are solely reliant on the Greenfields Bench aquifer for drinking water: the Tri-County Water District that serves 146 users, and the Greenfields School. In addition to the public water-supply users, more than 400 homes use the Greenfields Bench aquifer as the sole source of domestic water.

The industry in this region is primarily irrigated agriculture. In addition to irrigated alfalfa and irrigated pasture, about 70% of the Bench acreage is devoted to the cultivation of irrigated malting barley. The non-irrigated balance of the acreage is used for other small grain production, livestock operations, residential areas, and roads. Figure 4 shows the distribution of various irrigation methods on the Bench. Of the irrigated acreage, roughly 55%-60% of the land is flood-irrigated, while either center pivot or wheel-line sprinklers irrigate the remaining acreage.

Irrigation water is supplied to the Bench from Gibson Reservoir, about 35 miles to the west, via approximately 295 miles of canals and laterals (Osborne, 1983). The principal supply canals
Figures 2A and 2B. Mean monthly precipitation and temperature for the Greenfields Bench.
Figure 3. Generalized topographic profile and geologic cross-section across the Greenfields Bench. Trace (N-S) of diagram shown on geologic map (figure 6).
Figure 4. Map showing irrigation methods on the Greenfields Bench.
are the Main Canal and the South Canal. Irrigation return flows discharge chiefly to the Sun River via the tributary Muddy Creek, which borders the north and east flanks of the Greenfields Bench. A lesser amount of irrigation return flow occurs on the western edge of the Bench and drains to Freezeout Lake Wildlife Management Area.

A variety of agricultural chemicals are used on the Greenfields Bench including:

♦ Assert (imazamethabenz methyl) for the control of wild oats, mustard and buckwheat in barley and wheat,
♦ Achieve (tralkoxydim) for the control of grass weeds in barley, wheat, and grass seed crops,
♦ picloram which is used for broadleaf weeds and woody plants mostly in non-crop settings,
♦ 2,4-D used for broadleaf weed control,
♦ prometon, a ground sterilant, and,
♦ clopyralid used for broadleaf weed control.

The predominant weed control efforts are in the control of wild oats in the malting barley crops.

**PREVIOUS INVESTIGATIONS**

Maughan, (1961) prepared a geologic map of the Vaughn Quadrangle that includes the Greenfields Bench area. In his report on the geologic structure and stratigraphy of the quadrangle he described terrace gravel deposits, gravel thickness, and gradients on the First, Second and Third Benches, collectively referred to as the Greenfields Bench.

A number of hydrological investigations have been conducted in the Greenfields Bench area. Much of the work focused on the Greenfields Irrigation District and streambank erosion on Muddy Creek. Numerous reports by the U.S. Bureau of Reclamation (1967, 1974, 1976, 1981, 1982, 1983) discuss salt loading, irrigation effects, and proposed rehabilitation and structural erosion control alternatives on Muddy Creek.

Systems Technology, Inc. (1979) summarizes hydrological, water-quality, and biological investigations on Muddy Creek and discussed work performed by the U.S. Bureau of Reclamation, the Montana Department of Fish and Game (Hill, 1976), and the Water Quality Bureau of the Montana Department of Health and Environmental Sciences (Braico and others, 1974; Ingman and others, 1979). The primary concerns in Muddy Creek as outlined by Systems Technology, Inc. were identified as elevated nutrient and suspended solids concentrations, high water temperatures, hydraulic modifications such as streambank incision, and biological impacts.

Walther (1981, 1982) collected nutrient data on the Greenfields Bench. He noted that nitrate levels were frequently elevated in water sampled from domestic wells. In 1982 he presented nutrient data for Muddy Creek and wastewater drains on the Bench.

Bauder (1981, 1982) has conducted numerous studies that focus on assessing soil-moisture use patterns and plant-water use requirements on the Bench.

Osborne and others (1983) evaluated the contribution of ground-water discharge to Muddy Creek. His report provides an overall hydrologic budget for the Bench, describes aquifer characteristics, discusses ground-water quality, and evaluates the potential for ground-water re-use or conjunctive use applications.

A report by the U.S. Geological Survey (USGS) (Knapton, and others, 1988) documented occurrences of selenium concentrations higher than recommended levels in the Freezeout Lake Wildlife Management Area and the Benton Lake National Wildlife Refuge. Several subsequent investigations were undertaken by the USGS in cooperation with other federal agencies to evaluate the potential adverse effects on water quality in the Sun River Irrigation Project, Freezeout Lake Wildlife Management Area and Benton Lake National Wildlife Refuge (Lambing and others, 1994; Nimick and others, 1996; Kendy and Olsen, 1997; Nimick, 1997; Kendy and others, 1999). Results of the investigations indicate that
selenium has accumulated in aquatic plants and invertebrates, fish, and waterfowl, and that residues in some biological tissue exceeded biological risk levels.

Miller (1998) completed a water-quality and hydrogeological investigation for the Fairfield public water supply. The geotechnical information was used to delineate source-water protection boundaries and time of travel estimates for the seven wells used by the Town.


McDonald (2000) provides a comprehensive summary of the seasonal variability in water quality and quantity for the Muddy Creek and Sun River watershed. Her report summarizes existing water-quality and -quantity data and analyzes historical information.

**DATA-POINT NUMBERING SYSTEM**

Sites for monitored wells, springs, and stream locations are numbered according to geographic position within the rectangular grid system used in Montana by the U.S. Bureau of Land Management (figure 5). The first three characters specify the township and its position north or south of the Base Line. The next three characters specify the range and its position east or west of the Montana Principal Meridian. The next two numbers are the section number. The next four letters designate the quarter section (160-acre tract), quarter-quarter section (40-acre tract), quarter-quarter-quarter section (10-acre tract), and the quarter-quarter-quarter-quarter section (2.5-acre tract) respectively. The subdivisions of the sections are designated A, B, C, and D in a counterclockwise direction, beginning in the northeast quadrant. If two or more data points are located in the same tract, numbers are added as suffixes. It is important to note that the order of quarter-tract designations is exactly reversed from the order commonly used by surveyors; here the order begins with the largest quarter and progresses to the smallest. The process for locating an example site (22N02W26CDAA) is illustrated in figure 5.

**QUALITY ASSURANCE**

Quality-assurance practices for the collection and analysis of ground water and stream samples for inorganic analytes were defined by the MBMG Analytical Division Quality Assurance Manual, Rev.2.0 (September 2001). Wells were purged until field specific conductance, temperature, and \( \rho \) indicated that the sample was representative of aquifer water. For all samples collected for inorganic analyses, filtration and preservation of nutrient and trace metal samples were performed in the field to prevent geo- or biochemical water-quality changes prior to analysis.

Quality-assurance/quality-control procedures for collecting water samples for pesticide analysis were pursuant to the Montana Department of Agriculture (MDA) Technical Services Bureau Standard Operating Procedures (MDA QA/QC Manual) that govern field-sampling activities and data-reduction procedures. The MDA Laboratory’s EPA-approved Quality Assurance Project Plan governed analytical methods and procedures for pesticide analyses.
Figure 5. Data-point numbering system
HERBICIDE DATA EVALUATION AND RELIABILITY

Because the concentration of Assert herbicide in samples from domestic wells on the Greenfields Bench is extremely low, ranging from <0.2 µg/L to 5.0 µg/L, some analytical uncertainty exists. When establishing the presence or absence of a trend in concentration data in such low ranges, data reliability, reproducibility, and subjectivity to systematic error become critically important in data evaluation.

The Horwitz function (Horwitz, 1982) was used to estimate data reliability. For concentrations in the range of 0.1 to 1.0 µg/L, the coefficient of variation is 45%; for concentrations in the range of 1.0 to 10.0 µg/L, the coefficient of variation is 32%. For example, the actual value of a sample concentration reported to be 0.4 µg/L, may be ± 45% of the reported value; the actual value may range from 0.22 µg/L to 0.58 µg/L.

Estimates of data reliability are reflected as error bars in figures that present herbicide concentration data.

The analytical limit of quantitation (LOQ) is 0.2 µg/L.

GEOLOGY AND SOILS

The terrain surrounding the Greenfields Bench is a plain that is dissected by the Sun River and its tributary, Muddy Creek. The Bench itself is a plateau overlain by a series of terrace gravels that have been deposited by an ancestral Sun River (Maughan, 1961). The gravel-covered Cretaceous bedrock remains as upland terraces because the adjacent bedrock, unprotected by a gravel veneer, is more easily eroded. The contact of the gravel with the underlying bedrock is commonly associated with springs or seeps.

BEDROCK GEOLOGY

The bedrock surrounding and underlying the Greenfields Bench (figure 6) consists of sedimentary rocks of the Cretaceous Colorado Group and includes the Blackleaf Formation and the Marias River Formation. These formations are primarily dark gray shale with some interbedded siltstone, sandstone and bentonite. The combined thickness of these formations is about 1,500 feet. The Blackleaf Formation constitutes the lower 790 ft of the Colorado Group and is mostly a dark-gray shale with numerous sandstone beds, while the Marias River Formation composes the upper part of the Colorado Group (Maughan, 1961). Both the Blackleaf and Marias River Formations were deposited in marine environments.

The top of the Marias River Formation is an erosional surface formed prior to the deposition of Tertiary/Quaternary age gravels, leaving a gently eastward-sloping plain. The three benches were formed by periods of downcutting followed by periods of terrace gravel deposition by a pre-Wisconsin and early Wisconsin-stage Sun River. The present channels of Muddy Creek and the Sun River were formed later, probably during later Pleistocene time (Maughan, 1961).

SURFICIAL GEOLOGY

As shown on figures 3 and 6, three gravel terraces collectively comprise the Greenfields Bench. All are Quaternary and/or Tertiary in age and are interpreted as deposits of an ancestral Sun River, flowing in a more northeasterly course. The oldest and highest terrace (Ttsf) shown on figures 3 and 6 is Tertiary in age and is named the First Bench. The average topographic gradient of the First Bench is 24 ft/mile. The Second Bench, mapped as QTts2, lies 120 feet below the First Bench and has an average gradient of 19 ft/mile. Younger sediments (QTts1) overlie the Third Bench and lie about 75 ft. below the Second Bench.
Figure 6. Geology of the Greenfields Bench (Vuke and Colton, 2001), including trace of cross-section N-S (figure 3).
The Third Bench also has an average topographic gradient of 19 ft/mile (Osborne 1983). Two younger gravel terraces lie closer to the present Sun River channel and are called the Asheulot Bench (Qts2) and the Sun River terrace (Qts1). The gravel remnants rest upon eroded bedrock. Data obtained from drill holes and domestic-well indicate that the gravel thickness ranges from 3 to 50 ft. Bench-wide, the average gravel thickness is about 19 ft. The gravel is somewhat thicker on the west end of the Bench.

The moderately well sorted, poorly stratified gravel consists primarily of pebbles and cobbles of quartzite and argillite derived from rocks of Precambrian age exposed in the headwaters of the Sun River (Nimick, 1996). Pebble and cobbles sizes range from 0.5 to 3 inches in diameter and are usually well imbricated. Boulders exceeding one foot in diameter are often present on the western end of the Bench (Osborne, 1983). Caliche rind (calcium carbonate precipitate) coats the undersides of rocks in the upper 10 feet.

Figure 7 is a photograph of a road cut that shows gravel inter-mixed with medium-coarse sand. Gravels may also contain a heavy clay matrix. The unsorted gravel-clay matrix found in some areas of the Bench has a very low transmissivity and where present, can act as an aquitard that locally confines ground water and creates shallow, perched water-table conditions.

Vuke and Colton (2000) noted glacial or glacio-lacustrine (glacial lake) deposits on the northwestern edge of the Bench, suggesting that glacial deposits may overlay or be inter-tongued with the gravel beds.

SOILS

Most of the soils on the Bench are classified within the Rothiemay clay loam series (D. Bloedel, written commun., 1998). The Rothiemay-Niart clay loam and Varney-Rothiemay clay loam soil complexes are present within the series. Taxonomically, the Rothiemay series is described as a fine-loamy, mixed Aridic Calciboroll. The soils are described as well drained and alluvial in origin. The Ap horizon of the Rothiemay Series is typically 0 to 8 inches in depth, and is a grayish brown clay loam that turns very dark grayish brown when moist. The soil has a weak medium to fine subangular blocky structure and is also hard and friable. There are 5% pebbles and cobbles with many fine irregular pores. Generally, soil pH ranges from 7.4 to 8.6. The soil is slightly effervescent, indicating the presence of calcium carbonate.

GROUND WATER

OCCURRENCE

Ground water on the Greenfields Bench occurs in the terrace gravel deposits that overlie Cretaceous shale. Prior to the establishment of the Greenfields irrigation system in 1920, shallow ground water on the Bench was probably very limited in quantity and marginal in quality, with high total dissolved solids (TDS) when compared to current TDS concentrations. Some seeps and springs probably existed before irrigation; early settlers on the Bench dug shallow wells that periodically went dry. According to local residents, Cleiv Springs, located on the northeast corner of the Bench, supplied water to Native Americans.

After the delivery of irrigation water began, surface water (from the Sun River via Gibson Dam and Pishkun Reservoir) leaked into the terrace gravel deposits creating an aquifer that was productive enough to support withdrawals by domestic wells. As leakage continued, ground-water levels in the shallow gravel deposits rose, resulting in water-logged soils in places. Drains were subsequently constructed to reduce waterlogging of soil caused by ponding of ground-water discharges and surface-water runoff in low areas. The drains intersect various coulees on the Bench, most of which drain into Muddy Creek.
Figure 7. Photograph of a road cut showing gravel inter-mixed with medium-coarse sand.
The generally thicker deposits on the western portion of the Bench allow for more ground-water storage than in the thinner deposits in the idle and eastern portions of the Bench and has reduced the need for shallow drains on the western end (Osborne, 1983).

**WATER-LEVEL FLUCTUATIONS: RECHARGE AND DISCHARGE**

The hydrograph shown on figure 8 shows 10 years of water-level data for a well located at 22N03W15BAAD. Figure 8 illustrates the seasonal cyclicity of ground-water levels associated with the application of irrigation water. Shorter-term hydrographs shown in figure 9 also show that depth to ground water is highly dependent on the seasonal effects of irrigation and precipitation. During the irrigation season (generally from May through July), ground water is recharged and levels may rise to ground surface as is illustrated by the “Flood well” hydrograph in figure 9. From August to early May, water levels drop in response to ground-water drainage after the cessation of irrigation. In early spring prior to irrigation, ground water is at the lowest level. Depth to ground water commonly ranges from near ground surface to about 20 feet below ground surface, with depths of almost 35 feet below ground surface noted in deep wells.

Ground water flows from the higher western edge of the Bench to the lower eastern edge, and from the higher First Bench successively to the Second and Third Benches. Figure 10 illustrates ground-water flow conditions in December 1998, a period when water levels are falling in response to the cessation of irrigation. Flow paths converge at the coulees, drains, springs and seeps that constitute ground-water discharge areas. The hydraulic gradients across the First, Second and Third Benches were, 0.009, 0.005, and 0.003, respectively.

Sources of ground-water recharge include precipitation, canal losses (figure 11, photo A) and on-farm irrigation. Discharge occurs through extraction by pumping wells, as ground-water discharge via drains (figure 11, photo B), and as evapotranspiration including crop water demand. Of the total runoff from the Bench, Osborne (1983) estimated that about 65% occurred as ground-water baseflow into Muddy Creek.

Aquifer characteristics are indicative of a high degree of sensitivity to land-use practices. The protection of ground-water quality and quantity is critical to the protection of public health because the shallow ground water on the Bench is a sole-source aquifer. Also, the relationship between ground water and surface water highlights the importance of managing land-use practices to prevent ground-water contamination in a way that will ultimately protect the water quality of receiving streams.
Figure 8. Hydrograph for well located at 22N03W15BAAD.
Figure 9. Map showing short-term hydrographs for selected wells.
Figure 10. Water-level contour map for the Greenfields Bench, December 1998.
Photo A: The Main Canal is a source of ground-water recharge

Photo B: One of the many drains that act as ground-water discharge areas

Figure 11. Photographs showing irrigation structures that provide sources of recharge and sites for discharge.
**HYDRAULIC PROPERTIES**

Table 1 provides a comparison of transmissivity, storage coefficients, and hydraulic conductivity estimated from the results of aquifer tests performed on 13 wells across the Bench. Figure 12 shows the location of wells where aquifer test data were collected. Though variable, most estimates of aquifer transmissivity on the Bench are fairly high, ranging from $2.9 \times 10^3$ to $7.0 \times 10^4$ ft$^2$/day.

The variability in transmissivity values indicates heterogeneity in aquifer materials. For example, a notable difference exists between values of hydraulic conductivity for sites 22N02W26 and 22N02W26CDBD as shown on table 1 (19 ft/day using a pumping test versus 3,914 ft/day using a tracer test). This difference may be reflective of variability in geologic materials between the two sites. Clay matrices and/or caliche cementation shown on well logs for this area (Appendix B – well logs) can act as a semi-confining layer, causing perched water tables of limited areal extent. The hydraulic effects of this geologic heterogeneity may be expressed as higher horizontal hydraulic conductivity in deeper sands and gravels when compared to the horizontal conductivity in shallower, clay-rich, zones. Another explanation for the difference in estimated hydraulic properties may be that saturated thickness and hydraulic gradients were probably lower in October when Osborne conducted the pumping tests than in June when the tracer test was performed. Storativity ($S_y$) values shown in table 1 are reflective of an unconfined aquifer. Freeze and Cherry (1979) report that $S_y$ usually ranges from 0.01-0.30 for unconfined aquifers and from 0.005 to 0.00005 in confined aquifers. Zaluski and others (1984) calculated an average storativity of 0.07 for gravel deposits on the Bench.

Values for T and K are lower for those wells that were tested using a slug. An explanation for these lower values may be because of inherent bias in the test method itself. Since a very limited part of the aquifer is actually tested when a slug is used, the resultant estimates for T and K are expected to be lower than if a pumping test is used.

In summary, the Greenfields Bench aquifer is a productive aquifer with calculated values for hydraulic conductivity, K, that are comparable to clean sand and gravel (Freeze and Cherry, 1979).

### Table 1. Estimated hydraulic properties for the Greenfields Bench (see figure 12)

<table>
<thead>
<tr>
<th>Location</th>
<th>Well depth, ft.</th>
<th>$T$, ft$^2$/day</th>
<th>$S_y$, unitless</th>
<th>$K$, ft/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>22N02W24BABC*</td>
<td>50</td>
<td>$1.2 \times 10^4$</td>
<td>0.025</td>
<td>461</td>
</tr>
<tr>
<td>21N03W03CBBC*</td>
<td>26</td>
<td>$3.6 \times 10^3$</td>
<td>0.25</td>
<td>212</td>
</tr>
<tr>
<td>22N03W27</td>
<td>19.5</td>
<td>$1.6 \times 10^4$ (Osborne, 1983)</td>
<td>0.13</td>
<td>727</td>
</tr>
<tr>
<td>21N03W11ABAB*</td>
<td>24</td>
<td>500</td>
<td>0.016</td>
<td>36</td>
</tr>
<tr>
<td>22N02W14BBBBB</td>
<td>20</td>
<td>$8.1 \times 10^4$ (Osborne, 1983)</td>
<td>0.17</td>
<td>643</td>
</tr>
<tr>
<td>22N03W12</td>
<td>29</td>
<td>$2.3 \times 10^4$ (Osborne, 1983)</td>
<td>0.012</td>
<td>1,327</td>
</tr>
<tr>
<td>21N02W01DCC</td>
<td>23</td>
<td>$3.7 \times 10^4$ (Osborne, 1983)</td>
<td>0.11</td>
<td>236</td>
</tr>
<tr>
<td>21N03W03BDAC</td>
<td>40</td>
<td>$2.8 \times 10^4$ (Miller, 1998)</td>
<td>1.580</td>
<td></td>
</tr>
<tr>
<td>22N02W29CCCCC**</td>
<td>29.5</td>
<td>14.2</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>22N02W29CCCAA**</td>
<td>30</td>
<td>170</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>22N02W29CCCCB**</td>
<td>27.5</td>
<td>$2.9 \times 10^3$</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>22N02W24BADDD**</td>
<td>30</td>
<td>76</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>22N02W26</td>
<td>28</td>
<td>192 (Osborne, 1983)</td>
<td>19</td>
<td>3,914</td>
</tr>
<tr>
<td>22N02W26CDBD***</td>
<td>9</td>
<td>$7.0 \times 10^4$</td>
<td>19</td>
<td>3,914</td>
</tr>
</tbody>
</table>

*Transmissivity estimates represent an average of results obtained from Cooper-Jacob, Theis, Hantush and Papadopulos-Cooper analytical solutions.

** Estimates of transmissivity derived from slug tests using Bouwer and Rice (1976).

Figure 12. Map showing the location of aquifer-test sites.
In the following discussion, inorganic water-quality data are used to describe ground-water/surface-water interaction, including baseflow versus runoff conditions, and to characterize inorganic-constituent loading rates on surface water that receives ground water from the Bench.

Inorganic ground-water quality across the Bench appears to be highly influenced by the quality of the surface water that is delivered via irrigation canals and on-farm irrigation. As irrigation water has leached soluble minerals from the water-bearing gravel deposits, TDS concentrations have probably decreased over time. Subsequent water-quality changes occur in the subsurface, as surface water infiltrates below the root zone into the saturated zone. Drains, springs and seeps carry discharged ground water to surface-water bodies.

Water-quality information may be categorized as ground-water quality and surface-water quality (includes applied irrigation water and irrigation return flow). Figure 13 shows the location of all water-quality monitoring sites used in this investigation. Sixteen domestic wells (numbered 1 through 16), in addition to five drilled observation wells were used to characterize ground-water quality. The wells OW-1, OW-2, OW-3, OW-4, and OW-5 shown on figure 13 were installed on both upgradient and downgradient sides of the Main Canal at two separate locations. Well OW-5 was a dry hole and was not sampled. Lithology, well-completion, and hydrograph information for these wells is found in Appendix A.

Surface-water samples of recharge water (Main Canal) were also collected near the sites OW1 and OW4. Surface-water-quality samples were collected and flow measurements were performed on discharging drains, springs and from Freezeout Lake.

Ground-water quality data for the sites noted on figure 13 are found in Tables A-2 through A-4 in Appendix A. Surface-water quality data are found in Tables A-5 through A-7 in Appendix A. The analytical results include basic parameters such as specific conductance, pH, hardness, common ion analyses that include calcium, magnesium, bicarbonate, and nitrate, and a full suite of trace-metals.

**MAJOR CONSTITUENTS**

**Ground Water**

Figure 14 presents a diagrammatic comparison of the concentrations, in milliequivalents per liter (meq/L), of major water-quality constituents in four representative ground-water samples and in irrigation (recharge) water. The shapes of the graphs differentiate between various water-quality types. Total dissolved solids in ground water ranges from 246 to 2,219 mg/L. On average, TDS, bicarbonate and sulfate are three to four times higher in ground water than in irrigation (ground-water recharge) water (figure 14 and Tables A-2 through A-7). As irrigation water infiltrates through the soil profile into the aquifer, the TDS concentration increases because the soil and subsurface deposits provide a source of soluble minerals that are dissolved into the water as it migrates through the flow system. The pH of ground water is about 8 with field pH ranging from 7 to 9.3. Figure 14 shows that most of the ground water has a magnesium-bicarbonate type of water chemistry with low chloride and relatively little sulfate. The chemical characteristics of ground water as portrayed by the shape of the graphs, bear a resemblance to surface water (see figure 15). However, the average TDS of ground water (661 mg/L) is about two-thirds the average TDS concentration of surface water receiving ground-water discharge (1,009 mg/L) (Tables A-3 and A-6).
Figure 13. Map showing the locations of ground-water and surface-water quality monitoring sites.
Figure 14. Concentrations (meq/L) of major constituents in representative ground-water samples.
Figure 15. Concentrations (meg/L) of major constituents in representative surface water samples.
Well 4 is exceptional in that it contains 960 mg/L (20 meq/L) sulfate. Well 11 also exhibits slightly higher sulfate, at 7.8 meq/L. All of the other ground-water samples contained less than 3 meq/L sulfate. The probable explanation for this difference is that both wells are open to both the gravel and shale, mixing water from different geologic sources. Well 4 has an open-bottom that penetrates about 35 feet of the Colorado (Marias River Formation) shale, an abundant source of salts, including sulfate. Well-bore exposure to shale is more limited in other wells, with drilling depths into the shale ranging from only 1 to 13 feet. Well 11 penetrates about 2 feet of shale, according to the drillers’ log.

**Surface Water**

The surface-water chemistry of water applied as irrigation water is shown as the “Type 1, Irrigation supply (recharge) - Main Canal” curve on figure 15, and is very high quality, with a TDS of less than 200 mg/L. It is a calcium bicarbonate-type water with very low magnesium, sodium, chloride, and sulfate concentrations. The ratio of calcium to magnesium in milliequivalents per liter (meq/L) is 2.2, the highest Ca/Mg ratio of any water that was sampled. Total dissolved solids concentrations are less than 190 mg/L, but with moderate concentrations of alkalinity (about 100 mg/L as CaCO₃), the water is well buffered. The pH of the water samples from Main Canal is 8.2.

Figure 15 displays major ion concentrations for surface-water samples that are representative of four types of water chemistry. Type 1 is the calcium bicarbonate-type irrigation-supply (recharge) water (TDS=178 mg/L) that was discussed earlier. Type 2 is magnesium bicarbonate (TDS=565 mg/L), low sulfate (95 mg/L, 1.9 meq/L) water that occurs primarily during high-flow events. Type 3 is characterized as magnesium sulfate (TDS= 870 mg/L) water corresponding to low-flow conditions. Freezeout Lake (Type 4) is represented as sodium sulfate (TDS=4,897 mg/L) type water. Freezeout Lake is an internally drained basin so its water-quality characteristics are not expected to be typical of the flowing discharge sites.

Based on an evaluation of 28 water-quality samples, it appears that the chemistry of surface water in drains is dependent on flow stage. Surface-water quality samples from drains were collected concurrently with flow measurements (Tables A-5 through A-7) so that constituent loads can be estimated in surface water. Figure 16 shows typical graphs of TDS and loading rate versus flow at selected drain discharge sites. The site locations are shown on figure 13. For the graphs in figure 16, the flow (cfs) is reported below the date. As shown on figure 16, concentrations are usually highest during periods of low flow, yet the actual loading rate is at its lowest during low flow. Conversely, concentrations are lowest during high flow, but loading rates are at their peak during high flow conditions. It must be noted that ground-water discharge is probably the primary source of water during periods of low flow.

Figure 17 displays a relationship between flow stage and type of water contributing to in-stream flows. The Ca/Mg ratios of water from selected drain sites are illustrated with the respective discharge rates on figure 17. There seems to be a significant difference in Ca/Mg ratios between high flows and low flows. The average ratio of Ca/Mg in drain discharges during high flow is 0.84, while the average Ca/Mg ratio during low flow is 0.55. The low-flow ratio is more comparable to that of ground water (0.46 Ca/Mg) than to surface water applied as irrigation water (Ca/Mg ratio 2.2). This suggests a higher relative proportion of baseflow contribution to flow during low flow periods. Surface water under high flow conditions is also receiving a proportionately higher influx of surface water from overland flow. This suggests that the Ca/Mg ratios could be used as a marker in surface-water samples to indicate the relative contribution from baseflow.

This points out the importance of a carefully designed monitoring strategy when using water-quality data as a tool in planning remedial strategies, land-use management and TMDL development. If water-quality data are collected during low flow periods, they are probably most representative of ground-water-transported non-point sources of contamination from long-term land use practices. However, during periods of high flow, other sources of surface-water-recharge from overland flow, irrigation return-flow and point-sources, may become more important.
Figure 16. Graphs showing a comparison between surface-water discharge and total dissolved solids concentrations and loading rates.
Surface-water monitoring sites

Figure 17. Map showing discharge in cubic feet per second (cfs) and calcium/magnesium (Ca/Mg) ratios in surface water.
**NITRATE**

Since 1980, a large amount of nitrate data has been collected from ground water and surface water on the Bench. Table A-8 Appendix A presents nitrate results from 683 samples, including samples collected for this investigation. All of the data are expressed as nitrate as nitrogen in mg/L. Figure 18 A-C provides a graphical summary of these data. As shown in figure 18A, most of the data were collected in 1980.

Elevated nitrate concentrations have been reported in ground water across the Bench. Roughly 16% of the samples from 1980 to 1999 (Table A-8) contained nitrate in excess of 10 mg/L (figure 18B). The highest reported nitrate concentration was 44.7 mg/L. This sample (figure 18C), was collected from a well in Township 21N02W. Elevated nitrate concentrations were noted in samples from section 2 and section 9 of 21N02W (Table A-8 and figure 18C). One explanation for the elevated nitrate in this township (mostly First Bench) may be that there is proportionately more non-irrigated farming on this area of the Bench. Figure 18C compares nitrate concentrations in ground water underlying non-irrigated acreage versus irrigated acreage. While maximum values of nitrate were similar for both areas, wells located in non-irrigated areas displayed median values of nitrate at about 23 mg/L, while ground water underlying irrigated areas contained a median value of less than 5 mg/L. The process of saline ground-water development (dryland salinity/saline seep) may be occurring, increasing the overall salt load to the unsaturated zone. With the dryland saline seep process, salts that are leached from the soil and unsaturated zone into the ground water tend to reside in the aquifer because flushing or dilution does not occur as it would under irrigation. Nitrate is a salt commonly found in ground water affected by dryland salinity.

There are a number of possible sources of nitrate in ground water on the Bench, including fertilizers, septic tank discharge, soil organic nitrogen, or geologic sources. Variations in the natural abundance of the two stable isotopes of N (\(^{14}N\) and \(^{15}N\)) can be a valuable tool for semi-quantitatively resolving sources of nitrate in ground water. Sources of nitrogen from ammonia fertilizer, nitrate fertilizer, soil organic nitrogen, and animal or human waste have different isotopic signatures (Exner, 1994).

In December of 1998, the U. S. Geological Survey (D.A Nimick, written commun.,1998) collected water samples from 16 wells for nitrogen isotope analysis. The locations of the sampling sites and a chart showing the USGS analysis of the relationship between nitrate and \(^{15}N\) is shown in figure 19. The results suggest that the occurrence of nitrate in ground water is attributable to nitrogen fertilizer, ammonium fertilizer, soil organic nitrogen or a combination of these. About half of the sample results fall in the range for ground water affected by fertilizer use. The other results suggest that the source is nitrate fertilizer and/or soil organic nitrogen. The two samples that were collected from wells in non-irrigated areas of the Bench contained \(^{15}N\) levels that suggest soil nitrogen, nitrate fertilizer, or both as the source of nitrogen. Because of the limited sample population and the overlapping ranges of potential sources when using isotopic analyses, there is some degree of uncertainty as to the relative contribution of each source. A detailed evaluation of nitrate sources and nitrate mass transport was outside the scope of this investigation. This analysis did not identify the isotopic signature of naturally-occurring nitrate-nitrogen associated ground water in the Colorado shale, nor was the Colorado shale assessed as a potential source of nitrate. It is apparent that nitrate in ground water is likely derived from fertilizers or from natural sources such as soil organic matter or shale, and not from septic systems or animal waste. Additional, focused, data collection and analysis is necessary to characterize sources and mass transport of nitrate to the subsurface.

Nitrate loading in surface water from Bench drains is shown on figure 20. Figure 21 illustrates drain discharge in cubic feet per second (cfs) versus nitrate concentration. Surface-water monitoring sites S1 through S9 are shown on figure 13. Volumetric flow rates in the eight drains ranged from 0.27 cfs at S6 in April 2000 to 73.5 cfs at S8 in July 2000. Flows in Muddy Creek at Vaughn ranged from 24 cfs in April
2000 to 230 cfs in July 2000. Freezeout Lake is not a flowing drain and therefore discharge was not measured at this site.

Nitrate correlation to flow is similar to TDS correlation to flow. The lowest nitrate concentrations generally correspond to the highest flow rate. Conversely, the highest loading rates occur during periods of high flow.

A complete compilation of current and historic nitrate data for other surface-water bodies in the area can be found in McDonald (2000).
Figure 18A. Number of samples collected per year (1980-1999)

Figure 18B. Greenfields Bench nitrate data (1980-1999)

Figure 18C. Comparison of NO₃ concentrations in ground water under irrigated vs. non-irrigated acreage (1980-1999)

Wells in non-irrigated acreage located at 21N02W02 and 21N02W09

Figure 18 A-C. Nitrate data summary.
Relation of nitrate concentration, nitrogen isotope ratio, and land-use for ground-water samples collected in December 1998, Greenfields Bench, Source: USGS

Figure 19. Map showing locations of $^{15}$NNO$_3$ sampling from wells completed in gravel underlying the Greenfields Bench and relation of nitrate concentration, nitrogen isotope ratio, and land-use based on groundwater samples collected in December 1998 (Nimick, 1998).
Figure 20. Nitrate loading rates for surface water.
Figure 21. Surface-water discharge in cubic feet per second (cfs) versus nitrate concentration (mg/L nitrate as nitrogen).
HERBICIDE (ASSERT)

The aquifer’s shallow nature and its dependence on recharge from irrigation, render it particularly vulnerable to any agricultural chemical that can be mobilized and transported to the sub-surface. A quarterly ground-water sampling program was instituted in 1998 to characterize the occurrence of Assert in the aquifer. Concentrations of Assert and its acid metabolite, or daughter product, were detected in numerous wells tapping the aquifer.

Concentrations of Assert (parent compound) in 91 ground-water samples from 16 domestic wells ranged from 0.2 µg/L to 3.2 µg/L (Table A-9). The levels of Assert acid metabolite ranged from 0.2 µg/L to 5.0 µg/L. The average concentration of Assert in all domestic water samples is 0.51 µg/L and the average Assert/met concentration is 0.97 µg/L. Neither Assert nor Assert metabolite was detected in wells 3 or 5.

The highest concentrations of Assert and metabolite in domestic wells were found on the Third Bench (figure 22A). Concentrations in water samples from wells 10, 11, 15, and 16 consistently exceeded 1.2 µg/L. With the exception of well 13 on the Second-Bench, concentrations for the First and Second Bench were below 1.2µg/L (figure 22B). Although levels of Assert in well 13 were below 1.2µg/L, metabolite levels usually ranged from 2.0-4.2µg/L. The reason for consistently higher levels of Assert on the Third Bench is unknown. But, in addition to a hydraulic gradient towards the east as indicated by water-level contours (figure 10), there is also a head gradient driving ground-water flow from the more southerly First and Second Benches to the northernmost Third Bench. There is a possibility that since the Third Bench is receiving ground water from the First and Second Benches, that Assert is being transported to the Third Bench from the other benches, causing some accumulation of the herbicide as evidenced by the higher concentrations there.

In general, metabolite concentrations exceeded the concentration of the Assert parent compound, probably because the metabolite is more soluble than the parent compound and because there may have been sufficient time for the parent compound to degrade to its acid metabolite before being transported to the saturated zone.

There appears to be a possible statistical correlation between Assert (and/or its acid metabolite) and the occurrence of nitrate. Table A-9 in Appendix A displays ground-water levels (feet below ground surface) and concentration data for Assert and its acid metabolite (in µg/L), and nitrate (as N in mg/L). Statistical correlation coefficients, ρ, are also reported for Assert and/or metabolite versus nitrate and for Assert and/or metabolite versus water levels. Figure 23 illustrates a correlation between Assert and/or metabolite, and nitrate concentrations in Well 15. Additional correlation charts are found in figure A-5 in Appendix A.
Figure 22A. Assert concentrations and ground-water levels on the Third Bench.
Figure 22B. Assert concentrations and ground-water levels on the First and Second Benches.
A positive correlation means that as one variable increases, the other variable increases. A negative correlation means that as one variable increases, the other decreases. If \( \rho \) is either \(-1\) or \(+1\), the variables have a perfect linear relationship in that all of the points in a sample lie exactly on a line. If \( \rho \) is near \(-1\) or \(+1\), there is a high degree of linear association. In 9 of the 16 wells (56\%) the correlation coefficient, \( \rho \), exceeds \(+0.5\) suggesting a moderate degree of linear association. In six of the wells (1, 6, 10, 14, 15, and 16), a high degree of linear association was demonstrated, with \( \rho > 0.80 \) reaching a maximum of 0.98.

It must not be assumed that because these two variables are related, a change in nitrate or Assert causes a change in the other. A high degree of linear relationship does not prove a cause-and-effect relationship. Rather, the pattern of Assert concentration-change over time is similar to the pattern of nitrate concentration-change over time. Whichever factors are causing the transport of Assert, are also influencing the movement of nitrate through the flow system.

Correlation coefficients for Assert and metabolite versus water level are low, signifying that increases (or decreases) in one variable, do not correspond to increases (or decreases) in the other variable. Although there does not appear to be a high degree of correlation between Assert and water levels, the highest concentrations of Assert usually occur near the peak in water levels or on the falling limb of the hydrograph, suggesting that hydraulic loading is a predominant factor in the transport of Assert from the ground surface downward to the water table and through the ground-water flow system. As ground water rises to a level that is at, or near ground surface, Assert/metabolite and soluble nitrate (probably either from fertilizer or soil organic nitrogen) are dissolved in the soil organic layer, and transported into the saturated zone. The solutes are subsequently moved through the flow system and discharged through the various drains, springs and seeps along the edges of the Bench.

Surface-water concentrations of Assert and 2,4-D noted in surface-water sample sites S1-S9 are tabulated in Table A-10 in Appendix A. Figure 13 shows the locations of the water-quality monitoring sites for drains. Herbicide samples were collected in April and July 1999 and in April and July 2000. Flow in the drains was measured on the same day that samples were collected (Table A-10 in Appendix A). Herbicide samples were collected and flow measurements were also performed at the USGS gaging station, Muddy Creek at Vaughn, in April and July 2000.

In July 1999, 2,4-D was detected at 0.59 \( \mu \text{g/L} \) at S9. Levels of Assert and metabolite in drains were generally lower than levels found in ground water. Assert levels ranged from “no-detection at or above the “limit of quantitation (LOQ)” (0.00\( \mu \text{g/L} \) on spreadsheets) to 0.85\( \mu \text{g/L} \). Metabolite concentrations ranged from “no-detection at or above the LOQ” to 1.5\( \mu \text{g/L} \).

Figure 24 displays Assert and metabolite concentrations versus drain discharge rate. The results further illustrate the predominance of baseflow in drains during low flow periods. Ground water generally contains proportionately more metabolite than Assert parent compound. In general, high flow periods are characterized by proportionately more Assert parent compound than at low-flow periods. During high flow, surface water contributes a higher proportion of flow than at low flow periods. During low flow, ground water discharge to drains is the predominant source of flow.

The occurrence of herbicides in the Greenfields Bench aquifer is closely related to agricultural practices, the sensitivity of the aquifer to contamination, the interdependence of water-uses on the Bench, and the intensity of irrigation. Because voluntary measures are sought to decrease or eliminate herbicide residues in ground water, a field study was conducted comparing Assert migration to ground water under three irrigation methods with the intent of providing recommendations for long-term planning and changes in land-use management practices. The results of this study are presented below.
Figure 23. Graph for Well 15 that illustrates a high correlation coefficient for Assert and/or metabolite versus nitrate.

$p = 0.95$ for Assert and metabolite versus nitrate

$p = 0.92$ for Assert and metabolite versus nitrate

$p = 0.95$ for Assert, ug/L versus nitrate

$p = 0.92$ for Assert metabolite, ug/L versus nitrate

$p = 0.95$ for Nitrate, mg/L versus nitrate
Figure 24. Surface-water discharge in cubic feet per second (cfs) versus Assert/met. concentrations (ug/L).
EXPERIMENTAL STUDY OF HERBICIDE (ASSERT) TRANSPORT

Assert is an imidazolinone compound that contains the active ingredient Imazamethabenz methyl. It is a post-emergent herbicide used for control of wild oats, mustards and buckwheat in barley and wheat. After rapid absorption through foliage and roots, Assert is translocated through the plant where inhibition of amino acid synthesis and hence plant cell division of growing roots and shoots occurs. The application rate for Assert is 1.2 to 1.5 pints per acre. The application rate within this range is largely determined by density of weed infestation. Application rates need to be high enough to provide good control and minimize weed resistance yet from an economic standpoint, need to be as low as possible to minimize crop production costs. Herbicide efficacy is tied to application at the correct weed growth stage. This optimal window of application often coincides with crop moisture needs. In many irrigation seasons, this has resulted in crops being irrigated shortly after Assert had been applied. Assert is a 3:2 mixture of para- and meta-methyl isomers. When applied, Assert undergoes hydrolysis. It hydrolyzes slowly at pH ranges from 5 to 7, but rapidly in alkaline conditions, resulting in the de-esterified imazamethabenz acid. It is the acid that provides the weed control. The density of Assert is 0.3 g/ml at 20°C.

The organic carbon-water partition coefficient, $K_{oc}$, for the m-isomer of Assert is 66 and the $K_{oc}$ for the p-isomer is 35. Good soil-sorption occurs when $K_{oc}$ is 300 or greater. Optimal sorption of Assert occurs at lower pHs and in soils with high clay and organic matter content. However, Assert is a strong acid with an average dissociation constant ($pK_a$) of 2.9. When the $pK_a$ value of a pesticide is less than 3, the anionic pesticide species is dominant in the soil pH range of 5-8. Sorption will be reduced at pH greater than 3.9, being only weakly adsorbed in soils having high pH, such as the soil pH found on the Bench. When these conditions occur, the pesticide is very soluble and will be highly mobile in soil unless a chemical complex is formed (Wauchope et al, 1992) or unless binding occurs in soil clay and/or organic matter. The sorption of Assert to clay and organic matter is reversible.

With a reported soil half-life of 45 days, Assert has a moderate persistence. Its half-life is both pH- and temperature-dependent. Under dry conditions, imidazolinones are resistant to photolytic degradation. However, reported degradation in surface water occurs rapidly. The primary degradation process is from microbial decomposition. The water solubility (25°C) of the para-isomer is 857 mg/L and 1,370 mg/L for the meta-isomer. While previous studies indicate that Assert remains in the top 18 inches of the soil, suggesting limited mobility, EPA has noted that Assert has the potential to leach and contaminate ground water at very low concentrations. The application of organic fertilizer retards decomposition of Assert and its metabolite (Rouchard and Gustin, 1994).

In general, the processes that affect the transport of pesticides (inclusive of herbicides, fungicides, etc.) through the soil into ground water are dependent upon the pesticide properties and environmental conditions. Pesticides not metabolized by the pest (weeds in this case) remain in the environment until they are degraded. Pesticides that are not rapidly degraded by microbial, photolytic, hydrolytic, chemical, or other processes and that have moderate to high solubility, poor sorption and moderate to lengthy persistence will have the potential to leach to ground water. Agricultural practices such as irrigation methods may be altered to prevent, or reduce, pesticide occurrence in ground water.

The goal of the field study was to evaluate the mass transport of the herbicide, Assert, to ground water under three commonly used irrigation methods. Using an observation-well network and an intensive herbicide-sampling strategy, a field experiment was conducted on a malting-barley field (figure 25) to evaluate Assert concentrations in soil and ground water under irrigation by flooding, wheel-line sprinkling, and center-pivot sprinkling. Assert was chosen as the herbicide of interest because of its widespread use and consistent detections in wells on the Greenfields Bench.
Figure 25. Map showing the location of the experimental field study site.
STUDY SITE AND METHODS

The total field size, including both flood and sprinkle-irrigation (figure 26) is 148 acres. A 5-acre test plot was located in the sprinkle-irrigated field and another 5-acre test plot was located in the flood-irrigated field. In the year 2000, the northern 110 acres (inclusive of one 5-acre sprinkler test plot) were irrigated with a wheel-roll sprinkler and 38 acres (inclusive of the other 5-acre flood test plot) were flood irrigated. In the fall of 2001, the landowner replaced the wheel roll system with a center pivot that was capable of irrigating the entire field. During the irrigation season of 2001, the landowner was able to interrupt the pivot cycle so as not to sprinkle the flood plot. Only 8 acres (inclusive of the 5-acre flood test plot) were flood-irrigated in 2001 and 140 acres inclusive of the 5-acre sprinkle test plot, were irrigated using a center-pivot sprinkler system.

Twenty, 2-inch diameter PVC-cased observation-wells (Appendix B) were installed in March 2000. The wells were drilled using a hollow-stem auger fitted with a down-hole hammer. Sixteen of the wells were deep/shallow, nested pairs. The shallow wells were about 9 feet deep with screened intervals from 4 to 9 feet. The deep wells were drilled into weathered bedrock (15 to 20 feet below ground surface) with screened intervals ranging from 9 to 19 feet. The well pairs were designed to separately monitor the seasonally-saturated fine-grained shallow zone and the deeper, coarser-grained aquifer. It was anticipated that most of the Assert, which has a density about one-third the density of water (0.3 g/mL at 20°C), would be distributed in the upper portion of the aquifer. The following well designations represent deep/shallow well pairs, with the letter, “A”, symbolizing the deep well and the letter, “B”, symbolizing the shallow well.

- 1A/1B
- 2A/2B
- 3A/3B
- 4A/4B (Flood plot)
- 6A/6B
- 7A/7B
- 8A/8B
- 9A/9B (Sprinkler plot)

Wells 5, 10, 11, and 12 are deep wells, not paired with shallow ones. Wells 1 through 5 were used to monitor ground water under the 5-acre flood test plot and wells 6 through 10 monitor ground water under the 5-acre sprinkle test plot. Well 11 is located on the upgradient edge of the field, while well 12 is located on the downgradient edge of the flood plot. Continuous-monitoring, digitally recording, water-level recorders were used to measure water-levels in wells 1A, 3A, 6A, 8A, 9A, 11, and 12.

Well-completion methods included a sand pack surrounding the perforated zone followed by a bentonite seal from the top of the sand pack up to the ground surface. All wells were developed with an air compressor to remove fines from the sand pack and well bore except for those shallow wells that were dry at the time of installation.

Assert was applied to the fields on June 10, 2000 and on June 1, 2001. In the year 2000, Assert was applied aerially because wet field conditions precluded application using a field vehicle. It is important to note that irrigation occurred prior to application of Assert in 2000 and again after application, whereas in 2001 irrigation occurred only after application of Assert. In most years, when there is sufficient soil moisture to promote wild-oat emergence in the spring before irrigation, Assert is applied to the emergent weeds prior to irrigation. But in 2000, the field was so dry that neither barley nor wild oats would emerge without an irrigation cycle. In this case, it was necessary to apply the herbicide after an irrigation cycle. For both years, Assert was applied at the rate of 1.5 pints per acre.

Ground-water and soil samples were collected and analyzed by the Montana Department of Agriculture. For most of the observation wells, pre-irrigation/pre-Assert application samples were collected in early spring, weekly samples were collected through May, and then bi-weekly samples were collected throughout the irrigation season into early fall. This schedule was followed for well 8 in the year 2000 only; in the year 2001 only a pre-irrigation sample was collected from well 8. Likewise this schedule was followed for wells 11 and 12 in the year 2001.
Figure 26. Schematic showing test-plot design and a simplified geologic cross-section.
In the year 2000, wells 9, 11, and 12 were sampled pre-irrigation, then weekly in June and July. Wells 5 and 10 were only sampled prior to irrigation.

Composite soil samples were collected from the 5-acre flood and sprinkler plots. Each composite soil sample was composed of fifteen random sub-samples. Soil samples were collected prior to Assert application to determine textural characteristics and pre-application Assert levels. During the year 2000, additional soil samples were collected at monthly intervals during the growing season.

Reported mass flux values for ground water are reflective of those changes in concentration that occurred in excess of the analytical limit of quantitation (LOQ) of 0.2µg/L. The hydrograph separation method was used to estimate ground-water recharge at the various well sites. The durations of flood, wheel-line, and center-pivot irrigation events were 3 days, 12 days and 18 days, respectively. Accordingly, the values for duration-of-recharge-event as used in rate calculations were 3 days for flood events in 2000 and 2001, 12 days for wheel line sprinkling in 2000, and 18 days for center pivot irrigation in 2001.

A tracer test was conducted using lithium bromide (LiBr) to evaluate its effectiveness as a tracer for Assert and to characterize ground-water flow rate. In the year 2000, 1-kg of LiBr was applied to a 1-m² surface pit, 1-meter upgradient from well-pairs 1 (flood site) and 6 (sprinkler site), just prior to irrigation. In the year 2001, the same configuration and timing was used only for well-pair 1. Bromide ion concentrations were measured at four-hour intervals during irrigation using a bromide ion-specific electrode.

The project field-activities schedule summarized in Table B-1 in Appendix B reports the dates of pertinent field activities such as irrigation timing, precipitation events, and sampling activities.

DATA RELIABILITY

The concentration of Assert (or its metabolite) in water samples from observation wells in the study plots was extremely low, ranging from <0.2 µg/L to 10.0 µg/L. Herbicide-data reliability (analytical uncertainty) and the use of the Horwitz function to qualify numerical value was discussed in a previous section.

Assert metabolite concentrations were used for mass-flux computations because of the metabolite’s consistently higher concentration in ground water when compared to the parent Assert compound. As explained in a previous section, the higher the concentration, the more reliable the data. All mass-flux data must be accompanied with the caveat that the computations were based on reported values; actual values may vary by as much as ± 32-45%.

SITE HYDROLOGY AND SOILS

The saturated thickness of the aquifer during irrigation is about 18 feet. Depth to ground water ranges from ground surface to 10 feet below ground surface. The upper 6 feet of the aquifer consists of poorly-sorted gravel, silt, and sand embedded in a clay matrix, with the lower 12.5 feet generally composed of well-sorted sand, gravel and cobbles.

The soil “A” horizon (figure 27) is classified as a clay loam with pH of 7.4 and average total organic carbon content of 2.5%. The “A” horizon is usually 4- to 8-inches thick. Total organic
Figure 27. Schematic showing soil characteristics and texture.
carbon content decreases with depth, to an average of 0.25% in the “C” horizon. Conversely, soil pH increases with depth, to a maximum of 8.1 in the “C” horizon.

Ground water at the study site is primarily a magnesium bicarbonate type (Table B-2, Appendix B). Ranging from 253 to 389 mg/L, the average TDS of ground water is about 320 mg/L. The water is well-buffered; pH ranges from 7.3 to 8.2 and average hardness and alkalinity values were 246 and 253 mg/L as CaCO₃, respectively. Nitrate concentrations ranged from below the detection level to 2.3 mg/L Results from trace-element analyses do not indicate elevated concentrations and do not approach maximum contaminant levels for drinking water.

Prior to the irrigation season, ground water flowed in a southeasterly direction across the study field (figure 28). With the onset of flood irrigation, flow directions shifted to a more northeasterly direction at the flooded site in response to increased hydraulic head in the southern portion of the field. Ground-water levels on the flood plot usually rise to ground surface during irrigation. Ground-water flow direction under both wheel line and center pivot responds to the localized increase of head across the sprinkler site, resulting in a more marked southeasterly flow vector across the sprinkler site.

Before irrigation, the hydraulic gradient across the study site was 0.004. During irrigation, the hydraulic gradient across the entire field was 0.006, with gradients across the flood plot during flooding estimated to be as much as 0.008.

**STUDY RESULTS AND DISCUSSION**

In the year 2000 before herbicide application, Assert metabolite was detected in five wells, with the maximum concentration of 0.53 µg/L measured in well 11 (Table B-3 and figures B-7 through B-24 in Appendix B). Pre-application levels in 2001 were higher, ranging from the LOQ to 1.6 µg/L of metabolite in well 3B. It must be noted that prior to June of 2000, Assert had not been applied to this field since 1997. It is significant that Assert residuals were still found after 2 years of non-use. This probably explains the slightly more elevated pre-application levels in 2001; 2001 pre-application sampling occurred nine months after the 2000 application. Possibly because of its higher solubility (at 25°C, 1370 mg/L for metabolite vs. 857 mg/L for parent Assert), or because the parent compound had hydrolyzed to the acid metabolite, metabolite was generally found in higher concentrations than the Assert parent compound. Assert and metabolite concentrations were usually higher in shallow wells than in deep wells. In 2000, the highest concentration of metabolite (3.5 µg/L) was found in shallow sprinkler-well 6B. The highest concentration of metabolite (10.0 µg/L) was found in shallow flood-well 2B in 2001.

Assert may be preferentially distributed in the upper portion of the water column because the proportionately higher clay content in the upper portion of the aquifer is acting as a temporary reservoir for Assert. Other investigators have noted that in 2:1 clay soils subject to wet/dry cycles similar to seasonal changes on the Bench, that herbicides with chemical characteristics similar to Assert, will diffuse into the clay micropores about four times faster than diffusion out of the micropores after re-wetting has occurred. In other words, once the soil is re-wetted after a dry period, it may take up to four times longer for Assert to diffuse out of the clay micropores into the soil/water solution (Bryan Gentsch, BASF, oral communication, 2002). Another explanation for higher concentrations in the shallow zone may be the establishment of a shallow concentration gradient of (low density) Assert caused by insufficient mixing with the deeper flow system.

In the year 2000, ground-water samples collected from all wells at the beginning of the growing season indicate lower concentrations of Assert at the flood plot (figure 29A) than at the sprinkler plot (figure 29B).
Figure 28. Water-level contour maps for irrigation test plots.
Figure 29A. Hydrographs showing concentrations of Assert and Assert metabolite in flood wells.
Figure 29B. Hydrographs showing concentrations of Assert and Assert metabolite in sprinkler wells.
Assert breakthrough in 2000 generally occurred about 30 days after application in the flood-irrigated plot and about 40 days after application in the wheel line sprinkler-irrigated plot. In 2001, breakthrough in the flood-irrigated wells occurred about 30 days after application, with the exception of deep well 1A, where breakthrough lagged behind by an additional 30 days, or 60 days after application (figure B-7). In 2001, breakthrough of Assert did not occur under center-pivot sprinkler irrigation.

**Ground-water recharge**

Recharge (Table 2) was calculated using the following equation,

Feet of recharge = Δh × η,

where,

Δh = change in water level during irrigation event, feet, and,

η = Porosity, unitless, estimated at 25%

<table>
<thead>
<tr>
<th>Year and irrigation method</th>
<th>Recharge (feet)</th>
<th>Recharge volume (acre-feet)</th>
<th>Metabolite flux (grams)</th>
<th>Flux / Recharge ratio (grams/acre-ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 flood</td>
<td>1.0</td>
<td>38.0</td>
<td>22</td>
<td>0.5</td>
</tr>
<tr>
<td>2001 flood</td>
<td>1.1</td>
<td>8.8</td>
<td>25</td>
<td>2.8</td>
</tr>
<tr>
<td>2000 wheel line</td>
<td>0.3</td>
<td>31.5</td>
<td>61</td>
<td>1.9</td>
</tr>
<tr>
<td>2001 center pivot</td>
<td>0.1</td>
<td>13.2</td>
<td>0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Average estimates for ground-water recharge under flood irrigation are 1.0 ft and 1.1 ft for the years 2000 and 2001, respectively (Table 2 and figure 30). This corresponds to a recharge volume (hydraulic load) from flood irrigation of 38 acre-ft in 2000 when the total flooded acreage was 38 acres, and 8.8 acre-ft in 2001 when the total flooded acreage was 8 acres (figure 30). Ground-water recharge from the wheel-line sprinkler system in 2000 was 0.3 feet, corresponding to a recharge volume of 31.5 acre-ft (110 acres irrigated with the wheel-line sprinkler). By comparison with the wheel-line sprinkler, the center pivot sprinkler contributed only 0.1 feet or recharge, or 13.2 acre-feet in 2001 (140 acres irrigated by center pivot in 2001).

The deep and shallow flow systems, as measured by the deep/shallow nested well pairs, seem to exhibit slight differences in recharge (figure 31A). Recharge to the shallow system on the flood site was slightly less than in the deep flow system on the flood site (38 acre-ft vs. 39 acre-ft) in 2000. In 2001, the recharge in the deep and shallow flooded systems was identical. The total recharge on the flood site in 2000 was about 4 times more than in 2001.

A clay matrix in the upper zone of the aquifer may act as an aquitard and as a medium for temporary attenuation of Assert and metabolite. The hydraulic effects of the shallow clay matrix are accentuated by the higher hydraulic loading on the flood site in 2000. These results also suggest that horizontal hydraulic conductivity is greater than vertical hydraulic conductivity in the deep system. An evaluation of differences in water levels between nested pairs suggests that in general, the hydraulic gradient is upward, except during an irrigation event, when the gradient reverses to a downward trend. This suggests that the deeper wells tap a zone of higher permeability (supported by the lithologic reports on well logs). Subsequently, the higher permeability of aquifer materials in the deeper zone transmits the higher head from upgradient more rapidly than the clay-rich shallow zone. This may explain the additional 30-day lag in Assert breakthrough in well 1A following flood irrigation. During irrigation when the gradient is
Figure 30. A comparison of ground-water recharge and the mass-flux of Assert metabolite for the years 2000 and 2001.
downward, the clay-rich upper zone becomes the limiting factor in downward vertical flow, retarding flow and possibly temporarily adsorbing Assert onto clay micelles.

Mass-flux of Assert metabolite

This discussion of herbicide mass flux through the flow system is limited to an analysis of the metabolite of Assert rather than Assert parent compound. In the majority of observation wells where detections occurred, the metabolite concentrations were significantly higher than concentrations of Assert parent compound, thereby rendering the data for metabolite statistically more reliable, with lower coefficients of variability (see above section on Data Reliability). The low concentrations of parent compound in ground water carry such a high coefficient of variation (about 45%) that significant differences between concentrations are questionable, making it difficult to establish the presence or absence of concentration trends (see error bars on the hydrographs in figures 29A and 29B and in Figures B-7 through B-24 in Appendix B).

As reported in table 2, the average metabolite-mass flux on the flood site increased from 22 grams in the year 2000 to 25 grams in 2001. But the change in mass flux on the sprinkler site from 2000 to 2001 was more dramatic, decreasing from 61 grams under the wheel line sprinkler in 2000 to 0 grams under the center pivot in 2001.

There are a number of variables involved in calculating the recharge and mass flux attributable to any one irrigation method. The variables include,
1. Irrigation method, such as flood, wheel line, or center pivot,
2. Changes in the number of acres that were irrigated by a given method in a given year,
3. Reported ground-water concentrations under each irrigation method.

The expression of the ratio of unit mass flux per unit recharge is a method of describing Assert mass transport while accounting for these variables. Calculations for the unit mass flux / unit recharge ratio are reported in the last column in table 2.

Differences in metabolite-mass flux exist between deep and shallow parts of the aquifer. These differences are apparent in figure 31B where results are expressed in terms of unit mass flux per unit recharge (grams per acre-ft of recharge). Mass flux / recharge ratio is consistently higher in the deeper flow system than in the shallow system on both plots in 2000 and on the flood plot in 2001. The flux per unit recharge increased on the flood plot from 2000 to 2001, the flux per unit recharge decreased to zero on the sprinkler plot from 2000 to 2001.

Under a flood irrigation event, ground water rises almost to ground-surface, coming into contact with Assert-enriched soil. This provides an instantaneous influx of Assert to ground water. In the flood wells, as shown in figure 31B, the flux per unit recharge ratio was low in 2000; Assert concentrations were low, and recharge (hydraulic loading) was high. The lower mass loading in 2000 was probably due to dilution. Ground-water levels also rose to the soil zone in 2001, providing a source of Assert in ground water, but recharge was four times lower in 2001, resulting in higher concentrations and higher ratios of flux per unit recharge.

Under wheel line sprinkling in 2000, the mass flux / recharge ratios were 2.9 and 1.0 in the deep and shallow sprinkler wells, respectively. Apparently, the downward hydraulic gradient under the wheel line sprinkler was sufficient to transport Assert through the soil into the saturated zone, but the hydraulic loading was insufficient to reduce the concentrations through dilution, as was the case with flood irrigation in 2000. Mass flux / recharge ratios (figure 31B) for the center pivot sprinkler used in 2001 were zero for both the deep and shallow observation wells, indicating that the center pivot did not appear to provide sufficient hydraulic loading to transport Assert from the soil downward into the saturated zone.
Figures 31A and 31B. Graphs showing recharge and mass-flux:recharge ratios for flood and sprinkler wells.
Tracer test

A data summary and charts showing tracer-test results for 2000 and 2001 are found in Appendix B, tables B-5 and B-6 and in figures B-25 and B-26, respectively. Results of the tracer test were inconclusive for the flood plot in 2000. It is assumed that on the flood plot, the lithium bromide (LiBr) was flushed through the system at such a high rate that the bromide-ion sampling frequency was too low to detect the initial breakthrough.

But results from 6B (sprinkler plot) in 2000 indicate that bromide-ion breakthrough (6/24/00), occurred 2-days prior to the breakthrough of Assert on 6/26/00. The data show that although not appropriate for use as a surrogate indicator for Assert, LiBr is a conservative ground-water tracer.

The tracer test was repeated for the flood plot in 2001. The first concentration peak of bromide ion was measured in well 2B (160-feet down-gradient from well 1B), 12-hours before the peak was measured in well 1B (figure B-26). These results further support the assertion that horizontal hydraulic conductivity is much higher than vertical hydraulic conductivity. A second upward trend in bromide concentration began on 6/28/01, but insufficient data was collected to fully characterize the trend.

Estimates for transmissivity and hydraulic conductivity, calculated from the 2001 flood-plot tracer-test were $7.0 \times 10^4$ ft$^2$/day and 3,914 ft/day, respectively. It must be noted that the estimates were based on an 18-ft. saturated-thickness and a hydraulic gradient of 0.007 estimated during flood irrigation.

Assert residuals in soil

Prior to soil-sampling on 8-Mar-00, there had been no Assert application to the field for 26 months. Assert was applied to the field on 9-June-00 at the rate of 1.5 pints/acre. On 11-June-00, two days after Assert application, 30 days after sprinkler irrigation and 14 days after flood irrigation the soil concentrations were 1,800 $\mu$g/kg and 1,400 $\mu$g/kg in the sprinkler and flood plots, respectively (Table 3). Yet by 3-July-00, 24 days after application, roughly half of the Assert had either been metabolized by plants or microbes, photo-degraded, hydrolyzed, or transported from the soil either via surface-water runoff or by leaching to ground water. By 24-July-00, soil concentrations had decreased to about 300 $\mu$g/kg, two to four times the concentration in the pre-application soil.

Table 3. Assert concentrations in soil.

<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
<th>Flood plot</th>
<th>Sprinkler plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Assert, $\mu$g/kg</td>
<td>Met., $\mu$g/kg</td>
</tr>
<tr>
<td>8-Mar-00</td>
<td>Pre-application</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>11-Jun-00</td>
<td>2-day post-application</td>
<td>1,400</td>
<td>53</td>
</tr>
<tr>
<td>3-Jul-00</td>
<td>24-day post-application</td>
<td>810</td>
<td>110</td>
</tr>
<tr>
<td>24-Jul-00</td>
<td>45-day post-application</td>
<td>310</td>
<td>21</td>
</tr>
<tr>
<td>3-Mar-01</td>
<td>Pre-application</td>
<td>110</td>
<td>39</td>
</tr>
<tr>
<td>6-Aug-01</td>
<td>66-day post-application</td>
<td>480</td>
<td>36</td>
</tr>
</tbody>
</table>

In comparing 2000 pre-application levels of Assert and metabolite with those from 2001, it is noted that in general, concentrations were higher in 2001 than in 2000. Before the 2000 pre-application samples, there was a 26-month lapse between application and sampling, but for the 2001 pre-application sample the time lapse from application to sample was only 9 months, allowing less time for transport or degradation of the metabolite, leaving higher residual metabolite concentrations in 2001.

Concentrations of Assert parent were higher in the 6-Aug-01 post-application sample than in the 3-Mar-01 pre-application sample, but the metabolite concentrations had decreased from 3-Mar-01 to 6-Aug-01. The metabolite seems to be degraded or solubilized and transported through the soil at a much higher rate than the Assert parent compound.
In the two months following Assert application, soil concentrations were higher on the flood plot than on the sprinkler plot, but after 9 months, this trend reverses, and the sprinkler-soil residual exceed those of the flood-plot residuals. There may be some environmental or geological factors affecting differential soil attenuation between the flood and sprinkler site. For instance, irrigation water applied to the flood site may reduce soil temperatures such that microbial degradation of Assert was temporarily retarded. Or the soils on the flood plot may be slightly more clay-rich than those on the sprinkler plot, enhancing the temporary adsorption to clays on the flood soils. Clay adsorption is temporary so desorption would occur over time.

Persistence of Assert in the soil is very problematic. Assert had not been applied to the field plots for 26 months prior to the initial soil sampling on 8-March-00. Up to 120 µg/kg had been retained in the soil for longer than two years. The extreme persistence of Assert in soil was inconsistent with the 45-day half-life claimed by the chemical manufacturer. The soil appears to be serving as a “reservoir” for Assert, allowing the chemical to desorb or degrade at some rate dependent on a variety of environmental conditions.

Pool (1993) notes that microbial decomposition and adsorption are important factors affecting the degradation of Assert in soil. He showed that its persistence was related to the clay content and organic matter content of soils. However, Assert is anionic and therefore clay and organic matter account for minimal anionic adsorption. Pool also found that on its own, pH did not play a significant role in determining Assert activity, but noted that lowering the pH enhanced sorption in soils. Rouchard (1994) found that on non-irrigated sites in Belgium, organic fertilizer treatments retarded the soil metabolism of Assert and its metabolites.

Unlike the experimental field plots, Pool’s research was conducted on soil with a low pH (4.1-6.2 pH) and Rouchard worked on non-irrigated sites. The exact cause of Assert persistence in soil beyond the expected half-life is unknown. However, it is suspected that high soil pH associated with calcium bicarbonate buffering capacity enhances soil sorption and non-microbial hydrolysis that produces Assert acid metabolite.

Previous studies have shown that wildfire and prescribed fire in forests can alter soil biochemical properties and microbial populations. Choromanska and DeLuca (2001) found that heat generated during fire induces chemical oxidation of soil organic matter thereby altering carbon and nitrogen transformations. They found that higher temperatures resulted in greater microbial mortality and a greater release of soluble sugars and ammonia-nitrogen. Pietikainen (1999) cites that the most frequently reported pattern of response of the total microflora to burning is an immediate decrease in amounts of microbes after the burning. This is followed by a gradual recovery to pre-burn levels or higher, which usually occurs within days or months.

Because of uncertainty in the role of soil microorganisms in Assert biodegradation, a preliminary soil microbiological evaluation was conducted in the spring of 2001. The purpose of the microbial evaluation was to determine whether burning the crop residue (stubble) had an effect on overall soil-bacterial numbers.

The results (Table 4) show a one-log reduction of soil bacterial numbers after burning at all locations, including the site that was not burned. However, sampling site discrepancies occurred on the “never burned” site that suggest that the after-burn sampling site was not reflective of “A”-horizon soil. In any case, these results are highly preliminary and are included here for the purposes of suggesting a direction for further investigation.
Table 4. Results of preliminary microbiological sampling of soil. (Burns and Mitman, 2001)

<table>
<thead>
<tr>
<th></th>
<th>Before Burn, March 8, 2001</th>
<th>After Burn, April 25, 2001</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Live</td>
<td>Dead</td>
</tr>
<tr>
<td>Flood Plot</td>
<td>4.920 x 10^9</td>
<td>1.796 x 10^9</td>
</tr>
<tr>
<td>Sprinkler Plot</td>
<td>5.223 x 10^9</td>
<td>1.805 x 10^9</td>
</tr>
<tr>
<td>Never Burn 4 inches</td>
<td>5.584 x 10^9</td>
<td>1.620 x 10^9</td>
</tr>
<tr>
<td>Never Burn Surface</td>
<td>5.675 x 10^9</td>
<td>1.978 x 10^9</td>
</tr>
</tbody>
</table>

Additional microbiological work was performed to determine whether soil microorganisms could tolerate the presence of Assert in concentrations normally found in the soil. The results show that soil microorganisms survive on agar plates containing Assert in concentrations ranging from 50 to 2,000 µg/L, after being incubated at 5°C (Burns and Mitman, Appendix B, 2001).

Soil concentration data are revealing, but limited in quantity. Additional soil monitoring is suggested to better understand the role of soil characteristics such as organic content, clay content, and microbial ecology, in the adsorption/desorption and biodegradation of Assert.

The microbiological evaluation performed should be considered highly preliminary. A comprehensive experimental design based on deriving reproducible results from soil sampling should be undertaken before making any conclusions about soil health vs. crop-residue burning.
CONCLUSIONS

1. The dramatic fluctuation of ground-water levels across the Bench demonstrates a direct hydraulic connection to the surface water in the irrigation distribution canals, a condition that increases the aquifer sensitivity to land-use activities and has serious ramifications for source-water protection.

2. Concentrations of Assert and its acid metabolite are consistently higher in ground water on the Third Bench than on the First or Second Benches.

3. Assert and its metabolite are being discharged to receiving streams. Assert was detected in surface water, suggesting that photodegradation was not rapidly occurring.

4. There appears to be a correlation between the occurrence of Assert (and/or its acid metabolite) and the occurrence of nitrate. The factors that cause the transport of Assert also influence the movement of nitrate through the flow system.

5. The occurrence of nitrate in ground water appears to be attributable to nitrogen fertilizer, ammonium fertilizer, soil organic nitrogen or a combination of these.

6. Soils on the Greenfields Bench appear to be functioning as a “reservoir” for Assert and its acid metabolite, allowing the chemical to desorb or degrade at some rate dependent on a variety of environmental conditions.

7. Due to persistence and favorable environmental factors, low levels of Assert can be expected under any type of irrigation system, with the possible exception of center pivot.

8. A minimum threshold of hydraulic flux is required to transport Assert metabolite into the ground-water system. But at high levels of hydraulic loading, such as the flood event in 2000, dilution may result in low concentrations.

9. Ground water in the wheel line-sprinkled plot had higher concentrations of Assert and lower hydraulic flux rates when compared to ground water under a 38-acre flood irrigated plot. However, when the flooded acreage was reduced to 8 acres, and the wheel line was replaced by a center pivot, the mass flux trend reverses, and much higher concentrations of Assert were found in the flood irrigated ground water than in the center pivot irrigated ground water.
RECOMMENDATIONS

1. Initial efforts to implement Best Management Practices should be focused on the Third Bench where highest concentrations of Assert have been found. Data suggest that a northerly ground-water flow component may result in the transport of Assert from the First and Second Benches to the Third Bench.

2. When collecting water-quality and flow data for TMDL applications or other watershed evaluations, a carefully designed monitoring strategy should be developed to calculate the effects of ground-water baseflow on receiving streams. If water-quality data are collected during low flow periods, they are probably most representative of ground-water-transported non-point sources of contamination from long-term land use practices. However, during periods of high flow, other sources of surface-water-recharge from overland flow, irrigation return-flow and surface runoff from point-sources become more important.

3. Sprinkler irrigation results in lower Assert loading to ground water than flood irrigation. However, the need for high ground-water quality should be balanced with the need for sufficient ground-water quantity. Since Greenfields Bench ground water is currently the only source of domestic water, the amount of ground-water recharge attributed to the various irrigation methods should be considered before initiating a Bench-wide irrigation strategy. On a per acre basis,
   • Wheel line irrigation provides 1/3 the ground-water recharge of flood irrigation.
   • Center pivot irrigation provides 1/10 the ground-water recharge of flood irrigation.

4. Additional soil Assert concentration data should be collected to more fully characterize flux rates through the “A” horizon.

5. A comprehensive evaluation should be performed to determine the effects of agricultural practices, such as crop-residue burning and chemical fertilizer application, on soil health and soil microbial ecology.
REFERENCES


Pietikainen, J., 1999, Soil microbes in boreal forest humus after fire: Academic Dissertation in Forest Soil Science, Finnish Forest Research Institute, University of Helsinki, Finland.


Systems Technology, Inc., 1979, Muddy Creek special water quality project: Systems Technology, Inc., Helena MT.


U.S Bureau of Reclamation, 1981, Muddy Creek erosion problem, a coordinated strategy for federal action.

U.S Bureau of Reclamation, 1982, Muddy Creek study plan formulation review document.


