155 pp incl. refs

Final Report

For:

Olmsted County
Dye Trace Investigation

Prepared For:

Olmsted County, Minnesota

Volume 1 of 4: Text

April, 1991

Donohue ENGINEERS
ARCHITECTS
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FINAL REPORT
FOR
OLMSTED COUNTY DYE TRACE INVESTIGATION
OF THE
ORONOCO SANITARY LANDFILL

by

E. Calvin Alexander, Jr.
Technical Sub-Consultant
Dept. of Geology and Geophysics
University of Minnesota
Minneapolis, MN 55455

4/25/91
Date

Barbara J. Huberty
Site Manager
Olmsted County Public Works Dept.
2122 Campus Drive S.E.
Rochester, MN 55904

4/25/91
Date

Keith J. Anderson, P.E.
Project Manager
Donohue and Associates, Inc.
7200 Hemlock Lane N., Suite 300
Maple Grove, MN 55369

4/25/91
Date

Prepared by:

Donohue & Associates, Inc.

April, 1991

ACKNOWLEDGEMENTS

In addition to the residents who so faithfully participated in the Oronoco Dye Trace Study, over one hundred individuals had a direct role in the development or implementation of this project. Time and space do not permit acknowledgement of those individuals' contributions. However, we would like to take the opportunity to recognize the organizations which provided staff, equipment or support:

Agricultural Stabilization and Conservation Service
Donohue and Associates, Inc.
International Business Machines, Incorporated
Lindsay Water Conditioning
Mayo Clinic Biochemistry and Molecular Biology Department
Minnesota Department of Health
Minnesota Geological Survey
Minnesota Pollution Control Agency (Central and Regional Offices)
Olmsted Community Hospital Laboratory
Olmsted County Attorney's Office
Olmsted County Board of Commissioners
Olmsted County Central Services Department
Olmsted County Health Department
Olmsted County Human Resources Department
Olmsted County Telecommunications Consortium
Olmsted County Public Works Department (Finance,
Solid Waste and Survey Divisions)
Olmsted County Waste-to-Energy Facility
Oronoco Dye Trace Study Staff
Oronoco Landfill Staff
Oronoco Village Mayor and Town Council
Ottman Quarry
Ozark Underground Laboratory
Rochester Educational Services Center
Rochester Post Bulletin
Shamrock Enterprises
Traveler's Insurance Company
Twin City Testing Corporation
United States Environmental Protection Agency
United States Geological Survey
University of Minnesota (Department of Geology and Geophysics)

In addition, the following individual's contributions were important:

Representative Donald Frerichs
Dr. James Quinlan
Louis Reiter
Residents allowing property access to sampling sites

SPECIAL THANKS
ARE EXTENDED TO THE RESIDENTS
WHO PARTICIPATED IN THIS STUDY

Without their dedicated efforts,
this project would not have been possible.

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DOCUMENT ACRONYMS

Cl	Chloride
Cr	Chromium
Cu	Copper
EMS	Environmental Monitoring System
EPA	Environmental Protection Agency
Fe	Iron
HPLC	High Performance Liquid Chromatography
HRS	Hazard Ranking System
ID	Identification
MDA	Minnesota Department of Agriculture
MDH	Minnesota Department of Health
MGS	Minnesota Geological Survey
ml	Milliliter
MPCA	Minnesota Pollution Control Agency
OCH	Olmsted Community Hospital
OCHD	Olmsted County Health Department
OCPWD	Olmsted County Public Works Department
NOAA	National Oceanic and Atmospheric Administration
NO_3-N	Nitrate-Nitrogen
ppb	parts per billion (10^{-9} g/g = microgram per liter = ug/L)
ppm	parts per million (10^{-6} g/g = milligram per liter = mg/L)
ppt	parts per trillion (10^{-12} g/g = nanogram per liter = ng/L)
PEFS	Perkin-Elmer Fluorescence Spectrophotometer
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RAL	Recommended Allowable Limit
RPD	Relative Percent Difference
SO_4	Sulfate
SWL	Static Water Level
TDFF	Turner Design Filter Fluorometer
U of M	University of Minnesota
USCS	Unified Soil Classification System
USFWS	United States Fish and Wildlife Service
VOC	Volatile Organic Compound
Zn	Zinc

1.0 EXECUTIVE SUMMARY

The Olmsted County Landfill Dye Trace Study was initiated in April, 1989 and continues at the present time (March, 1991). This report is based primarily on data gathered between April, 1989 and September, 1990.

The Dye Trace Study was divided into two phases. Phase 1 extended from the initiation of the project through March 31, 1990. Phase 2 extended from April 1, 1990 to the present.

1.1 Background

The Olmsted County Sanitary Landfill, located approximately 10 miles north of Rochester, Minnesota, was purchased by the City of Rochester in 1969. A permit to construct a landfill on the site was granted by MPCA in 1970. Site development began in 1972. The City of Rochester operated the site until 1983, when the City and Olmsted County agreed to transfer the permit to Olmsted County.

The landfill has received waste from local refuse collection haulers serving residences throughout Olmsted and adjacent counties. Local commercial establishments, institutions, and industries, also have used the site. In addition to the usual refuse from these generators, the site also has received incinerator ash, utility ash, wastewater treatment plant sludge and sludge ash, miscellaneous industrial process sludges, and debris resulting from the 1978 flood. In March 1987, the landfill was closed to municipal solid waste, but continued receiving demolition, coal ash, and asbestos waste.

In 1983, analysis of water samples from monitoring wells at the site indicated the presence of VOCs. As a result, MPCA and EPA began Superfund actions at the site in 1986. Subsequently MPCA and EPA agreed to establish MPCA as the lead agency for remedial action. The MPCA negotiated a Response Order by Consent with the City of Rochester and Olmsted County which became effective in December 1989.

1.2 Site Geology and Hydrogeology

In the vicinity of the site, glacial overburden generally is less than 100 feet thick. Within the site, the overburden is 0 to 60 feet thick and includes sands and gravels, clay, and silt. Clay and silt units predominate in the southern part of the site. Sand and gravel underlies the central and northern part of the site, including the waste cells.

The first bedrock encountered under the site is the Prairie du Chien Group. It is approximately 250 feet thick and is predominantly dolomitic limestone. It is fractured, jointed, and contains numerous karst features. Underlying the Prairie du Chien Group is the Jordan Sandstone.

The main water table is encountered in the Prairie du Chien Group. In the vicinity of the waste cells, groundwater monitoring wells completed at the water table have static water levels at depths of 80 to 115 feet below ground surface. Groundwater flow in the vicinity is generally to the east or northeast. Residential wells in the vicinity draw water from both the Prairie du Chien and the Jordan aquifers.

1.3 Dye Trace Purpose and Methods

Groundwater flow velocity and direction in fractured and jointed limestone is difficult to predict because the exact nature of the fractures, joints and solution cavities in the limestone is unknown. Groundwater flow in these conditions can be studied by introducing dye at one or more locations and then monitoring the groundwater at many locations to see which direction, and how fast, the groundwater and dye are moving. This technique was used for the Olmsted County Landfill Dye Trace Study. The study's purpose was to determine groundwater flow direction and velocity near the landfill; to determine if the landfill monitoring wells would intercept any potential groundwater contamination from the site; and to identify private wells in the area which would most likely be affected by potential groundwater contamination from the site.

Rhodamine WT dye was selected for use in this study principally because of its ease and economy of analysis. Dye was introduced into limestone bedrock in a quarry west of the landfill in May 1989. A second introduction of dye was made in March 1990 in a sinkhole located east of the site.

A study area approximately 1.5 miles square was established. Groundwater samples initially were taken daily from approximately 100 residential wells and from the landfill monitoring wells. Springs, which had been located previously, and Zumbro River sites were sampled less frequently.

The residential wells were distributed throughout the study area. They included up-gradient wells, generally west and south of the landfill site, and wells north and east of the Zumbro River, a hydrogeologic boundary. Residential well samples were taken by the residents.

Springs were sampled because they were considered to be potential discharge points for dye. The Zumbro River was sampled in an effort to detect dye which might seep directly into the river. These samples were taken by County staff.

1.4 Results and Conclusions

As dye detection began to occur erratically at isolated, random locations, the number of residential wells in the study was expanded. Ultimately the number exceeded 200. It was determined that these scattered, short-term detections were a random phenomenon unrelated to the Rhodamine WT used in the study.

Rhodamine WT dye reached the first monitoring well less than 24 hours after introduction. Dye reached a total of six monitoring wells in the following weeks and months documenting a complex pattern of groundwater flow roughly from west to east under the waste cells. The continued presence of dye in the monitoring wells documents that they are working adequately. All of the positive monitoring wells are sampling the Prairie du Chien aquifer.

Rhodamine WT dye reached private well 151, north-northeast of the landfill, 77 days after introduction. Well 151 is located 1.2 miles northeast of the dye introduction point. The minimum speed the leading edge of the dye traveled to reach well 151 is 5.7 miles per year. Dye continues to emerge from well 151 as of January 1991. Dye reached private well 108, 1.5 miles northeast of the introduction point, in 207 days. Dye continues to emerge from well 108. Both wells are old, Prairie du Chien wells. These two positive wells document a groundwater flow path from the Phase I dye introduction point near the landfill to the north-northeast in the Prairie du Chien aquifer. Other flow paths may exist which may not go under the landfill.

Rhodamine WT from the first dye introduction has not been confirmed at any of the other monitoring wells, residential wells, springs, or river stations in the Dye Trace. Rhodamine WT from the second introduction of dye has not been confirmed at any sampling location.

The dye pulses in five of the six positive monitoring wells respond rapidly to recharge events to produce large fluctuations in the dye concentrations. The monitoring well breakthrough curves illustrate the complex nature of the groundwater system beneath the landfill. The Prairie du Chien aquifer under and surrounding the landfill has flow characteristics that are intermediate between those of mature, conduit-flow karst aquifers and porous-media aquifers.

The results of an anion survey conducted as part of the Dye Trace Study indicate that the Jordan aquifer is isolated from the overlying Prairie du Chien aquifer in the Study Area. In many parts of southeastern Minnesota these two aquifers behave as a single aquifer. In the Study Area, the Prairie du Chien aquifer contains elevated chloride and nitrate contents from a variety of surface sources. The Jordan aquifer, in contrast, shows very little evidence of surface impact. The pattern of dye movement revealed by the positive wells is consistent with the chemical data and with Study Area scale potentiometric mapping.

1.5 Recommendations

Additional geotechnical investigations should be undertaken at the site. Specifically, slug and pump tests should be performed on the existing monitoring wells. The response of monitoring wells within 500 feet of the pumped wells should be recorded. The source of the vertical head gradients at the site should be determined. Gamma logging of the monitoring wells and selected nearby private wells may prove to be a useful source of information. The existence and size of rapid pulses of contaminants in the monitoring wells should be investigated.

All of the existing monitoring wells should be maintained as part of the expanded EMS and private wells 151 and 108 should be added to the expanded EMS. There is a danger that access to samples from wells 151 and 108 could be lost as their owners seek alternative water supplies. The ability to sample wells 151 and 108 should be maintained.

Several new monitoring wells are needed. Several shallow water-table, mid-level Prairie du Chien and at least one Jordan monitoring well are needed in the northeastern part of the landfill site. Mid-level Prairie du Chien monitoring wells and another Jordan monitoring well are needed in the area between the landfill site and private well 151.

If the anion evidence for leachate pulses in the monitoring wells is confirmed, the ability of routine quarterly sampling to adequately define the contamination potential will need to be examined.

2.0 INTRODUCTION

Major portions of the text in Sections 2.1, 2.2 and 2.3 below have been taken verbatim or modified from RMT (1990).

2.1 Site Description

2.1.1 Location

The Olmsted County Sanitary Landfill is situated within Sections 27 and 28 of Township 108N, Range 14W (Oronoco Township). The landfill property includes 180 acres of the East one-half of Section 28 and 72 acres in the West one-half of the West one-half of the West one-half of Section 27. The landfill lies approximately 10 miles north of the City of Rochester, two miles southeast of the Town of Oronoco, east of U.S. Highway 52. Site access is via a county road off of Highway 52 (Figure 1).

2.1.2 History

In early 1968, the City of Rochester began the process of siting a new landfill. In October 1968, the City took an option to buy the Locoshonas farm, the current landfill site. The option was allowed to expire in January 1969. The Mayor of Rochester appointed an advisory committee in April 1969, to recommend a site for a sanitary landfill. In August 1969, the City purchased the Locoshonas farm.

On December 15, 1969, the City applied to the MPCA for a permit to construct and operate a solid waste disposal system. The MPCA issued the permit, No. SW-5, to the City dated February 9, 1970.

In March 1970, the City applied to the Olmsted County Planning Advisory Commission for a "special exception permit" to operate a sanitary landfill. The Commission refused to grant the permit. The City appealed to the District Court.

The Town of Oronoco and two nearby residents sought to restrict the City from operating the landfill by appealing the special exception permit that was issued as part of the original permit (MPCA Permit SW-5). The District Court denied injunctive relief and ordered a special exception permit from the County to be issued; both decisions were appealed to the State Supreme Court. The Supreme Court decision, dated April 18, 1972, upheld the decision of the District Court, and development of the site followed this decision.

The landfill was owned and operated by the City until 1983. Olmsted County requested that the permit be transferred to the County in December, 1982. An agreement was negotiated with the City, and following the required public notice and hearing, the permit was transferred on June 10, 1983.

2.1.3 Wastes Received

Waste has been received from throughout Olmsted County. Numerous local refuse collection services have used the site for mixed municipal and commercial refuse. Also, the site has been used by most local commercial establishments, institutions, and industries for various types and quantities of waste materials. Research by Donohue (1987) indicated that the site has received an unquantified amount of incinerator ash (from local hospitals, clinics, and institutions), utility ash, municipal wastewater treatment plant sludges and/or ash, miscellaneous industrial process sludges, along with the usual refuse flow from residential, commercial, and industrial generators. The original design capacity provided for 2,700,000 cubic yards of airspace for waste disposal. In 1984, the site was nearing site design capacity. On March 28, 1987, the site was closed to mixed municipal solid waste. Since that time, only demolition waste, coal ash, and asbestos were accepted on a regular basis.

2.1.4 National Priority List

The MPCA and the EPA began Superfund actions in September 1986 as a result of the detection of VOCs in monitoring wells in 1983. Analysis of water samples taken on May 17, 1983, from the groundwater monitoring wells at the site indicated the presence of volatile organic compounds.

The MPCA HRS score for the Olmsted County site was 34. If a site is scored by the MPCA, it is placed on the Permanent List of Priorities. The scoring was initiated in June of 1984. The HRS score was based upon the following factors:

1. The observed release of contaminants detected in the monitoring wells during the May 17, 1983, sampling event.

2. Dichlorodifluoromethane was the measured constituent with the highest toxicity and persistence ranking.

3. The groundwater in the area serves as the area's primary source of drinking water.

4. The proximity of populated areas.

The site was included on the State of Minnesota's 1984 Permanent List of Priorities.

A site must score a minimum value of 28.5 to be nominated for the National Priorities List. In addition to the scoring factors used by MPCA above, the EPA used information regarding metal hydroxide sludge disposal at the site in determining its HRS score. The EPA HRS score for the site is 41. The scoring was conducted during July 1985 to January 1986. The site was placed on the National Priorities List in June 1986.

In September 1989, the MPCA and EPA completed a Superfund Memorandum of Agreement that established the MPCA as the lead agency for remedial action. The City of Rochester and Olmsted County were identified as Responsible Parties by the MPCA. The search for additional Responsible Parties continues.

The MPCA negotiated a Response Order by Consent with the City of Rochester and Olmsted County under authority of the Minnesota Environmental Response and Liability Act; the order became effective December 19, 1989. In March, 1989, the site was ranked 395 on the EPA National Priorities List.

2.2 Geology

2.2.1 Regional

The landfill is located on the south end of the Red Wing-Rochester Anticline, which is located along the eastern reaches of the structural depression - Hollandale Embayment (Austin, 1972). Marine seas invaded this long, shallow embayment during early and middle Paleozoic times. The sea underwent nine cycles of advance and retreat depositing thick sequences of sedimentary strata. Upon the most recent regression, widespread erosion removed the upper part of that sequence. Erosion was the dominating geologic process acting upon the discussed area until the Quaternary period. In the Quaternary period, Southeastern Minnesota had repeatedly been covered by continental glaciers, which left a series of glacial and fluvioglacial sediments covering paleozoic sedimentary rocks (Figure 2).

Quaternary glacial drift is generally less than 100 feet thick within five miles of the landfill, except in the valley of the Zumbro River where unconsolidated sediments may be more than 250 feet thick (Olsen, 1988b). Quaternary sediments in most of Olmsted County form a geomorphic unit known as the Rochester Till Plain (Wright, 1972). The Rochester Till Plain consists of glacial sediments deposited before the most recent (late Wisconsinan) glacial advance. Texturally, the till is reported to be predominantly clayey as far east as the landfill site; east of this, till has been found to be silt rich (Hobbs, 1988). The surface of the Rochester Till Plain is gently rolling and has been dissected by erosion. Some of the unconsolidated sediments are cemented with calcite (Olsen, 1988b).

The Prairie du Chien Group is the first bedrock encountered beneath the unconsolidated deposits at and in the area surrounding the site (Olsen, 1988a). It is composed of two members, the overlying Shakopee Formation and the underlying Oneota Dolomite. These two members are difficult to distinguish from each other and are approximately 250 feet thick when combined. The Prairie du Chien Group is a thin to thick bedded, brownish grey dolostone to sandy dolostone interbedded with occasional sandstone and siltstones (Austin, 1969; Mossler, 1987; Sloan, 1987).

The underlying Jordan Sandstone is composed of three members. In descending order, these are the Sunset Point Member, an argillaceous and dolomitic quartz sandstone; the Van Oser Member, a white or yellow coarse- to medium-grained orthoquartzite; and the Norwalk Member, a yellow, silty, fine-grained quartzose sandstone. The Norwalk and Sunset Point Members may not be present locally (Austin, 1972).

The Jordan Sandstone is underlain by the St. Lawrence Formation, a dolomite siltstone and shale; which in turn is underlain by the Franconia Formation, a fine-grained glauconitic sandstone and shale (Olsen, 1988a). Neither unit is exposed at ground surface within 5 miles of the landfill.

Olsen's (1988b) study of Olmsted County geology found that bedrock and unconsolidated sediments are jointed near the site. Bedrock joints and fractures have influenced the orientations of surface streams in the area, including the South and Middle Forks of the Zumbro River. Olsen's (1988b) study measured joints in bedrock at an exposure just west of the landfill that strike predominantly north-northwest and east-northeast; similarly oriented fractures were measured by Olsen in overlying glacial tills.

Bedrock joints and fractures have led to the dissolution of carbonate rocks by groundwater. The bedrock has been subject to development of karst topography and sinkholes in the southcentral portion of the county, at and near the landfill site and in other scattered areas (Alexander and Maki, 1988).

2.2.2 Site

Over the past 20 years, unconsolidated materials at the landfill site have been investigated by five series of soil borings and two evaluation reports; data from these logs that appeared to be reliable were used to develop a description of unconsolidated materials at the site.

Unconsolidated materials at the site are 0 to 60 feet thick. They include stream alluvium, loess, tills, and glacial outwash deposits. Tills are of variable thickness; are generally medium-to-dark tan, clayey sands, clays, or silts; and are usually classified as SC (clayey sand) or CL (low to medium plasticity clay) in the USCS. Outwash deposits are described as fine to coarse sands that are light to orangish tan, with some silt or gravel. These deposits can be up to 25 feet thick and are usually classified as SP (poorly graded sand) or SM (silty sand) in the USCS. Stream alluvium (a heterogeneous, poorly sorted sand and gravel usually classified as SW [well-graded sand] in the USCS) and loess (a tan silt usually classified as ML [silt] in the USCS) are generally less than five feet thick. A dark, peat-like material, 5 to 20 feet thick, was encountered during the March 1990 excavation into fill that had been placed in a former sinkhole (B. Huberty, pers. comm., April 1990), but this material does not appear to be areally widespread at the site.

The subsurface occurrence of these units can be seen on Figure 3, a north-south geologic cross section of the site and on Figure 4, an east-west geologic cross-section of the site.

The cross-sections show that stratigraphic units are laterally discontinuous and have a complex vertical sequence. Clay- and silt-rich units (interpreted as till) make up the majority of unconsolidated materials in the southern part of the site. Sand or sandy silt underlies much of the center and northern part of the site. Predominantly sandy material underlies the area of waste disposal at the site, and extends approximately 500 feet beyond the southern boundary of the landfill cells. The locations of sand and till from site drilling data are consistent with the locations of outwash sand and till mapped at the site in a county map of surficial deposits (Hobbs, 1988).

A number of well borings, boreholes, and drillholes penetrate bedrock at the site. Uppermost bedrock at the site is the Prairie du Chien Group. The Prairie du Chien Group is largely dolomite beneath the landfill, although sandstone, sandy dolomite, and shale layers are common in the upper 30 feet. The deepest drillhole at the site (well 8, near the southern margin of the property) penetrates 287 feet of the Prairie du Chien Group and is completed 88 feet into the underlying Jordan Sandstone.

Several logs of borings, rock cores, and wells indicate that the uppermost part of the Prairie du Chien Group is weathered and fractured. Rock becomes progressively stronger and less fractured with depth. However, logs of monitoring wells MW-11A, MW-11B, MW-14B, MW-15A, and MW-15B report crevasses and clay zones as deep as 90 feet below the top of bedrock. These crevasses and clay zones may represent dissolution cavities. The degree of interconnection of fractures and cavities to each other, and their potential for transporting groundwater or potential releases from the landfill, have not been established through past investigations.

The top of bedrock is generally flat at the southern part of the site, at an elevation of 1,135 feet above MSL, or 35-60 feet below ground surface. The bedrock surface generally slopes downward to the north, as shown on Figure 3. A sinkhole south of the existing landfill cells which caused a ground surface depression of approximately 10 feet was filled with concrete during landfill operations in the 1970s.

Early studies of site structural geology identify northeast and northwest-trending sets of vertical faults (Hogberg, 1973 and Hogberg and Gilmer, 1976). However, later investigators of Olmsted County bedrock geology believe this interpretation to be open to question (e.g., Olsen, pers. comm., April 26, 1990). The postulated vertical bedrock displacements are not apparent on available cross sections from the above studies. The directions of the faults generally coincide with the directions of fracture sets observed in a bedrock exposure immediately west of the site (Olsen, 1988a). However, it does not appear that the discrete fault zones and vertical bedrock displacements identified by Hogberg's studies occur at the site.

Geophysical surveys at the southern portion of the site were reported to include resistivity traverses, resistivity soundings, and seismic refraction soundings (Hickok and Associates, 1982). Hickok's report includes a map showing apparent soil resistivity determined from resistivity data. The map was used to infer that soils in low-resistivity areas in the south of the site were clay rich, while high-resistivity soils immediately southeast and southwest of the landfill represented either sandy soil or shallow bedrock. The report did not give any other interpretation of the resistivity traverses, nor of the resistivity soundings. Seismic data were not presented or interpreted in the report. Although the report claims to use resistivity and seismic survey data in developing a bedrock surface contour map, there are no apparent geophysical data included in this map, which appears to be developed using soil boring data only. The geophysical information does not appear to have been interpreted to any meaningful degree, such as to modeling the depth to bedrock, locations of fractures, or thickness of stratigraphic units within the unconsolidated materials.

2.3 Hydrogeology

2.3.1 Regional

The bedrock Aquifers in this portion of Minnesota are the only important sources of water for residential, municipal and industrial users. The St. Peter-Prairie du Chien-Jordan Aquifer system is the first bedrock aquifer in the area, but the St. Peter Sandstone portion of the aquifer has been removed by erosion from the region beneath and around the landfill. The Prairie du Chien Aquifer typically has moderate to high potential yields in area wells primarily from solutionally enlarged joints, fractures and cavities in the dolomite (Kanivetsky, 1988). Due to evidence of surface contamination, area residents generally are no longer permitted to complete wells in the Prairie du Chien Aquifer (Minnesota State Well Code 4725; Olmsted County Public Health Regulation 40). However, numerous old Prairie du Chien wells exist in the area. The Jordan Aquifer is the shallowest usable bedrock aquifer in the area. The Jordan Aquifer typically gives moderate to high potential yields in area wells.

The St. Peter-Prairie du Chien-Jordan Aquifer has traditionally been mapped as a single hydrogeologic unit (Kanivetsky, 1988) due to the similarity of the potentiometric surface in adjacent water wells developed in the different formations. The aquifers were thought to be hydraulically interconnected with no significant aquitard between the formations. However, as part of a Jordan Aquifer sensitivity study, MGS staff has demonstrated that the St. Peter-Prairie du Chien-Jordan Aquifer has hydraulically significant internal structure. The area in northern Olmsted County which contains the landfill is particularly unusual (Dale R. Setterholm, private communication, 1990). The large vertical gradients within the Prairie du Chien Aquifer beneath the landfill (see 2.3.2 below) indicate the presence of hydraulically significant aquifer heterogeneities in the area.

Regionally, groundwater flow in the bedrock is northeast towards the Zumbro River. The Zumbro River appears to capture much of the flow in the combined St. Peter-Prairie du Chien-Jordan Aquifer from this area as the water table slopes toward the river from both sides (Kanivetsky, 1988). Precipitation falling on the area is the principal source of recharge to the bedrock aquifers. Thus, all of this area is basically a recharge zone and the Zumbro River is the discharge zone for at least part of the flow.

In the general vicinity of the landfill, the surficial deposits generally do not contain enough water to be of economic use except in areas close to the Zumbro River. Here, valley - fill deposits may be thick enough to make it likely a saturated sand lens is encountered which can provide an adequate water supply. Some of the buried bedrock valleys may contain enough water to be of use for a domestic water supply, but this is unknown, as many of the well logs in the area do not identify the water - bearing formation.

In addition to the surficial aquifers in the valley fills, several small springs and shallow dug wells are present high in the topography away from the valley fills. This demonstrates the presence of small discontinuous perched aquifers in the soil and underlying glacial deposits. These glacial deposits form the ridges north and south of the landfill and extend into at least the southern portion of the landfill property. One of these small, high spring complexes emerges in and near the pond on the west boundary of the landfill.

Water movement through these surficial materials generally follows the surface topography. Water movement is thus towards the local surface drainages, to the northeast towards the confluence of the Middle and South Forks of the Zumbro River (Figure 5). Much of the water also percolates downward to recharge the bedrock aquifers. The many sinkholes found in this area serve as conduits from the surface to the bedrock, thus aiding in the recharge process.

2.3.2 Site

Studies of site groundwater occurrence and flow at and near the site (e.g., Hogberg, 1973; Hickok and Associates, 1983a and 1983b; Kanivetsky, 1988) indicate that the water table is encountered within the Prairie du Chien Group. These studies indicate that, from 1973 to the present, the horizontal hydraulic gradient has been generally toward the east or northeast within five miles of the landfill.

The Prairie du Chien Group and underlying Jordan Sandstone are conventionally thought to be hydraulically interconnected, and are usually mapped as a single aquifer (Kanivetsky, 1988). Since 1988, water levels have been measured in a network of wells to characterize horizontal hydraulic gradients within this aquifer in the vicinity of the landfill.

Initially, the network consisted of about 31 residential wells and nine on-site monitoring wells. In February 1990, another 11 residential wells were added (Donohue, 1990b). Water levels in the well network were measured approximately once per month through December 1989, except during winter months. Water levels have been measured quarterly since the additional wells were added (see Appendix C).

The shallowest groundwater at the Olmsted County landfill site occurs in perched zones within fine-grained, unconsolidated sediments in the southern part of the site. Drilling records note water flowing into six of seven auger holes drilled south of the landfill cells in 1984. Water inflow was also noted in logs of 10 of 20 auger borings in the southern part of the site drilled in December 1982. Logs of test pits 14 to 20 feet deep dug in fine-grained material in the southern third of the site for a 1989 investigation of clay borrow materials recorded water inflow through sandy layers in two of the 16 pits. A spring located near the western boundary of the site was reported to flow northward into a pond at a rate of 0.5 gallon/min in April 1970. The pond was reported to flow to the west into a surface drainage at 1 gallon/min at this time; both spring and pond are believed to be supplied from seepage from a perched groundwater zone.

Perched zones in unconsolidated materials in the southern part of the site probably resulted from infiltration of water to sandy intervals within the predominantly silt- and clay-rich till.

Perched water zones were only rarely encountered by drilling in unconsolidated materials in the northern part of the site, including the area where the landfill cells are located. Records of auger borings drilled in unconsolidated materials in the area presently occupied by cell #4 noted groundwater inflow in only six of 99 holes drilled in September and October 1975 by Soil Exploration Company. No groundwater inflow was recorded in four auger borings drilled in preparation for rock boreholes immediately west of cell #4. The sandy material underlying the northern part of the site (including the landfill cells) apparently allows infiltrated precipitation to migrate downward into bedrock, without encountering low-permeability layers over which perched zones could accumulate.

It does not appear that the perched water zones encountered in the southern part of the site are hydraulically connected with the landfill. A slight swale separates the spring and pond on the west boundary of the site (and presumably the perched zone that supplies them) from the landfill cells. Auger borings 82-1, 82-2, 82-3, 82-4, 82-6, and 82-7 (the northernmost 1982 borings drilled closest to the landfill) did not record groundwater inflow. If any leachate has been released from the landfill, it is likely to move vertically downward through the underlying soil, rather than laterally into perched zones in sandy layers within the clayey till in the southern part of the site.

The main water table occurs within the Prairie du Chien Group. In the vicinity of the waste cells, groundwater monitoring wells completed at the water table have static water levels at depths of 80 to 115 feet below ground surface.

Potentiometric surface maps developed for the water table and the deeper groundwater zones using on-site monitoring wells show that horizontal gradients in both zones were east-northeast in April 1986, and east-southeast from April 1987 through November 1988. These contour maps include some inaccurate contours with respect to recorded water level measurements, but correctly identify general trends in horizontal gradients. Separate potentiometric surfaces developed using water table wells and piezometers show hydraulic gradients ranged from 0.001 to 0.005 during this time. (All gradients in this report are expressed as a dimensionless ratio of feet per feet.)

Gradients observed in on-site wells in 1987 and 1988 do not coincide with area horizontal gradients determined from off-site measurements. This may be due to nearby groundwater pumping or irregular flow paths in the fractured dolomite of the Prairie du Chien Group.

There is considerable evidence of downward vertical gradients at the site. Data from well nests MW-13A,B; MW-14A,B; and MW-15A,B; all located on the east side of the landfill, indicate downward vertical gradients of 0.09 to 0.14 from 1986 to 1990 (Braun, 1989b, c, e, f, 1990; C. Alexander, written comm., May 1990). A downward vertical gradient of 0.10 was also observed in well nest MW-13A,B in March 1983. Vertical gradients in the MW-11A,B nest were variable, ranging from essentially no vertical gradients to a downward gradient of up to 0.30 in measurements taken between March 1983 and February 1990.

The available evidence indicates that vertical gradients are about two orders of magnitude greater than horizontal gradients in the upper 100 feet of the Prairie du Chien at the landfill site. Downward gradients in the uppermost parts of aquifers are often observed in areas of groundwater recharge. If the downward gradients are produced by some type of downward increasing permeability then enhanced vertical recharge will occur. In karst aquifers such as the Prairie du Chien, however, the permeability typically decreases downward and the vertical gradients are more often due to local perching within the epikarstic or subcutaneous zone (Williams, 1983). These perching phenomena are complicated by solutionally enlarged vertical joints and fractures that are partially or totally filled with glacial sediments. The resulting flow patterns are complex. The epikarstic or subcutaneous zone is a storage zone or reservoir between the surface and the completely saturated zone.

2.3.3 Climate

The landfill is located in a continental climatic zone characterized by hot summers and cold winters. Meteorological data are collected by NOAA at its weather station at the Rochester Airport, approximately 16 miles south of the landfill. Over the period of 1951 to 1980, average daily temperatures

at the Rochester Airport station ranged from a low of 10.8°F in January to a high of 70.7°F in July, and annual precipitation averaged 28.26 inches (NOAA, 1982).

Figure 6 was constructed from the monthly rainfall record at the Rochester Airport from January 1972 through February 1990. The bar graphs across the bottom show the monthly total rainfall in inches (see the vertical axis on the right side of the graph). The most apparent feature of the monthly rainfall is the large annual variation. The winter months are dry and most of the precipitation occurs in the late spring, summer and early fall.

The heavy line across the upper portion of Figure 6 shows the cumulative departure from normal precipitation for the period. The cumulative departure increases during wetter than average periods, decreases during drier than average periods, and is level during periods of average precipitation. The precipitation was relatively normal in 1987. In 1988 and 1989 the precipitation was below normal at the Rochester Airport and in the Study Area. Between January 1988 and December 1989 the area received about 12 inches less than normal precipitation. The drought did not break until the late spring of 1990. The Dye Trace Study, therefore, began 16 months into what proved to be a 28 month period of below-average precipitation.

Daily readings from a rain gage at the landfill have been recorded by Olmsted County since 1982. Snowfall was not recorded at the landfill station before the winter of 1989-90. Daily precipitation recorded at the landfill and precipitation recorded by NOAA (1990) at the Rochester Airport varies considerably.

Figures 7 and 8 are graphs of the daily precipitation at the landfill. Figure 7 covers the same time period as the Phase I graphs in Appendices D, E, F and G and has the same horizontal scale. Figure 8 covers the same time period as the Phase II graphs in the Appendices. The rainfall data from the landfill is tabulated in Appendix Q.

2.4 Dye Trace Background

2.4.1 Purpose for Implementing a Dye Trace

The "Olmsted County Sanitary Landfill: Background Data Evaluation and Preliminary Hydrogeologic Investigation Workplan" (Donohue, 1987) identified the need for karst hydrogeologic investigations of the site. Recent texts emphasize the complex and unusual behavior of karst hydrogeology (White, 1988; Ford and Williams, 1989). A growing body of scientific literature (Aley, 1977, 1988; Quinlan and Ewers, 1984, 1985; Quinlan and Alexander, 1987; Quinlan, Ewers and Field, 1988) addresses the special problems associated with monitoring for contaminant flow from sites in karst terrains. An EPA protocol document on groundwater monitoring in karst terrains is now available (Quinlan, 1989). All of these documents emphasize the necessity of tracer investigations in the design, implementation and verification of groundwater monitoring systems in karst terrains.

The purpose of the Olmsted County Landfill Dye Trace Study was fivefold.

I. To determine the local directions and velocities of groundwater flow beneath and adjacent to the landfill.

II. To determine if the existing network of landfill monitoring wells would intercept any potential groundwater contamination emanating from the site.

III. To identify the private wells among the surrounding residences most likely to be impacted by potential groundwater contamination emanating from the site.

IV. In general, to provide the information necessary to design a more effective Environmental Monitoring System for the site.

V. To identify data gaps which could be addressed with additional hydrogeologic investigation as part of the subsequent Remedial Investigation and Feasibility Study of the site.

2.4.2 Chronology of Pertinent Events

The actual implementation of the Oronoco Dye Trace Study involved several interested parties and began in earnest in early 1987. Alterations in the study have continued since the introduction of dye in May 1989, as dictated by study results.

Below is an outline of the events which led to the inception, implementation and alterations of the Oronoco Dye Trace Study. Copies of documents relating to the events listed below are on file with the Olmsted County Public Works Department.

Date	Event
6/15/84	The Oronoco Landfill was ranked by MPCA staff and received a Hazard Ranking Score of 34, placing it on the Minnesota Permanent List of Priorities.
12/6/84	MPCA submitted its site ranking information to EPA, which subsequently gave it an HRS score of 41 and then placed it on the National Priorities list in June 1986.
5/6/86	Olmsted County retained the consulting firm of Donohue and Associates, Inc. to complete a preliminary Evaluation Report of the Oronoco Landfill as part of their Remedial Investigation and Landfill Closure contract.

1/87 to 9/87 Several meetings involving Olmsted County Commissioners, Dr. Calvin Alexander (U of M), staff from the Olmsted County Health and Public Works Departments, the state and regional MPCA offices, Martha Kuehn (as the Oronoco Township citizens' representative and as a Solid Waste Advisory Committee member), and Donohue staff were held to discuss a dye trace and the forthcoming Response Order by Consent for the Oronoco Landfill (Abrams, Alexander, Kuehn, et. al. pers. comm. December, 1990).

3/87 Static water level monitoring of area residential wells and landfill monitoring wells began.

4/28/87 In their completed Preliminary Evaluation Report, Donohue recommended a secondary field investigation phase to likely include a karst geology expert experienced in dye-tracing and other karst monitoring methods.

6/26/87 Meeting with MGS, U of M, OCHD and Donohue representatives at MGS to discuss the requirements for an investigation of the karst hydrogeology of the landfill area.

7/20/87 Dr. Alexander submitted a conceptual outline for a dye trace to Donohue.

7/21/87 MPCA staff contacted MDH staff concerning the necessity of conducting a Health Assessment for dyes used in hydrogeological investigations, like the proposed Fountain, MN dye trace.

7/28/87 Representatives from OCHD, OCPWD, MPCA, U of M, Donohue and Oronoco Township met to discuss the Oronoco Dye Trace proposal. MPCA staff decided a Health Assessment for Rhodamine WT would be necessary.

7/31/87 MPCA formally requested a Health Assessment from the MDH for the use of Rhodamine WT, Lissamine FF, fluorescein, and lithium salts as tracers for the Fountain, MN dye trace.

9/9/87 Summary notes from a multi-agency meeting held to discuss the proposed dye trace documented an MPCA request to add the Oronoco Study to the Health Assessment being conducted for the Fountain Study.

9/17/87 Dr. Alexander formally requested permission to meet with MDH and MPCA staff to provide input into the Health Assessment process before it was completed.

9/22/87 Dr. Alexander submitted copies of literature articles indicating the non-toxic nature of Rhodamine WT and fluorescein when used in water tracing applications to MPCA and MDH.

9/23/87 Letter of inquiry sent from Dr. Alexander to Dr. Sharon Abidi (USFWS) regarding her 1982 work with Rhodamine dyes.

9/28/87 Response from Dr. Abidi to Dr. Alexander concluded the controlled use of Rhodamine dyes in natural areas would not lead to the formation of carcinogenic diethylnitrosamine.

10/87 Dr. Alexander met with MDH and MPCA staff to discuss the Health Assessment of Rhodamine WT. Reference materials were exchanged (Alexander pers. comm. December 1990).

10/15/87 Dr. Alexander met with OCPWD and Donohue staff to formulate a dye trace study proposal.

10/16/87 Draft proposal to conduct a dye trace study submitted by Dr. Alexander to Donohue.

10/28/87 MDH issued a memo to MPCA indicating a lack of sufficient information to establish human exposure guidelines or to determine if Rhodamine WT could produce toxic reactions or toxic breakdown products. MDH staff recommended that Rhodamine WT not be used in the Olmsted County landfill investigation.

11/3/87 Donohue submitted a proposal to conduct a dye trace to MPCA.

11/9/87 MDH formally transmitted its response to the MPCA 7/31/87 and 8/87 requests, which included a copy of its 10/28/87 memo recommending that Rhodamine WT not be used for a dye trace and that all other tracer substances should be subject to a complete assessment of health risks. This document effectively terminated the 11/3/87 proposal to conduct a dye trace at the Oronoco landfill.

1/26/88 Letters from the chairmen of the Olmsted County Board of Commissioners and the Solid Waste Advisory Committee were sent to local Congressmen requesting an addition to the Clean Water Act which would allow the proper use of dye tracers.

2/2/88 MPCA submitted the draft Response Order by Consent for the Oronoco Landfill to Olmsted County.

3/11/88 EPA responded to Eric Kuehn recommending the use of Rhodamine WT only intermittently and for short periods of time when no other suitable tracers were available.

3/14/88 Dr. Alexander submitted a letter to Rep. Don Frerichs suggesting reconsideration of the use of Rhodamine WT.

3/22/88 Rep. Frerichs forwarded Dr. Alexander's 3/14 letter to MDH and the MPCA.

3/29/88 MDH responded to Rep. Frerichs upholding their earlier recommendation to prohibit the use of Rhodamine WT.

4/5/88 MPCA responded to Rep. Frerichs upholding their earlier recommendation to prohibit the use of Rhodamine WT.

4/15/88 Letter sent from Dr. Alexander to Rep. Frerichs regarding the use of Lissamine FF as an alternative dye tracer.

4/28/88 Ten residential wells were tested by MPCA for VOCs at the request of the Olmsted County Board of Commissioners. No VOCs were detected.

5/3/88 Rep. Frerichs made a request of MPCA to require the review of Lissamine FF for use in a dye trace.

5/31/88 MPCA responded to Rep. Frerichs indicating they would review a proposal for a dye trace using Lissamine FF submitted by Olmsted County.

6/9/88 An internal staff meeting was held with representatives of MDH, MPCA, and MDNR to discuss the implications of MDH's recommendation to prohibit the use of Rhodamine WT for the Olmsted County dye trace on research being conducted or planned by agency staff. MDH staff acknowledged their agency had no legal power to ban the use of Rhodamine WT in groundwater tracing. The conflicts were not resolved.

6/17/88 Rep. Frerichs requested a decision from the MDH regarding which tracer would be acceptable for a dye trace at the Oronoco Landfill.

7/1/88 MDH responded to Rep. Frerichs, approving the use of Lissamine FF as an acceptable dye tracer.

7/14/88 MPCA responded to Rep. Frerichs, approving Lissamine FF for inclusion in a dye trace proposal.

8/2/88 EPA's Science and Technology Branch division chief responded to Crompton and Knowles (manufacturers of Rhodamine WT) with a temporary advisory guidelines of 0.1 micrograms per liter for Rhodamine WT.

8/30/88 Olmsted County requested a meeting with MPCA and MDH staff to re-evaluate the use of Rhodamine WT in light of the newly released EPA temporary advisory guideline for Rhodamine WT.

9/19/88 A meeting was held to discuss the use of Rhodamine WT. The following parties were represented: Donohue, OCPWD, OCHD, MDH, MPCA, the Olmsted County Board of Commissioners, the U of MN, and the Environmental Quality Board. Joint agreement was reached to use Rhodamine WT for a dye trace of the Oronoco Landfill.

9/30/88 Dr. James Quinlan made a site visit of the landfill to investigate potential dye input locations.

10/17/88 MPCA Commissioner Willet approved the use of Rhodamine WT in a response letter to Rep. Frerichs, if three steps were taken: preparation of a QAPP, arrangement for provision of bottled water to area residents, and establishment of community relations to discuss the proposed study.

11/3/88 to 11/29/88 Meetings were held with Oronoco Township residents to educate them on the need for the dye trace, to solicit information on the locations of springs and sinkholes, and to seek their cooperation for the project.

12/22/88 MPCA received Donohue's "Proposal for Conducting a Dye Trace Study", which included provisions for alternative drinking water supplies for participating residents and bottled water for residents with Rhodamine WT dye and a QA/QC Report.

12/29/88 MPCA forwarded a copy of the Dye Trace Study Proposal to MDH.

2/10/89 Staff from MPCA, OCHD, OCPWD, and Martha Kuehn participated in a conference call during which verbal comments from MPCA and MDH for the "Proposal for Conducting a Dye Trace Study" were transmitted and discussed.

2/28/89 Dr. Calvin Alexander was retained to complete a search of springs in the study area.

3/3/89 In response to an agency comment, Donohue contacted the MDA in regard to the effect of the dye trace on livestock drinking water supplies.

3/4/89 Weekly conference calls were instituted for better project management.

3/9/89 MPCA and MDH submitted written review comments for the 12/88 Dye Trace Study Proposal to Olmsted County.

3/10/89 Dr. James Quinlan was retained by Donohue as the technical subconsultant for the Oronoco Dye Trace Study.

3/29/89 MDA responded to Donohue's 3/3/89 letter.

3/31/89 Donohue submitted a Dye Trace Study Addendum in response to MPCA and MDH written review comments of 3/9/89.

4/3/89 MDH rescinded its earlier decision to prohibit the use of Rhodamine WT, in light of the provisions outlined in the 12/22/88 proposal.

4/3/89 MPCA received a QAPP for the Dye Trace Study from Donohue.

4/4/89 Dr. Alexander was retained by Olmsted County to provide technical services with respect to fluorometric analysis and spring sampling.

4/5/89 Distribution of monthly progress reports prepared by Dye Trace Study staff was initiated.

4/6/89 A public meeting was held to outline the project workplan and to train participating residents in the sampling procedures.

4/11/89 Background sampling began at initial monitoring sites.

4/25/89 MPCA provided a written response to the 3/31 Addendum and 4/3 QAPP to Olmsted County and conditionally approved the 12/88 Dye Trace Study Proposal contingent upon the submission of responses to the remaining comments.

5/1/89 Donohue submitted the spring search results (the 2nd iteration) to MPCA.

5/5/89 MPCA gave verbal approval to Gene Avery, Solid Waste Manager for Olmsted County, to proceed with the scheduled introduction of dye.

5/8/89 QAPP revisions were submitted to MPCA by Donohue, along with a letter confirming the 5/5 conference call proceedings.

5/9/89 Olmsted County sent letters to area residents informing them of the OCHD decision to utilize carbon filters to remove Rhodamine WT should it appear in their wells during the study.

5/10/89 124 pounds of a 20% solution of Rhodamine WT dye was introduced into the Prairie du Chien Aquifer in a quarry floor crevice approximately 600 feet west of the landfill boundary.

5/15/89 Olmsted County staff began researching the availability of technology at the Mayo Clinic to assist with the Rhodamine WT confirmation process.

5/25/89 Donohue and Dye Trace staff began preparations for a second introduction, using fluorescein dye.

5/30/89 Written approval from MPCA to conduct the dye trace was received.

6/7/89 As the potential second site for dye introduction, a successful percolation rate test was conducted at the Reiter sinkhole east of the landfill.

6/14/89 Dr. Alexander completed tests on charcoal filter units to determine their effectiveness in removing dye from water supplies.

7/5/89 Site visit by Dr. Jim Quinlan which resulted in his conclusion that refrigeration of samples was necessary and that use of Mayo's scanning spectrofluorophotometer was inadequate.

7/89 to 9/89 The study area was expanded, according to the workplan, as fluorescence was detected in representative wells and wells near the study boundaries (see Section 3.4.4 below).

7/24/89 MDH provided written approval for the use of fluorescein in a second dye introduction, provided the same filter installation plan was followed as with the first dye trace.

7/25/89 Request for Response Action to prepare a Response Order by Consent for the Remedial Investigation and Feasibility Study of the Oronoco Landfill approved by the MPCA Citizens' Board.

7/27/89 Olmsted County decided to make Dr. Alexander the primary technical sub-consultant for the project.

8/89 Sub-studies to investigate the random detection phenomenon were initiated. As questions were answered and new ones developed, new sub-studies were created (see Section 5.1).

8/10/89 Dr. Alexander, Mayo Clinic, and County staff met and established an acceptable analytical protocol for the PEFS.

8/17/89 A moratorium on study area expansion was called by Donohue and Olmsted County staff when the size of the study doubled and became unmanageable. It continued until investigations underway could determine whether or not these random detections were due to the appearance of Rhodamine WT.

9/14/89 MPCA requested Olmsted County submit a plan for interim VOC analysis in residential wells.

9/20/89 EPA sent a Superfund Memorandum of Agreement authorizing MPCA to act as the lead agency for Superfund investigations at the Oronoco Landfill.

9/21/89 Olmsted County made the decision to add VOC testing from wells 151 during the regular fall round of monitoring well sampling. MDH was asked to pursue sampling of community supply well 159 during the same time period.

10/1/89 Dr. Alexander recommended to Olmsted County that the stream sites be dropped, that spring sampling be reduced to three sites and that use of bugs at springs be dropped.

10/5/89 Donohue submitted a request to MPCA, which was forwarded to MDH, to amend the project workplan in two ways: to install filters only in homes with continuous dye detections and to fix the study area at its 10/5/89 size.

10/5/89 MPCA staff were added as weekly conference call participants. During this call, Olmsted County authorized the addition of HPLC analysis by Twin City Testing to the analytical plan.

10/6/89 A proposal for criteria to select wells for an interim residential well VOC Sampling plan was submitted by Donohue to MPCA.

10/11/89 MPCA staff gave verbal approval to drop stream sampling. The other recommendations made 10/1/89 were denied.

10/17/89 MDH responded to the 10/5/89 request for a workplan addendum; fixing the study area size was approved, but the proposed modifications for filter installation were rejected. A counter-proposal for modifications in the installation policy was provided.

10/26/89 MPCA gave verbal agreement with the 10/17/89 MDH decision.

10/27/89 An interim response action plan to be utilized in the event contaminants were detected in residential wells as a result of VOC sampling was submitted to MPCA by Olmsted County.

11/2/89 Approval of criteria for selecting residential wells for VOC sampling was received from MPCA by Olmsted County.

11/7/89 Dr. Alexander confirmed the presence of Rhodamine B on seed corn.

11/30/89 In response to MPCA comments of the 10/27/89 proposed interim response action policy, Olmsted County submitted a modified proposal.

11/30/89 Olmsted County made a formal written request for MPCA to allow a change in the frequency of static water level monitoring from monthly to quarterly.

12/13/89 MPCA approved the interim response action plan to be implemented if VOCs were detected in residential wells, on the condition that MDH would be asked to conduct a health assessment if compounds without RALs or in excess of RALs were detected.

12/13/89 MPCA agreed to change the frequency of static water level monitoring from monthly to quarterly.

12/19/89 MPCA, Olmsted County, and the City of Rochester executed a Response Order by Consent to govern the Remedial Investigation and Feasibility Study for the Oronoco Landfill.

12/21/89 MPCA obtained permission to consult with Malcolm Field (EPA) on karst dye trace technical matters.

1/24/90 Meeting with staff from MPCA and Donohue, Dr. Alexander and Malcolm Field to discuss the Dye Trace results, to date.

1/25/90 A site visit was made by Malcolm Field, Dr. Alexander, staff from MPCA, and Donohue. A meeting followed with these parties and OCPWD staff to outline future options for a second dye trace. Consensus was reached on the following points:

- a second dye trace was warranted based on the ambiguous nature of the water table information east of the landfill.
- Rhodamine WT would be an acceptable dye choice for a second dye introduction because it would still define groundwater flow in the vicinity of the landfill without incurring extensive, new work plan development or laboratory costs (therefore, further investigation of the feasibility of using fluorescein dye was dropped); and
- the on-site sinkhole should be excavated and a percolation test conducted to see if it would be an acceptable second dye introduction site, before committing to the Reiter sinkhole.

1/25/90 Donohue submitted a letter to MPCA outlining necessary modifications for the Dye Trace Study which included a proposal to reduce the size of the study and to introduce ten times the amount of Rhodamine WT in a second dye introduction.

2/12/90 In answer to questions raised about the potential for Rhodamine WT degradation into Rhodamine B, Dr. Franklyn Pendergast, Director for Research in Mayo Clinic's Biochemistry and Molecular Biology Department presented the expert opinion that light transformation of Rhodamine WT to Rhodamine B, or vice versa, is an implausible chemical transformation.

2/12/90 Directive from MPCA sent to Olmsted County recommending a second dye introduction and requesting a detailed proposal for this portion of the workplan.

2/22/90 Donohue submitted Dye Trace Workplan addendum to MPCA.

3/8/90 The excavation and failed percolation test at the landfill sinkhole was discussed during a conference call and the decision to use the Reiter sinkhole was made.

3/19/90 MPCA accepted the elimination of monitoring points as proposed in the 2/22/90 document and provided documentation of their approval to eliminate stream sites from the monitoring plan.

3/22/90 Interim data summary submitted to MPCA by Donohue.

3/23/90 Olmsted County submitted a proposal to conduct an anion study to MPCA.

3/28/90 MPCA provided verbal approval of the Anion Study Workplan.

3/29/90 Anion sampling of 133 sampling sites was begun to provide information helpful to set criteria for future study area reductions.

3/30/90 Introduction of 1,000 pounds of 20% Rhodamine WT solution occurred in the Reiter sinkhole.

4/12/90 MPCA provided verbal approval of the Phase II Workplan, its QAPP and Addendum.

4/16/90 Donohue submitted a response to MPCA regarding the continued use of bugs, as an addition to the QAPP.

6/26/90 Dr. Alexander submitted the Random Detections Report and the Anion Report to MPCA.

6/26/90 Letter sent to residents with carbon filter units summarizing the random detections phenomenon and the resulting change in filter installation policy.

7/6/90 Olmsted county contracted with Mr. Tom Aley of the Ozark Underground Laboratories as a technical subconsultant to review bug analysis and interpretation techniques.

7/25/90 Letter sent from OCPWD to MPCA confirming the submittal of the Random Detections Report, the Anion Report, the change in the filter installation policy, and an outline of the 8/90 reduction plan.

8/6/90 Analytical services transferred from the OCH to the U of M, Department of Geology Laboratory.

8/30/90 Based on results of the Rhodamine WT degradation experiment, staff assigned to the Dye Trace Study verbally agreed that refrigeration of samples was unnecessary.

10/25/90 MPCA gave verbal approval for the preparation of a maintenance mode plan for the dye trace.

11/5/90 Olmsted County formally submitted a maintenance mode plan for the Dye Trace to MPCA.

1/14/91 MPCA provided written documentation of their earlier verbal approvals of the 8/90 reduction plan, the transfer of analytical services to the U of M, and the maintenance mode sampling plan.

3.0 DYE TRACE METHODOLOGY

The methods, procedures and QA/QC plan for the Dye Trace Study are described in detail in Donohue (1988, 1989a, 1989b, 1989c, 1990a, 1990b, and 1990c). Donohue (1989b) is the initial QAPP. As the Dye Trace Study developed, modifications to the methodology of the trace became necessary. These modifications were discussed in weekly conference calls between various agency staff assigned to the dye trace. Requests for significant modifications were submitted by Olmsted County staff and/or by Donohue staff to the MPCA for approval as necessary. The accumulation of several modifications, as well as the plans for the second dye introduction, necessitated the major revisions outlined in Section 2.4.2.

3.1 Choice of Dye

The references listed in 2.4.1 above uniformly conclude that fluorescent dyes are by far the most effective, economical, and efficient of the range of potential tracer materials. Because the Olmsted County Landfill Dye Trace Study was designed to reach the private domestic water supply wells in the residences surrounding the site, the non-toxicity of the dye was an overriding concern. The secondary factors included stability of the dyes, resistance to adsorption in the aquifer, natural background levels of fluorescence, and ease and economy of analysis.

3.1.1 Non-toxicity of Rhodamine WT

The current comprehensive review of the toxicity of fluorescent dye tracing agents is Smart (1984). Smart (1984) concluded that Rhodamine WT, fluorescein and Tinopal CBS-X are the three safest dyes for tracer work. A.H. Perler (1988), Chief, Science and Technology Branch Criteria and Standards Division, EPA, issued temporary advisory guidelines designed to prevent "any adverse health effects resulting from the use of Rhodamine WT as a fluorescent tracer in water flow studies". The Olmsted County Dye Trace methodology outlined in the QAPPs are more conservative than the EPA guidelines. The most recent evaluation of Rhodamine WT's toxicity (Steele, 1989) concludes that the use of Rhodamine WT in dye tracing "presents a *de minimus* health risk ($<1 \times 10^{-6}$)" to potable water supplies.

Abidi (1982) raised an important question about the safety of Rhodamine WT as a surface water tracer. She reported that under laboratory conditions Rhodamine WT could react with concentrated solutions of *nitrite* (not nitrate) to produce diethylnitrosamine, a known carcinogen. However, Steinheimer and Johnson (1986) demonstrated that Abidi's proposed reactions simply did not occur under a variety of natural conditions in surface waters. Abidi (1987) acknowledged that under the conditions present at the Olmsted County Landfill the production of diethylnitrosamine would not occur.

3.1.2 Physical and Chemical Properties of Dyes

The most comprehensive review of the chemical and physical properties of fluorescent water-tracing dyes is Smart and Laidlaw (1977). The toxicity concerns described above restricted the choice of dyes to Rhodamine WT, fluorescein, and Tinopal CBS-X. The secondary factors in the choice of dyes included: 1) the stability and ease of analysis of the dyes, 2) the natural background levels of fluorescence for each dye, and 3) the dyes' resistance to adsorption in the aquifer.

Rhodamine WT and fluorescein have long been used in tracing studies in karst areas and both have been used in successful quantitative dye traces in Minnesota (see for example: Mohring and Alexander, 1986; Foster and others, 1990). Most of the quantitative tracing work in Minnesota has used Rhodamine WT, however. Tinopal CBS-X has not been used extensively in Minnesota as a tracing agent.

Tinopal CBS-X is an optical brightener whose major use is in detergents. All of the residences in the Study Area are on private septic systems. These septic systems quite likely are introducing optical brighteners into the groundwater systems. The interpretation of positive optical brightener results would, therefore, always be ambiguous. In addition, Quinlan (pers. comm., 1989) indicated that it was very difficult to quantify Tinopal CBS-X in direct water samples. Given the lack of history of successful tracing work in Minnesota using Tinopal CBS-X, the septic tank problem, and the difficult analytical techniques necessary to analyze for it, Tinopal CBS-X (and other optical brighteners) did not appear to be appropriate for this study.

The issues of dye stability and ease of analysis are interrelated. Smart and Laidlaw (1977) and numerous other workers have shown that fluorescein is very susceptible to photo-degradation when exposed to light. This is not a problem as long as the tracer is underground but becomes a major logistical problem once the samples are collected. In addition, this photo-degradation complicates the preparation of standards for the analysis of water samples containing fluorescein. In contrast, Rhodamine WT is not very susceptible to photo-degradation. In section 5.2.2 below, a series of measurements are presented which show that Rhodamine WT in natural water samples is stable for months to years under normal laboratory conditions. The most significant problem in the analysis of Rhodamine WT is the large temperature coefficient (-2.6 percent per °C) on its fluorescence. This problem was avoided by equilibrating the samples and standards to the same temperature before analysis.

The available information from Rhodamine WT tracing in Minnesota groundwaters indicated that the background fluorescence in the red portion of the spectrum typically corresponds to < 10 ppt. This was shown to be true for the Study Area during the background sampling of the initial wells (see section 5.2.1 below). In contrast, the background fluorescence in the green portion of the spectrum is often higher and much more variable. Section 5.2.5 below presents the information that shows this to be true in the Study Area.

Although Rhodamine WT and fluorescein have been used extensively in karst tracing work, both are subject to adsorptive losses when exposed to fine-grained materials in soils or aquifers. Neither dye is as conservative as chloride or bromide ions, for example.

Rhodamine WT was selected for the first dye input (May 10, 1989) based primarily on its stability, ease of analysis and low background in the Study Area.

Rhodamine WT was also selected for the second dye input (March 30, 1990) for the same reasons. However, the second selection was more difficult. The major advantage of using Rhodamine WT for the second trace was that no changes were necessary in the analytical system in place at that time. The use of fluorescein would have more than doubled the analytical costs and effort. The major disadvantage was that it would be impossible to tell the two traces apart. After the second dye introduction, a positive detection could be due to either dye input. Nevertheless, Rhodamine WT was chosen, in consultation with the MPCA, MDH, EPA, and Olmsted County staffs, for the second dye input. The amount of dye introduced in the second input was increased by almost a factor of ten from the first dye input. It was hoped that the larger dye input would increase the concentrations of the dye detections in Phase II.

3.1.3 Economics

The economics of the analyses required for the Dye Trace Study was a major factor in the selection of a fluorescent dye as the tracing agent. It also factored in the decision to use Rhodamine WT for both phases. The primary analytical technique, filter fluorometry, was economical relative to any other available analytical technique. All of the samples were first screened on the TDFF. The cost of TDFF Rhodamine WT analyses from the Olmsted Community Hospital and University of Minnesota Laboratories was 50 cents per sample. The sample bottles were used only once and added another 20 cents to the real cost of each analysis.

Samples that indicated any significant fluorescence on the TDFF were then analyzed by scanning fluorescence spectrophotometry. Only a small percentage of the samples collected needed this second level of analysis. The commercial cost of such analyses would have been about $25 per sample. However, the Mayo Clinic staff generously allowed Dye Trace staff to use their PEFS when it was not in use (in the evenings, for example), at no charge. This allowed the second level of analysis to proceed at only the cost of staff time. There was only a limited amount of time available on the PEFS, however, and it would have been impossible to screen all of the samples through the PEFS.

A third level of analytical confirmation was used in a few dozen cases. This third level consisted of HPLC analyses via a commercial laboratory at the cost of about $125 per sample.

The combination of the three levels of analysis resulted in a net analytical cost that averaged about $1 per sample. A trace of the magnitude of this study would not have been economically feasible with any other tracer technique. A trace using a conservative ionic tracer such as chlorine or bromide ions would have required analytical techniques costing 10 to 20 times more per sample. Even the use of fluorescein in the second trace would have more than doubled the analytical costs per sample. The added analytical costs of using fluorescein was a major factor in the decision to use a larger amount of Rhodamine WT in the second trace rather than fluorescein.

3.1.4 Filters

As noted in section 2.4.2, the initiation of the Dye Trace Study was originally hindered when MDH recommended in November 1987 that Rhodamine WT not be used as the dye tracing agent. It was the opinion of their staff that information sufficient to establish human exposure guidelines was lacking, due in part to the unknown ability of Rhodamine WT to produce toxic reactions or toxic breakdown products.

In August 1988, the division chief of EPA's Science and Technology Branch provided the manufacturers of Rhodamine WT with a temporary advisory guideline for Rhodamine WT of 0.1 micrograms per liter. The existence of this EPA guideline produced a multi-agency agreement in September 1988 to proceed with a dye trace of the Oronoco Landfill using Rhodamine WT. However, because MDH still had concerns about the potential health effects of Rhodamine WT, the MPCA Commissioner stipulated that the use of Rhodamine WT would be suitable only if bottled drinking water was supplied, for a reasonable length of time, to residents potentially affected at the time Rhodamine WT was introduced into the groundwater.

The "Proposal for Conducting a Dye Trace Study" (Donohue, 1988) contained the following provisions to meet this stipulation:

> "Olmsted County is proposing to provide all residents within the study area free access throughout the investigation to potable water wells close to their area, which are completely free of any potential for the presence of Rhodamine WT. These water wells will be available for use by any potentially affected parties until all potential for dye entering their own wells is past. Additionally, Olmsted County will provide, at County expense, bottled drinking water to any resident who has a confirmed detection of Rhodamine WT in their well. The drinking water will be provided within 24 hours of detection and continued until two weeks after dye is no longer detected in the well."

Cost proposals for supplying bottled water were obtained from area vendors as part of the detailed preparations for the Study in early 1989. OCHD staff suggested that using commercially available carbon filter units could be an economical alternative to bottled water, if the filters could be shown to effectively remove Rhodamine WT from aquifer water supplies.

OCHD contracted with Dr. Alexander to proceed with this investigation in April 1989. His analysis indicated that the Ecowater Systems Water Master XLC1 under-the-sink carbon filter unit could effectively remove over 99.99% of the Rhodamine WT, even at concentrations 1,000 to 10,000 times greater than expected during the study (see Appendix K). The results were presented to area residents at the April 1989 public meeting.

A cost comparison of filter systems vs. bottled water was then completed. Since the provision of filter units in lieu of bottled water would entail considerable savings, OCHD staff recommended the use of under-the-sink carbon filter units (specifically the Water Master unit, with its proven efficiency) as an alternative to providing bottled water to residents with confirmed detections of Rhodamine WT. This recommendation was made as part of the Donohue response to MPCA and MDH comments of the "Proposal for Conducting a Dye Trace Study" in the March 31, 1989 addendum to the proposal, which was submitted to both MPCA and MDH. Procedures for testing the continued effectiveness of installed filter units were also outlined in this response document.

MPCA granted verbal approval of the 12/88 proposal, its 3/89 addendum and 5/89 QAPP, and thereby the use of carbon filter units to remove dye, on May 5, 1989. Letters were subsequently sent to residents informing them of the decision to provide carbon filters instead of bottled water to assure the availability of dye-free drinking water for those residents with confirmed exposures to Rhodamine WT. The procedures for installation of filter units were also discussed in this letter along with notification of the availability of potable water supplies from the Elton Hills or Silver Lake Fire Stations to any residents in the Study Area.

MPCA granted written approval of the 12/88 proposal, its addendum and QAPP on May 30, 1989.

As the Study progressed, detections of dye began occurring in residential wells in a random, isolated fashion, at very low concentrations. None the less, filters were offered to all residents with dye detections in their water supply. Installation arrangements were made with those residents wishing filters as soon after the confirmed detection as possible. (The first filters were installed in July 1989.) After installation, residents were asked to take both before-filter and after-filter samples once per week to verify the continued effectiveness of the filter.

In August 1989, as the random detection phenomenon began to become more evident, it became clear that installation of filters in homes with random detections was providing negligible protection against Rhodamine WT, at a great financial cost. Therefore, an amendment to the workplan was submitted to MPCA and MDH in October 1990 requesting that the county be required to install filters only in homes whose wells exhibited one of three circumstances:

1) continuous dye detections (i.e. three consecutive daily samples showing a detectable level of Rhodamine WT);
2) five or more intermittent appearances of dye; or
3) detections greater than 0.100 ppb.

MDH rejected this proposal on the basis that dye may have been reintroduced to private water supplies during pumping at non-sampling times, therefore resulting in the potential for the intermittent presence of dye and unacceptable chronic exposure. MPCA concurred with the MDH decision.

Further investigations were undertaken to determine whether or not these random detections were due to the introduction of Rhodamine WT into the aquifer. The results of those investigations (see sections 5.1 and 6.1, below and Appendix M) provided evidence that the random detections were not Rhodamine WT, but were more likely Rhodamine B from some undetermined source. Therefore, the county could now show that the filter units were being provided to residents because of the presence of a dye in the aquifer for which the County was not responsible.

Simultaneous with the finalization of the Random Detections Report (see Appendix M), a new filter installation policy was also being prepared, in consultation with MPCA and MDH staff. The new policy allowed the installation of filter units only in those homes where the presence of Rhodamine WT was determined. Staff, at all agency levels, would evaluate information on the dye's location, duration, and concentration to make this determination.

Residents were notified of the policy change for filter installation at a public meeting on June 26, 1990, as well as by individual mailings and notices posted at the sample drop-off locations. The MPCA received written confirmation of the policy details in July 1990.

A summary of carbon filter use may be seen in Appendix K. During the course of the study, 114 residential wells experienced random detections, 2 of which experienced continuous pulses of Rhodamine WT. The detections in these wells impacted over 360 individual residences. (In many cases, more than one home is served by one well. See Appendix B.) Filters were offered to all residents whose wells showed random detections, but only 140 accepted them. (Four residents with random detections already owned their own filter unit.)

When the June 1990 filter policy was instituted, 69 of the 140 residents decided to have their filter purchased at county expense and maintained at their own expense. At this time, only the two residential wells with continuous dye detections (wells 151 and 108) continue to receive replacement filter units at county expense. Their filter units were purchased by the county, on their behalf, and are no longer rented on a month-to-month basis.

The total expenditure for filter installation, monthly rental, filter cartridge replacement, associated service and repairs, unit purchasing, and de-installation between July 1989 and July 1990 (the end of the implementation period for the filter policy changes) was approximately $37,500.00. Had the filters been installed only in the homes with evidence of the continuous dye pulse, the estimated cost to protect public health would have been $800.00. The lack of technical justification for the level of filter use and the need for study area expansion unnecessarily increased the cost of the study without contributing significantly to the outcome.

3.2 Rationale for Dye Introduction Locations

The first dye introduction location was selected based on the available potentiometric maps and on field work to find karst features suitable for dye introduction. The potentiometric information available in the fall of 1988 was fragmentary but suggested that some type of groundwater flow divide might be located near the landfill. Initially, three potential areas of dye introduction were investigated.

A sinkhole located about 800 feet east of the landfill was investigated. It was alluviated with soil eroded from the surrounding fields but was actively taking water from several tile drains and acted as the sink point for surface runoff from several hundred acres. A backhoe was used to excavate the sinkhole and water was dumped into the sinkhole to see if the bedrock in the bottom would accept water. The sinkhole accepted water readily. The location of this sinkhole, known as the Reiter sinkhole, is shown with the star symbol east of the landfill on Figure 9.

Carbonate bedrock is at the surface on the landfill property immediately north of the cells. During field work in September 1988, several locations were investigated by scraping off soil cover with a backhoe and then pouring water into crevices to see if they would accept water. No crevices were found which would accept significant amounts of water. No suitable dye input points were identified in this area.

Immediately west of the northwestern portion of the landfill property, there is an active limestone quarry. Several crevices were visible on the bare bedrock quarry floor. Inspection of the quarry floor indicated that water had ponded after precipitation events in several low areas but had not ponded around one creviced area. Water tests indicated that the crevice took water readily and that crevice was selected for the first dye input. The location of the crevice was surveyed and is shown as the star off the northwest corner of the landfill on Figure 9. Active quarrying has continued at the site since May, 1989 and it is not clear if the crevice is still accessible.

As the results of the first dye trace began to accumulate over the summer of 1989, it became evident that the groundwater from the Phase I introduction point flowed generally east and northeast. The first dye input yielded no evidence of north or northwest flow from the first dye input point. Interest then shifted to the possibility of east or southeast groundwater flow from the south or southeast part of the landfill.

Early plans for the landfill indicated the presence of a filled sinkhole immediately south of the existing cells. During the winter of 1990 an extensive effort was made to excavate that filled sinkhole. The sinkhole was located and excavated to a depth of greater than 60 feet. The sinkhole would not accept any significant amount of water, however. Water poured into the excavation simply ponded in the bottom for several days. The inability to get the excavation to take water into the subsurface eliminated this area as a potential dye input point. The location of the excavated sinkhole was then surveyed and is shown by the "+" symbol inside the landfill on Figure 9. The excavated sinkhole was then backfilled with clean fill.

The Reiter sinkhole east of the landfill was therefore selected on March 8, 1990 for the second dye input. The sinkhole was re-excavated in March 1990. The resulting excavation revealed a distinct crevice filled with glacial cobbles in the bedrock beneath the sinkhole. That crevice swallowed water readily. The second dye input occurred on March 30, 1990. The second input was selected to be on the opposite side of the landfill from the first input point and to test for evidence of a south or southeastern groundwater flow from the site.

The surveyed locations of the Phase I dye introduction point (Quarry), Phase II dye introduction point (Reiter sinkhole), and the filled sinkhole on the landfill property are given below.

Feature	Easting	Northing	Elevation
Phase I input (Quarry)	392,203.13	116,578.80	978.88
Phase II input (Reiter Sinkhole)	395,820.92	114,304.58	1010.4
Landfill Sinkhole	394,573.90	114,953.06	1011.0

Notes: All coordinates are in feet. Eastings and Northings are in the Olmsted County Project Coordinate System.

3.3 Methods and Timing of Dye Introduction

3.3.1 Phase I

The first dye introduction occurred on May 10, 1989, at the base of the quarry face about 600 feet west of the landfill property (Figure 9). No excavation was necessary at this site to facilitate dye introduction. A non-chlorinated, potable water supply was obtained from a quarry 1.5 miles west of the landfill property.

At 9:40 a.m. on May 10, approximately 3,000 gallons of non-chlorinated potable water was introduced into the crevice to increase saturation within the rock. Complete uptake of this water occurred within approximately 20 minutes. Approximately 500 gallons of additional water was introduced at 12:10 p.m., followed by approximately 124 lbs. of a 20 weight percent Rhodamine WT solution. Immediately thereafter, 5,500 gallons of water were added to flush the dye into the aquifer. At 2:45 p.m., an additional 3,000 gallons of water were introduced to bring the total volume of added water to 12,000 gallons. If all 12,000 gallons of this water had mixed completely with the 124 pounds of 20 weight percent Rhodamine WT solution, the dye concentration in the resulting mixture would have been about 250 ppm. Throughout the entire dye introduction process, the water and dye went into the Prairie du Chien formation with very little ponding.

3.3.2 Phase II

The second dye introduction occurred on March 30, 1990, at the Reiter sinkhole located about 850 feet east of the landfill property (Figure 9). This site was excavated prior to introduction using a backhoe to approximately 35 feet deep, with basal measurements of eight feet by ten feet.

At 10:20 a.m., approximately 2,800 gallons of non-chlorinated potable water were introduced to help saturate the area. At one point, water depth in the base of the pit reached about one foot, but water could be heard draining. It completely disappeared within 20 minutes. At 1:00 p.m., 1,000 lbs of a 20 weight percent Rhodamine WT solution were introduced into the base of the pit. The dye barrels were rinsed out in the pit to remove the dye from the barrels. The introduction of approximately 3,200 gallons of additional water occurred at 2:00 p.m. This time, the water depth in the base of the pit reached approximately two feet. By 3:40 p.m. the pit had drained. Towards the end of this phase, the crevice in the base of the pit had enlarged to the size of a football.

On April 1, 1990, an additional 6,000 gallons of water were introduced to flush the dye into the aquifer. According to the tanker operators, the water went down the sinkhole faster than the truck could pump it out. The total volume of water introduced was approximately 12,000 gallons. If all 12,000 gallons of this water had mixed completely with the 1,000 pounds of 20 weight percent Rhodamine WT solution, the dye concentration in the resulting mixture would have been about 2,000 ppm.

The sinkhole was backfilled with one foot of pea rock at the base of the pit. A piece of corrugated culvert was then used to create a column of pea rock above the rock base, removing the culvert as it was brought up to grade. The area surrounding the pea rock column was backfilled with the native soils previously excavated from the site and also brought up to grade. Two feet of culvert were left at the surface of the hole to mark the site. The entire area was then regraded, a snow fence put around the perimeter of the sinkhole site, and no trespassing signs were posted.

This sinkhole is the receptor of surface drainage from farm fields to the south that are in the Conservation Reserve Program. There are also three field drainage tile lines that drain into the sinkhole.

3.4 Limits of Study Area

3.4.1 Boundaries

The criteria used to establish the study area boundaries were based on the need to have:

- a distribution of sampling points around the landfill so that areas both up-gradient and down-gradient from the site would be included;
- a sampling array capable of detecting radial flow; and
- wells across the two forks of the Zumbro River to determine if they served as hydrogeologic boundaries.

Selecting an area approximately 1.5 by 1.5 miles met all these criteria and provided a sufficient supply of data points.

3.4.2 Upgradient and Downgradient Wells

During 1987 and 1988, static water level measurements were taken from landfill monitoring wells and selected residential wells to determine general groundwater flow directions in the vicinity of the landfill. In general, groundwater flow was found to be northeast from the landfill (Figure 5). Therefore, upgradient wells were those wells west, south and southeast of the landfill, while those north, northeast and east were considered to be downgradient wells (Figure 5).

3.4.3 Wells Across Hydrogeologic Boundaries

All wells north of the Middle Fork of the Zumbro River and east of the South Fork of the Zumbro River were considered to be across hydrogeologic boundaries (Figure 9).

3.4.4 Representative Wells

In areas with larger concentrations of private residential wells of similar construction, a limited number of wells were selected to serve as representative wells. Equal representation of Prairie du Chien and Jordan wells was the most significant factor in the selection of wells, since little well construction information was available. If a resident's well was not selected as a representative well, but the resident wished to participate, they were given the opportunity to do so. It was also understood that if dye was detected, any wells within a one-half mile radius not included in the study would be asked to join.

3.5 Monitoring Points and Sampling Frequency

3.5.1 Springs

3.5.1.1 Purpose

Springs are land surface expressions of groundwater flow systems. They were selected as monitoring points because of their potential to act as discharge points for dye.

3.5.1.2 Spring Search

A search was conducted by Dr. Calvin Alexander along the Middle and South Forks of the Zumbro River during the winter of 1989 and spring of 1990 to locate springs within the proposed study area (see Appendix A).

Several methods were employed in locating spring sites. Initially, potentiometric and topographic maps were used to predict areas with greater potential for spring sites. Local residents were also interviewed to assist in locating spring sites. Sites identified in this way were then field checked by walking the valleys and the river edges and by boating the river itself. Some springs were identified by observing open areas in the river ice during the winter months, while others were found by watching for flowing or seeping water in likely areas. During the river search, digital thermometers and conductivity meters were used, with little success, to seek temperature and specific conductance anomalies, which can occur where groundwater enters the river system (Donohue, 1989b). Snow melt, ice flows, spring floods, and seepage from bank storage hampered the spring search.

3.5.1.3 Spring Locations

The springs were identified with 41X, 41X.X, 42X, and 42X.X numbers in the Dye Trace Study. Most springs were found on the banks of the river at varying distances. Spring sites were selected as monitoring points for the study based on their location with respect to the landfill and expected groundwater flow directions, their elevation with respect to the dye introduction point, and their discharge volumes. Figure 10 shows the location of the springs selected for the study. A second site was added at

springs 411, 416 and 423 (labeled 411.5, 416.5 and 423.5) to maximize the retrieval of charcoal sampling devices at these important sites. (Note: Computer program limitations resulted in an incongruous labeling system for these second sites. In the data tables, 411.5 = 431, 416.5 = 426 and 423.5 = 433. The same system was utilized for the bug samples collected from these sites: 511.5 = 531 [for site 411.5], 516.5 = 526 [for site 416.5] and 523.5 = 533 [for site 423.5]). Spring site 425 was also added later, for a short time, as part of the random detections sub-study. Other springs identified, but not utilized as sampling points, are listed in Appendix A.

3.5.1.4 Sample Types

Two types of samples were obtained from the spring sites: direct water samples collected in 30 ml glass vials and charcoal "bug" samples which had to undergo chemical extraction to release the dye from the charcoal prior to analysis. The direct water samples are designated by their 41X, 41X.X, 42X, and 42X.X numbers while the bug samples are designated by corresponding 51X, 51X.X, 52X, and 52X.X numbers.

Variable field conditions affected both types of sample collection which were monitored in two ways: field forms to record field conditions at the time of sampling; and monthly check-in forms to summarize the collection event.

3.5.1.5 Sample Frequency

The rate at which water samples were collected varied, depending on the stage of the study. The collection frequency for spring water samples is shown on Table 1.

If a spring became dry, frozen, or was determined to be less important to the outcome of the study over time, sampling was discontinued. Dry or frozen springs were checked on a monthly basis and resumed when the conditions permitted.

Spring 416.5 was identified by Dr. Quinlan as the spring most likely to show the first pulse of dye. An automatic sampler, borrowed from the Rochester regional office of the MPCA, was set at site 416.5 to maximize the possibility of intercepting dye, should it move through the groundwater quickly. It was placed on May 10, 1989, and set for hourly sample collection. The automatic collection interval was lengthened over the course of the following six weeks.

On June 26, 1989, the automatic sampler was moved to site 411 which had been identified as the next most likely site to intercept the dye. The automatic sampler remained there until October 2, 1989. As no dye was detected during this time period at either of these sites, further use of the automatic sampler was deemed unnecessary.

The sample collection interval set on the automatic sampler for each site is summarized below:

SITE	DATES	COLLECTION INTERVAL
416.5	5/10/89 - 5/18/89	hourly
	5/19/89 - 6/2/89	4 hour intervals
	6/3/89 - 6/25/89	8 hour intervals
411	6/26/89 -10/2/89	12 hour intervals

Retrieving water samples progressed relatively smoothly. High water or severe storms prevented some samples from being taken. However, collection of bug samples was sporadic. Despite bugs being set on a regular basis, they were more vulnerable because they were left in place at the spring site for an entire week. Low water, flooding, tampering by humans and animals (fish, raccoons, cows) were some reasons why bug samples were lost.

Following the second dye introduction on 3/31/90, collection of water samples at the remaining spring sites was increased to five times per week to minimize the possibility of missing the dye. This frequency was maintained for six weeks before resuming the earlier rate.

Bug samples were set and retrieved at all active spring sites twice per week from 4/10/89 to 7/16/89. Since then, the frequency of bug collection has remained constant at once per week unless weather or high water conditions inhibited field activities.

3.5.1.6 Evolution of the Spring Sampling Program

The choice of sites for spring sampling evolved during the course of the study. This variability is summarized in Table 1.

At the beginning of the study, 14 sites were used for sampling. Due to drought conditions during the summer of 1989, Site 418 became dry and sampling was discontinued in July, 1989. It regained enough water by April, 1990 for sampling to be resumed. In December 1989, springs 411 and 422 froze and sampling was discontinued. Site 411 was replaced with a flowing site located 600 feet downstream and labeled 411.5. Sampling at site 422 was resumed at the end of March 1990.

Other factors also led to the addition or deletion of springs during the study. As the direction and speed of dye movement from the first introduction became more apparent, it became clearer which sites could be dropped from the sampling program. The only spring on landfill property, site 421, was eliminated 7/27/89 because it was an upgradient site, unrelated to the flow of dye. In October, 1989 sampling of site 415 was discontinued for several reasons: it was across a hydrogeologic boundary,

it had low flow, and grazing cattle often rendered the samples worthless. In November and December, 1989, sampling at sites 414 and 413 ended, as they were across a hydrogeologic boundary and unlikely to produce useful data.

A major reduction in sampling took place in August 1990. As part of the the reduction plan, sampling at spring sites was reduced to 410, 411.5, 412, 416.5, 419, 422 and 423.5 The maintenance mode of sampling adopted in December 1990 eliminated sites 419 and 422 from the sampling plan.

3.5.2 Streams

3.5.2.1 Purpose

The spring search found very few concentrated discharge points (springs) emerging directly into the rivers. However, the two forks of the Zumbro River have been alluviated by the lake behind the dam which is north of the study area, and the possibility remained that significant amounts of dye could emerge in undetected springs or seeps in the rivers. As a precaution against the possibility of any type of unmonitored discharge into the rivers, a series of seven sampling locations, designated as "stream sites" were established along the Middle Fork and South Fork of the Zumbro River.

3.5.2.2 Stream Locations

The seven stream sites, labeled 401 through 407, were distributed evenly along the two river segments within the study area boundaries. Their geographic location is noted in Figure 10.

3.5.2.3 Sample Types

Direct water samples and eluted samples derived from charcoal "bugs" were obtained from stream sites.

Field conditions, such as changes in water level, algae blooms, or turbidity were recorded on field forms.

3.5.2.4 Sample Frequency

Beginning in April 1990, water samples were collected twice per week. Bug samples were also set and retrieved twice per week from 4/19/89 to 7/17/89. After that, bug collection was reduced to once per week. Sampling continued largely uninterrupted through 10/20/89. The use of stream sites was discontinued at this time because useful data was not being produced. First, the presence of other organic materials in the river water made interpretation of the analytical results ambiguous. Second, once the low concentration of dye in the monitoring wells was evident, the probability of being able to detect dye in the more diluted stream samples declined.

3.5.3 Monitoring Wells

3.5.3.1 Purpose

Eleven monitoring wells are currently in operation at the Oronoco Landfill. Ten of the monitoring wells were installed into the Prairie du Chien Formation and the eleventh well was drilled as a water supply well into the Jordan Formation. All eleven monitoring wells were selected as Dye Trace sampling points to determine if they intercept groundwater flowing beneath the site and can thereby act as detection points for potential leachate leaks.

3.5.3.2 Monitoring Well Locations

The locations of the monitoring wells are shown in Figure 11. For the purpose of the Dye Trace Study these wells have been given numbers from 301 to 311. For most other landfill monitoring purposes the monitoring wells have a different numbering system. The conversion is as follows: 301 = 8, 302 = 1, 303 = 11A, 304 = 11B, 305 = 12, 306 = 14A, 307 = 14B, 308 = 13A, 309 = 13B, 310 = 15A, 311 = 15B.

Ten of the 11 wells (302 - 311) are in the Prairie du Chien Aquifer. Well 302 does not have an annular seal. The remaining wells are cased and grouted. When the wells were installed, the water table under the landfill was at about the 960 to 980 foot elevation. Wells 303 and 304, 306 and 307, 308 and 309, and 310 and 311 are adjacent, paired wells. Wells 303, 306, 308, and 310 contain 40-foot screens installed to intercept the top of the water table. Wells 304, 305, 307, 309, and 311 contain 10-foot screens installed about 60 feet below the water table. Well 302 is an open hole from about 80 to 180 feet below the water table. The eleventh well, 301, contains a 27-foot, open hole interval in the Jordan Aquifer about 300 feet below the original water table. In the spring of 1990, the water table under the landfill was at about the 940- to 950-foot elevation. The construction of the monitoring wells is summarized in Figure 12.

3.5.3.3 Sample Types

Only direct water samples were collected from the monitoring wells.

3.5.3.4 Sample Frequency

Beginning in April 1989, sampling occurred daily at the monitoring wells until June 9. By that time, the persistent nature of the dye pulses in the monitoring wells was well established, so sampling was reduced to three times per week. On 3/30/90, following the second dye introduction, sampling was increased to five days per week for two weeks to ensure that short-duration pulses would not be missed. In the absence of immediate detections, sampling three times per week resumed in mid-May. In August 1990, sampling was reduced to twice per week. Beginning in December 1990, sampling was reduced to once per week. Field conditions affecting sample collection were recorded on field forms.

3.5.4 Residential Wells

3.5.4.1 Purpose

Residential wells were selected to provide an areal array of sampling points necessary to determine groundwater flow directions, paths, and flow rates within the Prairie du Chien and Jordan Aquifers over a wide geographic area in the vicinity of the landfill.

Several wells were specifically selected to test the hypothesis that the local rivers were discharge zones which served as hydrologic boundaries for potential leachate migration from the landfill (Donohue, 1988). These test cases were wells north of the Middle Fork and east of the South Fork of the Zumbro River.

3.5.4.2 Residential Well Locations

The locations and other available information for all of the wells sampled in the Dye Trace are listed in Appendix B. The locations of the various wells are shown on Figure 13. The private wells are identified with 1XX, 2XX, 6XX, and 7XX numbers. The Quincy Control Area wells (see section 5.1.5.1 below) are designated with 9XX numbers.

3.5.4.3 Well Selection Criteria

Residential wells were initially selected to provide:

- areal distribution within the defined limits of the study area;
- equal representation of Prairie du Chien and Jordan wells;
- representative wells in areas with large concentrations of similar wells or wells serving multiple residences;
- representation for the few Quaternary and Franconia wells in the study area; and
- control wells upgradient and across hydrogeologic boundaries.

However, virtually any resident wishing to participate in the study was given the opportunity to do so. If a resident whose well was particularly important to the study chose not to participate, efforts were made to either recruit that individual or gain permission to have county staff collect samples from their well. The vast majority of residents proved willing to participate without any recruitment.

3.5.4.4 Sample Types

Only direct water samples were collected from residential wells. Conditions affecting sample collection were recorded by the individual well user on their purge forms.

3.5.4.5 Sample Frequency

Beginning in early April 1989, residents collected samples on a daily basis. If a resident missed sampling day(s), they were not asked to collect multiple samples later as replacement samples. There simply would be a loss of data for the length of the absence. In cases when residents were absent for long periods of time, arrangements were made to have county staff collect the samples. Conditions affecting sample collection were recorded by the individual well user on their purge forms.

Beginning in August 1990, sampling was reduced to twice per week and by December 1990, sampling was further reduced to one day per week.

3.5.4.6 Evolution of the Residential Well Sampling Program

Residents at 101 locations (represented by identification numbers in the 100s and 200s) began collecting samples between 4/11/89 and 5/25/89. The majority of these samplers began at least three weeks prior to the introduction of dye on 5/10/90 (Figure 9).

The size of the residential well sampling network remained constant for the first four months of the study. After that time, several changes occurred. Some residents quit the study because they expected results sooner and they became tired of the daily task. At about the same time, the first random residential well dye detections occurred. As detections occurred in wells serving as "representative wells", neighboring wells which had not previously been part of the study were added, as per the workplan. Also, new wells at the perimeter of the study area were incorporated due to the presence of dye in their neighboring wells. Within a three month time span, approximately 100 new residential wells (with identification numbers in the 600s and 700s) were added to the study (Figure 13).

When the study size began expanding rapidly, several sub-studies were initiated to evaluate the unexpected random detections of dye (see Section 5.1 below). Expansion of the study area ceased at this time. The efforts ultimately resulted in the identification of another dye, Rhodamine B, in samples with random detections.

After freezing the rapid addition of wells, the size of the study was re-evaluated. Eventually a reduction to 54 residential wells was implemented in August 1990 (Figure 14). A further reduction to 38 residential wells was implemented in December 1990 (Figure 15).

Appendix B presents the start date and end date for each participating resident. Although it is difficult to determine the number of participants on any given date, the landmark dates noted above give a clear indication of the fluctuations in study size which occurred. The total number of residents who participated for any length of time during the study was 203 (Figure 13).

3.5.4.7 Field Blanks

The large number of residential wells selected as Dye Trace Study sampling stations were located in all directions from the landfill. During the planning and initial phases of the Study it was assumed that many of these private wells would become de facto field blanks. (In this study, the term "field blank" refers to a sample vial filled with groundwater in the field which was not expected to contain Rhodamine WT dye.) As noted above, several wells were deliberately selected that were beyond the conventional hydrologic boundaries of the local flow system. A few wells were selected that were cased and grouted into the Franconia Aquifer which is separated from the Prairie du Chien/Jordan Aquifer by the St. Lawrence aquitard (Kanivetsky, 1988).

Residential well 182, southeast of the landfill, and residential well 200, northwest of the landfill, were initially selected to provide daily samples which would serve as designated field blanks for the study. These wells were assumed to be outside the area which had any potential to be reached by dye. Samples serving as field blanks were collected and analyzed using the identical protocols as the rest of the residential wells.

The validity of these assumptions was brought into question as isolated dye detections began to show up in the various field blanks. Indeed, it was the presence of isolated dye detections in these field blanks that contributed to the eventual identification of the random detection phenomenon (see section 5.1 below).

As the random detection phenomenon became better understood and as the groundwater flow direction from the first dye introduction became evident, the original assumptions were validated. Almost all of the private wells are currently de facto field blanks. The wells across hydrologic boundaries and in the Franconia Aquifer have served their intended purpose. Over 90% of the samples analyzed in this project are, in effect, field blanks.

3.6 Sampling Procedures

Sampling procedures for springs and streams, monitoring wells, residential wells, and static water levels are discussed in Donohue (1988, 1989a, 1989b, 1989c, 1990a, 1990b, and 1990c).

3.6.1 Springs and Streams

3.6.1.1 Sampling Personnel

Samples collected from the springs and streams were collected by Dye Trace Study field technicians. Several other staff members were also trained as back-up staff for this duty.

3.6.1.2 Sampling Procedures

3.6.1.2.1 Bug Sampling Procedures

An activated charcoal packet (termed a bug) was placed by one of two different methods at all spring and stream sites. In the first method, a ten-inch high, hydrodynamically stable stand (termed a gumdrop) was placed at each spring or stream site with high flow conditions. The bug was suspended from the gumdrop, then the entire unit was placed into the flow. Gumdrops were secured to nearby trees or bushes using black nylon cord and remained in place for the duration of the study, unless flow conditions changed or external problems (vandalism, flooding, etc.) rendered the gumdrops useless. The second method was used at low flow spring sites. Rather than using gumdrops, the bugs were situated in "traps" fabricated by sticks or rocks to keep the bug saturated within the flow from the site.

One week after placement, the bugs were collected and analyzed for fluorescence, and new bugs were left at each site. When collected, the bugs were placed in separate four-inch by four-inch ziplock bags. The site identification number, collection date and time were written on the bag with a waterproof marker. Field conditions affecting sample collection were recorded on the spring and stream field form and the sample information was logged in on the appropriate chain-of-custody form. After collection, the bugs were rinsed of organic matter using a non-chlorinated water supply. Initially, this was done at a private well south of the study area. Later, this was accomplished at the Dye Trace Study office using deionized water. Samples were transported in county or staff vehicles. After sample check-in procedures by staff at the office, they were stored in the freezer until delivery to the laboratory.

Appendix C of the QAPP (Donohue, 1989c) presents gumdrop and bug construction diagrams, while Appendix A details sampling procedures.

3.6.1.2.2 Direct Water Sampling Procedures

Direct water samples were collected in 30 ml vials. Each vial was rinsed three times and then filled with water from the spring or stream site. A blue label was affixed to the vial and the identification number, collection date and time were written on the label using a waterproof pen. Field conditions affecting sample collection were recorded on the spring and stream field form and the sample information was logged in on the appropriate chain-of-custody form. Samples were transported in county or staff vehicles. After sample check-in procedures by staff at the office, samples were refrigerated until delivery to the laboratory.

3.6.1.3 QA/QC Measures

Background samples were collected for at least two weeks prior to the first dye introduction. During this period, bugs and direct water samples were collected twice weekly. These samples were collected and analyzed to determine existing levels of natural, background fluorescence in the red part of the spectrum where Rhodamine WT is detected.

One randomly selected field duplicate was collected per ten sampling sites for both the bug and direct water samples. To collect the bug duplicates, two bugs were placed over the same sampling site. Upon collection, these duplicate samples were packaged separately and labeled one minute apart. Direct water sample duplicates were collected at the same location, one minute apart.

Collection of field blanks was not required for spring and stream samples. Instead, one materials blank was analyzed for each one pound can of charcoal used to make the bugs. This materials blank was made at the same time as the bugs used for sample collection. It was placed in a ziplock bag, labeled and analyzed using the same procedures as for the field samples. The amount of fluorescence detected in the materials blank served as a reference value with which comparisons to field samples using bugs made from that batch could be made.

Results are presented in Appendix H.7.b.

3.6.2 Monitoring Wells

3.6.2.1 Sampling Personnel

Samples collected from the monitoring wells were collected by field technicians from the Dye Trace Study trained in proper procedures. Back-up staff were also trained for this study.

3.6.2.2 Sampling Procedures

Groundwater samples were collected from 11 on-site monitoring wells at the Oronoco Landfill.

Prior to sample collection, monitoring wells were purged to obtain water samples representative of the aquifer. At least three well volumes were removed, as required by MPCA guidelines. Information from well logs and initial stabilization tests conducted by Donohue staff was used to determine the purge time for each well. If well recharge rates were insufficient to conduct continuous pumping, the wells were pumped dry and a sample obtained soon after recharge (see Appendix D.2).

At weekly intervals, when static water level measurements were taken, the volume to be purged was recalculated. If the recalculated volumes differed from the original calculated volumes by more than 20%, the amount of water to be purged would have been changed to the recalculated

volumes. Additionally, the volume actually being purged was remeasured weekly with a graduated bucket. If the volume differed from the original stabilization test results by more than 20%, the protocol would have been changed to reflect the changed conditions.

Groundwater samples were collected in 30 ml vials immediately following the purging process. Each monitoring well contained a dedicated pump. Sample containers were rinsed three times with well water prior to collection. Samples were then logged in on the appropriate chain-of-custody form, and notes of conditions affecting sample collection were recorded on the field form. Samples were transported by staff to the Dye Trace Office. The samples were checked in and refrigerated prior to delivery for analysis.

A green sample label containing the identification number, date, and time of collection was used for the monitoring well samples. Field duplicates were distinctly identified by noting a time one minute later than the regular sample. Upon collection, these samples were labeled and placed in a vial collection rack.

3.6.2.3. QA/QC Measures

To obtain background information, the monitoring wells were sampled daily for four weeks prior to the first introduction of dye into the aquifer. The purpose of these samples was to determine the natural level of background fluorescence.

Two field duplicates were collected from the on-site monitoring wells each sampling day. These sites were selected randomly at the beginning of each week.

3.6.3 Residential Wells

3.6.3.1 Sampling Personnel

Residential well owners sampled their own wells after instruction by Dye Trace Study staff. In cases where more than one residence was utilizing a well, the residents determined among themselves who would take the daily samples. When a well owner was unable to take their daily samples, the well owner made personal arrangements with a neighbor or Dye Trace staff to continue with the sampling.

3.6.3.2 Sampling Procedures

Chemical preservatives, light protection and refrigeration were considered unnecessary. However, refrigeration of samples was included in the sampling protocol until results from a Rhodamine WT degradation study were completed. Once results of this study were available, refrigeration was no longer required, although most residents continued to store their samples in the refrigerator out of habit and convenience. The samples were not permitted to freeze. The maximum holding time for these samples exceeds one year, based on a degradation study (see Section 5.2.2 below).

A copy of the sampling procedures given to participating residents may be found in Donohue, 1990c.

3.6.3.3 QA/QC Measures

Residential wells were sampled daily for two to four weeks prior to the introduction of dye into the aquifer, depending on the individual well user. The purpose of these samples was to determine the natural level of background fluorescence present in groundwater.

Due to the large volume of samples and type of sample collection, field duplicates were not required. Rather, a laboratory duplicate was selected within each batch of 40 samples analyzed. However, during one stage of the study, a sub-study of duplicate sample collection was instituted (see Section 5.1.5.3).

Collection of field blanks is discussed in Section 3.5.4.7.

3.6.4 Static Water Level Measurements

3.6.4.1 Personnel

SWL measurements were taken by Dye Trace field technicians with several other staff trained as back-ups.

3.6.4.2 Procedures

SWL measurements were taken from selected residential wells and 11 monitoring wells (see Figure 5). Measurements were taken on a monthly basis through early December 1989. From that point on, quarterly measurements were taken (see Appendix C).

An electric water level tape and steel tape were used in measuring. The type of well construction determined which tape was used. Both tapes were decontaminated prior to use and between wells to avoid cross-contamination between wells. Decontamination of the electric water level tape consisted of two distilled water rinses. The steel tape was decontaminated with isopropyl alcohol swabs.

Access to each well was determined by the type of cap on the well. Either the entire cap or the cap plug was removed to gain access.

Static water level measurements were taken using procedures set forth in the QAPP (Donohue, 1989b). See Appendix C.

3.7 Sample Transportation/Chain of Custody

3.7.1 Residential Wells

All residential well samples were transported as often as possible by the resident to one of five convenient drop off points. At each drop off point, the resident recorded their name, their well ID#, a listing of the samples delivered by date sampled, and the date and time samples were left on the appropriate chain-of-custody form. Samples were collected as often as necessary from the drop off points by a Dye Trace Study staff person and delivered to the office for sample check in and laboratory preparation. These sample acceptance procedures are outlined in Donohue 1990b.

Sample custody usually followed these steps:

1. The resident collected and labeled the sample.

2. Each resident delivered their samples, transferring custody to the drop off location by logging in their sample on the appropriate custody forms.

3. Dye Trace staff obtained custody when accepting the samples from the drop off points and delivering them to the Dye Trace Study office for subsequent handling. Both the transporter and the staff person receiving the samples signed the chain-of-custody form.

4. Dye Trace personnel delivered samples to laboratory personnel along with the chain-of-custody forms. After analysis, all samples and custody forms were returned to Dye Trace staff for storage until project's end.

3.7.2 Monitoring Wells, Springs, and Streams

Spring, stream, and monitoring well direct water samples and bugs were handled and transported directly by Dye Trace staff.

Chain of custody began in the field with sample labeling and completion of the appropriate chain-of-custody form. This form included the sample identification number, the date, and time the sample was delivered to the Dye Trace Study Office for sample check in and laboratory preparation. When transferring possession of the samples, the individuals relinquishing and receiving the samples signed, dated, and noted the time on the custody form.

Samples were delivered with their chain-of-custody forms to the analytical laboratory. When samples were not taken immediately to the laboratory, they were stored in a locked office or a locked refrigerator, with their chain-of-custody form.

Once the samples reached the laboratory, the analyst was responsible for their security. The laboratory was locked when not in use. While the samples were being analyzed, they were within sight of the analyst. After analysis, the samples were returned to the Dye Trace office for long term storage by the Dye Trace staff, who were responsible for filing and maintaining chain-of-custody records.

3.8 Analytical Procedures

Analytical procedures are discussed in detail in Donohue 1988, 1989b, 1989c, 1990a, 1990b, and 1990c.

3.8.1 Sample Preparation

3.8.1.1 Water Samples

Direct water samples were obtained from monitoring wells, residential wells, spring sites and stream sites. Once samples reached the laboratory for analysis, they were placed in a room temperature water bath for thirty minutes prior to analysis, so equilibration could occur. Since the fluorescence of Rhodamine WT decreases by 2.6% per degree Celsius, it was important to maintain a constant temperature of the samples. For each batch of samples analyzed, 1.0 degree Celsius was the maximum allowable temperature difference between the beginning and end of analysis.

3.8.1.2 Bug Samples

Bug samples, obtained only from springs and streams, were eluted prior to filter fluorometric analysis using a 5:2:3 "Smart Solution". The exact make-up of the elutant solution and the specific elutant procedure may be found in Donohue (1990b, Appendix B, sections 6.0 and 8.2.3).

3.8.2 Turner Design Filter Fluorometer

3.8.2.1 Purpose

The TDFF was used to separate samples with fluorescence in the red part of the spectrum (therefore samples potentially containing Rhodamine WT dye) from those samples without red fluorescence. Residential and monitoring well samples with fluorescence levels detected above 0.005 ppb on the filter fluorometer were then passed on to additional levels of analysis, using other instruments.

3.8.2.2 Theory and Operation

Sections one and two of Appendix B, "Laboratory Protocols for Dye Analysis", in the QAPP (Donohue, 1989b) outline the theory and operation of the filter fluorometer.

3.8.3 Perkin-Elmer Fluorescence Spectrophotometer

3.8.3.1 Purpose

The PEFS was used as a second analytical technique after filter fluorometry identified the presence of fluorescence in samples. This level of analysis distinguished between red rhodamine dyes and other types of red fluorescence. Four categories were used to classify analytical results from the PEFS. They were:

1. Negative (-): The scan showed the absence of rhodamine dye in the sample.

2. Interference (i): When the scan depicted peaks or elevated baselines which interfered with conclusive interpretation of the presence of rhodamine, results were classified as interference. Depending on the type of scan produced, four sub-categories of interference were identified:

   - interference/left showed a peak to the left of the rhodamine wavelength,

   - interference/right showed three peaks to the right of the rhodamine wavelength,

   - interference/middle showed a peak in a slightly off-set position from the expected rhodamine peak position, and usually with a different shape, and

   - interference/elevated showed an elevated base-line which could potentially hide any small rhodamine peaks present.

Combinations of the above categories of interferences were common.

3. Trace (t): If a rhodamine peak was present, but the calculated signal to noise ratio (see analysis procedures in section 3.8.3.2) was less than 3:1, the sample was classified as a trace.

4. Positive (+): When the fluorescence peak was of the correct shape, in the correct position (wavelength of 550 nanometers), and had a signal to noise ratio greater than or equal to three, the sample was classified as positive for rhodamine.

Summary results are presented in Appendix J. Individual PEFS results for each sampling point are presented on the individual graphs in Appendices D, E, F and G.

3.8.3.2 Theory and Operation

Appendix E of the QAPP (Donohue, 1990b) contains the description of the theory and general operation of the PEFS. A detailed description of PEFS operating procedures is contained in Appendix J.2.

3.8.4 High Performance Liquid Chromatography

3.8.4.1 Purpose

The PEFS could not distinguish between different types of rhodamine dyes. Therefore, a third level of analysis was added on a limited basis. HPLC analysis was used to confirm the presence of Rhodamine WT dye in samples. HPLC analysis was only used to a limited extent because the detection limit was approximately 0.050 ppb, a value significantly greater than the concentrations of dye in most samples. It was valuable, however, in isolating samples with larger concentrations of Rhodamine B, or a mix of Rhodamine B and Rhodamine WT.

3.8.4.2 Theory and Operation

Techniques for HPLC isolation and separation of rhodamine dyes were developed by the Twin City Testing Corporation of St. Paul, Minnesota. The procedure involved the extraction of Rhodamine WT-tetrabutylammonium ion pairs using liquid-solid extraction techniques. Rhodamine WT was then eluted from the extraction cartridge and analyzed using HPLC/Fluorescence. Assuming a 100 ml sample, this method provided detection limits in the 20 to 50 ppt range due to the high inherent fluorescence of Rhodamine WT and the sample concentration factor resulting from the use of liquid-solid extraction. Given only 25 ml of water the detection limit corresponded to 50 to 100 ppt of Rhodamine WT. The presence of Rhodamine WT in water samples was confirmed by comparison of HPLC retention times with analytical standards. The technique was capable of cleanly separating Rhodamine WT from Rhodamine B. The proprietary rights to the specific methods developed for this analytical method are held by the Twin City Testing Corporation.

The brief description of the technique's Supplies and Equipment and Methodology supplied by the Twin City Testing Corporation is included at the start of Appendix I.

3.9 Data Handling and Reporting

3.9.1 History

At the start of the study, analysis sheets were manually developed and the sample data was entered into a computer spreadsheet program (Symphony, Lotus Development Corporation) for data manipulation and monthly graph generation. Data was entered into the spreadsheet from the analysis sheet, a printout was generated and then proofed, with subsequent corrections entered and proofed.

Later in the study, computer programs were developed by Oronoco Dye Trace Study and OCH staff for data handling and reporting. These programs were developed in Easytrieve (Pansophic Corporation) and Symphony. The Easytrieve programs were used by the laboratory to generate analysis forms and for data entry. The Symphony programs were used for data manipulation.

The reporting process also changed through time. Line graphs were initially used and later x-y graphs were used. Line graphs displayed the data evenly along the x-axis, while x-y graphs spaced the information along the x-axis according to the date. The switch to x-y graphs was done to more easily identify data collection gaps.

3.9.2 Laboratory Data Processing

The Easytrieve programs were developed to assist the laboratory in data handling and reporting. The first programs were designed so that the sample ID#, date, and time would be entered by the analyst to generate a laboratory bench sheet. The analyst then checked the ID#, date, and time on sample vials with the bench sheet prior to analyzing each sample. Any ID#, date, or time corrections identified were made at this time.

After each batch of samples was analyzed, the uncorrected results obtained were entered into the computer. The program calculated the correction factor for each standard, the mean correction factor, percent standard deviation, relative percent difference for the laboratory duplicate sample, and the corrected values for the samples. A final analysis sheet was then printed so the laboratory supervisor could check the information on the computer-generated analysis sheet against the laboratory bench sheet to make sure the data were correct. After review, the laboratory supervisor signed the analysis sheet and returned it along with the samples and the chain-of-custody form to the Dye Trace office.

3.9.3 Data Proofing

The analysis sheet was checked against the chain-of-custody form to ensure that all sample information corresponded. Any discrepancies were checked with the vials themselves. The other QA/QC checks that were done at that time included the following:

1. The start temperature and finish temperature were compared to ensure that they did not vary more than 1° Celsius.

2. The correction factor, mean correction factor, and percent standard deviation were checked to identity discrepancies and to watch for degrading calibration standards.

3. The relative percent difference value for the duplicate samples was checked to verify that it fell within control limits.

4. Control standards were identified and percent recovery was calculated to verify that they fell within control limits.

5. Any charcoal or vial blanks were identified and the information was recorded on the summary sheet.

6. Samples with results greater than 0.005 ppb were identified as samples to be analyzed by the PEFS. (Note: once analysis moved to the U of M, samples with concentrations greater than or equal to 0.010 ppb were identified to be analyzed on the PEFS.)

The analysis sheets were signed by the person checking the chain-of-custody form and by the staff person responsible for other QA/QC checks.

3.9.4 Converting Data from Easytrieve to Symphony

After laboratory analysis of fifty batches of forty samples was completed, a file was closed. This facilitated the conversion of a manageable set of sample results from Easytrieve into Symphony for data manipulation in a spreadsheet format.

The program name and only five of the different fields (ID number, date, time, batch number, and result) were selected for conversion. The data were transferred into Symphony and checked against the analysis sheets for those batches to locate and correct typographical and transfer errors.

Once the data were in Symphony, they were sorted by well number and collection date so they could be utilized to generate monthly tables and graphs. Easytrieve was not capable of generating monthly data tables and graphs.

All records converted from Easytrieve into Symphony also remained in the Easytrieve directory as a back-up.

3.9.5 Monthly Table and Graph Generation

3.9.5.1 Macro-program Development

The data stored in Symphony were manipulated using three macro-programs created for this project: wellcom4, wellgraf, and xygraf.

The wellcom4 macro was developed to combine all data, using the well ID number as the unique field. Wellcom4 organized the data for each well ID number into its own spreadsheet.

Wellgraf was the first graphing program used during Phase I of the Dye Trace Study. This macro-program was written to generate line graphs using 75 percent less time than manually generated line graphs.

The xygraf macro-program was produced to enable the generation of x,y graphs, which sorted dates mathematically, instead of line graphs.

Details on the development and operation of specific macros can be obtained from OCPWD staff.

3.9.5.2 Proofing Monthly Tables and Graphs

On a monthly basis tables were generated from Symphony for those wells with data for that month. The tables were proofed against the monthly check-off table, which was used to summarize the chain-of-custody process. Any discrepancies between the two tables were checked with the chain-of-custody forms and the analysis sheets. Any corrections were made in the Symphony spreadsheet.

Once the tables were proofed, graphs were generated. Results from samples collected after an under-the-sink carbon filter unit were not graphed.

Sample results from the PEFS were added to the graphs manually, along with a key for those results. Once completed, the graphs were dated in the lower right hand corner, and mailed to the residents.

3.9.6 Final Table and Graph Generation

In addition to the graphs which were prepared for monthly residential reports, cumulative tables and graphs for Phase I (April 1989 through March 1990) and Phase II (April 1990 through September 1990) were prepared. These were prepared as a means to evaluate the data and for summary presentation in the final report.

The system used to produce the final tables and graphs was different for the Phase I and Phase II documents. During Phase I, the data generation and handling system underwent a considerable amount of developmental evolution. At the start of Phase I, most of the data handling was manual. By its end, the computerized data system was fully developed and integrated. The preparation of Phase I documents, therefore, involved a considerable level of effort to merge the monthly data summaries and graphs. Phase II document preparation was more straight forward.

An outline of the document preparation steps is listed below for each Phase.

Phase I:

1. Draft cumulative tables were printed for each well ID number.
2. The draft cumulative tables were proofed against the monthly tables, analysis sheets, chain-of-custody forms, purging records, damaged sample list, re-run sample list and the actual sample vials.
3. Corrections were written on the draft cumulative table during the proofing process, then entered into the computer's spreadsheet for each well.
4. Data from the PEFS table was merged into each well's spreadsheet.

5. Corrected draft cumulative tables were printed with the PEFS results added. At the same time, draft cumulative graphs were generated and printed. (Results from samples collected after the carbon filter units were presented on the tables, but not the graphs.)
6. The corrected draft cumulative tables were proofed against the graphs.
7. Corrections on tables and graphs were entered and final tables and graphs were produced for publication.

Phase II:

When the computerization of the data base took place, the data proofing process also changed. Rather than proofing the data after it had been entered into tables, proofing and entry of corrections began when the analysis sheets were returned from the laboratory. Data were not entered into the spreadsheets until it had already undergone the proofing steps outlined in number 2, above. Also, the PEFS results were merged into the spreadsheets as they were obtained.

1. Draft cumulative tables, with PEFS results, were printed for each well ID number. Graphs were generated and printed at the same time.
2. The corrected draft cumulative tables were proofed against the graphs.
3. Corrections on tables and graphs were entered and final tables and graphs were produced for publication.

To reduce the bulk of this report, only the graphs of Phase I and Phase II results are included. Monitoring well graphs are in Appendix D; graphs of spring results are in Appendix E; Appendix F contains the graphs of the stream results; and residential well graphs are in Appendix G. All graphs are presented in numerical order, according to their Dye Trace Study ID number. The corresponding data tables are available for review from the following organizations:

Olmsted County Public Works Department
Solid Waste Division
2122 Campus Drive S.E.
Rochester, MN 55904

Minnesota Pollution Control Agency
Groundwater and Solid Waste Division
Solid Waste Section, Enforcement Unit
520 Lafayette Road North
St. Paul, MN 55155

Dr. E. Calvin Alexander, Jr.
University of Minnesota
Department of Geology and Geophysics
30 A Pillsbury Hall
Minneapolis, MN 55455

3.10 Interim Volatile Organic Compound Analysis

Testing for landfill constituents was not included as part of the Dye Trace Study. However, sometime during the subsequent Remedial Investigation activities, testing residential water samples for contaminants would occur at some level. Because wells with confirmed detections of Rhodamine WT showed a direct connection to the groundwater flowing beneath the landfill, MPCA requested the preparation of an interim sampling plan for those wells in September, 1989.

MPCA defined the interim period during which residential wells would be sampled for contaminants from 10/89 until the Consent Order stipulations were in place, which occurred on 12/19/89. Sampling would occur as a one time event whenever a residential well reached five or more consecutive days with dye detections confirmed on the PEFS, regardless of concentration. Olmsted County contracted with Braun Environmental Laboratories to collect a sample for immediate VOC analysis and a total metals sample to be held and analyzed only if VOCs were present. Simultaneously, Olmsted County staff were to collect a sample for anion analysis and conduct an on-site survey for potential contaminant sources.

The plan outlined and approved by MPCA follows:

1. MPCA will receive copies of all test results received as part of the interim sampling plan.

2. If any VOCs are detected, MPCA and Olmsted County will jointly analyze these results and the results of any other pertinent background water quality information from this or surrounding wells to determine the need for resampling. If deemed necessary, resampling will occur as soon as arrangements can be made with the contract laboratory. This resampling is to confirm the results of the first test.

3. When the decision is made to resample for VOCs, the preserved metals sample collected during the first VOC sampling event will be submitted for analysis.

4. At the time of the second VOC sample collection, a water sample will also be collected to analyze for fecal coliform bacteria.

5. If more than one VOC is detected, MDH will be asked to conduct a health assessment to evaluate possible synergistic effects.

6. When results from the second round of sampling are returned, Olmsted County, MPCA, and MDH will confer to determine the implications of the findings and the necessity for further actions.

The initial sampling, following this plan, took place in October, 1989 at well 151. In December 1989, well 108 also became positive for dye and was sampled in January 1990.

The intent of the interim contaminant testing plan was to collect only one sample from a residential well positive with Rhodamine WT until the Remedial Investigation workplan was approved and implemented. However, residents with Rhodamine WT dye in their wells felt contaminant testing should continue on the same schedule as the monitoring of the landfill wells. Olmsted County adopted this plan in lieu of the earlier plan proposed to MPCA, and began residential well sampling concurrent with monitoring well sampling in the summer of 1990.

The choice of parameters for which samples were analyzed also went through an evolutionary process. Initially, at well 151, samples were collected for VOCs, total metals, and anions as per the MPCA plan. Later, metals and anions were dropped only to resume the metals later. The selection of analysis parameters continues to occur on an event by event basis. Results are discussed in section 5.8 below.

3.11 Anion Analyses

As part of the Remedial Investigation of the Oronoco Landfill, the anion contents of selected wells and springs were surveyed. The purpose of this survey was to: 1) help characterize the ground water quality in the vicinity of the landfill, 2) identify those wells most susceptible to surface pollution, and 3) obtain data that might guide selection of wells for the later phases of the Dye Trace Study. The results of these anion analyses are summarized in Appendix L.

An area roughly bounded by U.S. Highway 52 on the west, the Middle Fork of the Zumbro River on the north, the South Fork of the Zumbro River on the east, and Olmsted County Road 14 on the south was selected for this survey. This area surrounds the Oronoco Landfill. The areal distribution of wells and springs is shown in Figure 1 of Appendix L.

Samples were obtained from 111 residential wells, 11 monitoring wells and 10 springs. The samples were collected in batches during a one month period between March 25, 1990 and April 25, 1990. The residential well samples were collected by the individual well users. Appendix 1 of Appendix L is a copy of the sampling instructions supplied to the residents. The monitoring well and spring samples were collected by Dye Trace Study personnel. All samples were collected in pre-cleaned 60 milliliter plastic vials. The vials were kept cool and transported to the Geochemical Laboratory at the Geology and Geophysics Department of the University of Minnesota in Minneapolis. The samples were analyzed within one to three days of collection.

At the Geochemical Laboratory, the water samples were analyzed on a Dionex Ion Chromatography unit. This analytical procedure measures fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3-N), phosphate (PO_4-P), and sulfate (SO_4^{-2}) ions. The detection limit of the procedure varies slightly from ion to ion and from day to day but is generally between 0.005 and 0.050 ppm. The results of these analyses are summarized in Table 1 of Appendix L. Also shown in Table 1 is information on the aquifer from which each water sample was obtained. The aquifer information was compiled by Dye Trace Study personnel from well logs and from interviews with the well owners.

4.0 PUBLIC PARTICIPATION AND INTERAGENCY COMMUNICATION

Throughout the study, it was necessary to maintain communication with approximately four hundred families and over sixty representatives of interested governmental units or technical consulting firms. Several methods were employed to keep interested parties informed about the development and progress of the study.

4.1 Public Meetings

The cooperation and participation of study area residents was critical to the success of the study. Public meeting efforts began in November and December of 1988. Through several small group meetings, residents were informed of the need for the study and recruited to assist with it.

Once the study was ready to begin, public meeting notices were sent to all study area residents who had returned well survey forms. In addition, before the first large scale public meeting took place on April 6, 1989, a special effort was made to distribute flyers announcing the meeting agenda, time and location to every resident. An outline of the study workplan was presented and proper sample collection training was given at this meeting.

Several meetings which were scheduled on an "as needed" basis followed. Their dates and topics are outlined below:

8/31/89 review project goals, changes, and current results

10/18/89 project update and description of Olmsted County's residential well water testing program

12/5/89 project update and explanation of the newly adopted scanning fluorescence spectrophotometer and high pressure liquid chromatography techniques

1/31/90 project update, future project plans and description of additional upcoming remedial investigation work

3/14/90 review changes in the sampling, reporting, and filter installation procedures, discuss an anion testing sub-study, the proposed reduction in the study area size, and the second dye introduction

6/26/90 project update, anion study results, 8/90 reduction plan, random detections report summary, and updated filter installation policy

9/19/90 project update, future dye trace study plans, landfill closure progress and upcoming remedial investigation work plans

11/14/90 project update, "maintenance mode" study size reduction plan, remedial investigation progress

All meetings were held on an informal basis. One of the objectives in hosting these meetings was to have the technical project consultants and agency staff available for individual questions.

Public meeting attendance varied. Approximately 87 people attended the 4/6/89 meeting, but attendance declined steadily as the project declined in size and increased in length. The last two meetings had only 17 and 6 residential well locations represented.

4.2 Monthly Residential Reports

Participating residents were regularly mailed copies of their results, presented in the form of monthly graphs. Accompanying each graph was an informational letter which detailed the progress of the study, documented changes in the study, and summarized study results.

4.3 Sample Collection Site Notices

If the distribution of information was needed between residential letters or public meetings, notices or updates were posted at each of the collection points where residents brought their samples.

4.4 Community Liaison

Residential involvement in issues surrounding the Oronoco Landfill stemmed from the day the Locoshonas farm was proposed as a new landfill site. A strong contingent of residents played an important role in gaining support for the implementation of a dye trace study. Martha Kuehn, an Oronoco Township resident, long active in the landfill issues, was appointed community liaison specialist to promote and maintain residential involvement in and support for the Dye Trace Study. Martha proved to be an important link between the agencies and the residents. She provided insight to the project staff regarding resident's needs and concerns. She was also available to further explain study policies, plans and changes to the residents. Residents with extended absences made arrangements with Martha to collect their samples to maintain data collection consistency.

4.5 Project Coordination Conference Calls

Four key groups of people were responsible for project coordination throughout the study: Olmsted County staff, Donohue consultants, MPCA staff and Dr. Alexander, the technical sub-consultant. To keep everyone abreast of each other's progress and to facilitate joint decision making, weekly conference calls were established in December of 1989. This was maintained until September of 1990 when conference calls were reduced to twice monthly.

4.6 Agency Progress Reports

Several other individuals representing a variety of interests wished to be kept informed in the study's progress, but were not directly involved in the ongoing proceedings. An "agency" mailing list was developed to keep these

interested parties up-to-date. Examples of the types of individuals on this list included county commissioners, appropriate staff from the MDH, OCHD, OCPWD, as well as technical consultants and Dye Trace staff members. Names were added to the list by individual request.

Distribution of monthly progress reports began in December 1989.

4.7 Media Coverage

Coverage of the Oronoco Dye Trace Study by local television, radio and print media staff was extensive. Television coverage was limited to feature reports, public meeting coverage and interviews at the beginning of the study. Radio reports and interviews were consistent throughout the study, generally at milepost events. The most extensive coverage was provided by the local daily newspaper, the Rochester Post Bulletin. From March 1989 through November 1990, 21 feature articles, updates and letters to the editor were printed about the Dye Trace Study and its related landfill investigations.

4.8 Other Presentations

Periodic updates were presented to the Olmsted County Board of Commissioners at their public board meetings. Additional requests for presentations were made by service groups, realtors and schools.

4.9 Scientific Publications

The initial results obtained in this study have been presented at two scientific meetings. Alexander and others (1990a) was presented at the 11th Friends of Karst Meeting held in Decorah, Iowa, April 5-7, 1990. Alexander and others (1990b) was presented at the Geological Society of America 1990 Annual Meeting held in Dallas, Texas, October 28 - November 1, 1990.

5.0 SUMMARY OF DYE TRACE INVESTIGATION RESULTS

5.1 Random Dye Detection Phenomenon

Nine days after the May 10, 1989 dye introduction, private well 217, which is located 2.1 miles southeast and upgradient of the first dye input point, recorded a single positive dye detection. In mid-June 1989, isolated and apparently random dye detections began to occur frequently. By the end of March 1990, 114 private wells had recorded at least one of these events. These random detections were unanticipated and a number of different kinds of data were accumulated on the characteristics of these random detections. An interim summary of the work done to define the characteristics of the random detection phenomenon is attached as Appendix M.

The random detection phenomenon was seen in the direct water samples that were collected from private and monitoring wells and from springs primarily in the summer and fall of 1989. The distinguishing characteristic of the random detections was that they were only one sample long. After a series of samples from one location showed background levels, one sample would test positive for rhodamine while the next sample would be back to background levels. Figure 1 of Appendix M is a plot showing the measured dye concentration as a function of time for the samples collected from Well 154. The data from Well 154 show eight random detections and illustrate the phenomenon.

5.1.1 Dye Concentration in Random Detections

Figure 2 of Appendix M is a histogram showing the distribution of the concentrations of the random detections in those samples which have tested positive on the PEFS. Two hundred thirty-six random detections were identified between May 19, 1989 and the end of March, 1990. The concentration of dye in most of the random detections was extremely small -- the peak of the distribution was in the 15 to 20 ppt samples. Only 29 (12.3%) of the random detections contained more than 50 ppt of dye. Only nine (3.8%) random detections contained more than 100 ppt and only three (1.3%) contained more than 200 ppt.

5.1.2 Time Distribution of the Random Detections

Figure 3 of Appendix M is a histogram showing the time distribution of the random detections from the start of the dye trace through the end of March 1990. The random detections were not seen during the month-long background sampling in April and May, 1989. The phenomenon was first observed on May 19, 1989 and did not become common until July 1989. The absolute number of random detections peaked in late August 1989; dropped off during the fall; jumped back up in early December 1989; and finally disappeared during January, February, and March, 1990. The largest number of random detections, 19, occurred during the week of August 20-26, 1989. Those 19 random detection corresponded to about 1 of every 75 residential well samples collected that week.

There were fewer wells being analyzed by the summer of 1990, but many of those wells were ones in which the random detection phenomenon was common during the summer and fall of 1989. The random detection phenomenon did not recur during the summer and fall of 1990 anywhere near its 1989 rate. While 236 random detections occurred between mid-May 1989 and March 1990, fewer than half a dozen random detections occurred during the rest of 1990.

5.1.3 Spatial Distribution of the Random Detections

Figure 4 of Appendix M is a map showing the Oronoco Dye Trace Study Area. The February 1990 potentiometric surface is shown on the map. The potentiometric surface indicates a generally north-easterly flow direction of groundwater under the landfill. Figure 5 of Appendix M shows the spatial distribution of the random detections. Random detections are seen in all directions from the dye input point -- across hydrologic boundaries as well as up, down, and parallel to the potentiometric gradients. The pattern appears to be random and does not appear to be controlled by any known hydrogeologic factors.

5.1.4 Vertical Distribution of the Random Detections

Four aquifers are in use in the Dye Trace Study Area: Quaternary aquifers, the Prairie du Chien Aquifer, the Jordan Aquifer, and the Franconia Aquifer. Table 1 of Appendix M summarizes the distribution of the random detections between the five classes of wells based on the information known in late 1989. The random detections are seen in a majority of the wells in each aquifer.

The Prairie du Chien and Jordan Aquifers are the major aquifers used in the study area. Most hydrogeologic work in southeastern Minnesota has treated the two aquifers as a single hydrogeologic unit primarily because the water levels in the two aquifers tend to be indistinguishable in any given area. However, the anion survey data (see section 5.9 below) in over 100 wells in the Study Area indicates a distinct difference in the water quality of the Prairie du Chien and Jordan Aquifers. The random detections are seen in similar fractions (69% and 56%) of the wells in both aquifers, i.e. there is very little correlation between the clear difference in water quality between the two major aquifers and the distribution of random detections.

The presence of random detections in two of the three Franconia wells (758 and 149) in the study area is particularly revealing. The Franconia Aquifer in the Dye Trace area is isolated from the overlying aquifers by the St. Lawrence aquitard. As part of other projects, isotopic age determinations have been made on wells 758 and 149. Both wells contain no detectable ^{3}H (tritium). The absence of tritium indicates that the wells contain no significant component of water which entered the ground since 1954, therefore it is improbable that rhodamine dye from the Dye Trace Study reached these wells via the aquifer.

5.1.5 Additional Testing to Define the Characteristics of the Random Detections

As the random detections began to manifest themselves in the summer of 1989, a number of different special studies were initiated to help define the characteristics of the phenomenon.

5.1.5.1 Quincy Township Control Area

In the original QAPP, it was assumed that a large fraction of the private wells would be upgradient from the groundwater flow paths and would, therefore, serve as field blanks. In particular, wells 182 and 200 were the designated field blanks. (These two wells are indicated by circled locations on Figure 4 of Appendix M.) When random detections began to appear at wells in all directions and particularly when random detections appeared in 182 and 200, a new, distant control area was established. (See Figure 16).

An area in Quincy Township in the northeastern corner of Olmsted County was picked as the control area. The hydrogeology and land use of the Quincy area is similar to that around the Oronoco Landfill, but the area is over 20 miles away and across several hydrogeologic boundaries. Owners of fifteen wells in Quincy Township collected daily water samples between October and the end of December 1989. The locations of these Quincy Township wells are shown in Figure 17. A total of 974 samples were collected and analyzed. The Quincy Township control wells were identified with 9XX sample numbers. These wells were sampled and analyzed under the normal sampling protocols. Construction information on these wells was unavailable.

Two PEFS positives (Well 916 on 11-Oct-89 and Well 902 on 06-Dec-89) and one trace (Well 915 on 10-Nov-89) were observed in these samples. The observation of random detections in the control area clearly indicated that the phenomenon was not necessarily related to the Rhodamine WT introduced by the Dye Trace. Two random detections in 974 samples analyzed corresponded to an occurrence rate of about one in every 500 water samples analyzed.

The data summarized in Figure 3 of Appendix M indicates that the random detection rate in October through December 1989 in the Dye Trace Study Area averaged about 1 in every 200 water samples analyzed. The random detection phenomenon occurred in the Quincy Control Area at about 40% of the rate seen in the Study Area.

5.1.5.2 Multiple Sampling per Day of Wells 106, 132, and 185

In an effort to measure the duration of each random detection, three well owners were asked to collect samples three times a day, generally morning, noon, and night. Prairie du Chien well 106 (southeast of the landfill), Jordan well 132 (east of the landfill), and Jordan well 185 (northeast of the landfill) were selected. This sampling protocol

extended from early August 1989 through January 1990. During this interval, well 106 recorded four PEFS positives, and wells 132 and 185 recorded one PEFS positive each. All six positives were one sample long, i.e. the samples immediately preceding and following each positive were at background levels. The samples preceding and following each positive were often separated by only two or three hours from the positive sample.

Figure 7 of Appendix M is a plot of apparent rhodamine concentration versus time for the data from well 106. Note that none of the positives shown in Figure 7 extends through more than one sample. Dye distributed in an aquifer would not be expected to move through the aquifers and water systems on such a short time scale. This behavior is consistent, however, with what would be expected if fluorescent materials were in the vials or were introduced into the samples after the water has left the homeowners' faucets.

5.1.5.3 Duplicate Sampling of Wells 112, 139, 142, 147, 149, 154, and 192

In an attempt to isolate the source of the extraneous fluorescent materials, a duplicate sampling system was established for seven of the wells at which random detections frequently had been observed. These wells were also selected in all directions from the landfill and represented both Prairie du Chien and Jordan Aquifer wells. In addition to the regular Oronoco Dye Trace Study sample collection and analysis system, these seven residents were provided with a completely separate set of sample vials which were distributed by, returned to, and analyzed using identical procedures by U of M staff with a second TDFF. When a sample in either set yielded more than five to ten ppt on the TDFF, that sample was then analyzed on the PEFS in Rochester. When a sample in either set tested either trace or positive on the PEFS, the corresponding duplicate sample also was analyzed on the PEFS.

Duplicate samples were collected from well 149 between September 30, 1989 and December 10, 1989. Between mid-November 1989 and mid-April 1990 duplicate samples were collected and analyzed from the other six private wells. The duplicate sampling was discontinued after the rate of random detections dropped essentially to zero in February and March 1990.

A total of 854 pairs of samples were collected and analyzed by the two independent collection and analysis teams. Table 2 of Appendix M is a summary of the analyses of those pairs of samples in which a positive or trace PEFS result was obtained. Two PEFS positives and four traces were observed. In no case did the positive or trace appear in the corresponding duplicate sample.

The two positives were in Olmsted County samples. The four traces were evenly split between the Olmsted County and U of M samples. With only two PEFS positives, the odds are one in four that both would be in one sampling system or the other by random chance. Given the even split of the four traces, a conclusion that the random detection phenomenon is confined to the Olmsted County sampling system is not justified.

Two PEFS positives in 1,708 samples corresponds to an occurrence rate of 1 per 854 samples. This rate is not representative, however, because many of the samples were collected after the random detection phenomenon had apparently ceased.

5.1.5.4 Light - Cold Sampling of Well 182

To evaluate the stability of samples under light and cold conditions, duplicate samples of water were collected from well 182 on July 30, 1989. One of these samples was stored at room temperature in ambient light while the second sample was stored in the dark in a refrigerator. During a two week period both samples were reanalyzed six times on the TDFF. The data from these analyses is summarized in Table 3 of Appendix M.

The sample being stored in the light yielded 0.000 ppb (part per billion, 10^{-9} g/g) values the first three times analyzed on the TDFF and then yielded values of 0.010, 0.005, and 0.010 ppb the next three times it was analyzed. The sample being stored in the refrigerator yielded 0.000 ppb values in all six analyses. It is important to note that the smallest division on the dial of the TDFF corresponds to 0.020 ppb under the operating conditions of these analyses. The uncertainty in reading the dial at this level is about 0.005 ppb. On August 15, 1990 both samples were subjected to PEFS scans. The sample which had been stored in the light was a trace while the sample stored in the refrigerator was a negative. This sequence illustrated the difficulty in working near defection limits with the TDFF.

5.1.5.5 Weekly QA/QC Checks on the Efficacy of the Charcoal Filters

The QAPP for the Dye Trace Study required that alternative water supplies be provided for those wells in which dye was detected. Detection of the dye was operatively defined as a single PEFS positive. When a PEFS positive was found, all of the users of that well were offered under-the-sink charcoal filters which remove more than 99.99% of the Rhodamine WT from water which moves through the filters (see Appendix K.2). The residents of homes with charcoal filters collected a sample before and after the filter on a weekly interval. The before-and-after-filter samples from wells 108 and 151, in which continuous pulses of dye were observed, were an ongoing check of the efficacy of the charcoal filters. The before-and-after-filter samples from other residential wells did not test the efficacy of the filters because there was no reason to expect that dye was in the water system when the filtered and unfiltered samples were collected. These pairs, however, provided useful information about the random detection phenomenon.

Table 4 of Appendix M lists all of the before-and-after-filter sample data from wells 151 and 108 and from those pairs of samples from other wells in which a PEFS positive or trace has been observed. After the start of the continuous pulses at each well, all of the unfiltered samples have contained dye on the TDFF while none of the filtered sample have contained dye.

Three PEFS positives and five traces have been observed in the filtered and unfiltered sample pairs from the wells without continuous dye pulses. These data are shown as the last group in Table 4. One of the positives was in an unfiltered sample -- two were in filtered samples. Two of the traces were in filtered samples -- three were in unfiltered samples. The random detections were evenly split between the filtered and unfiltered samples.

5.1.5.6 QA/QC Checks of Sample Vials

The sample vials were purchased from commercial vendors in gross (144) boxes. The sample vials were not washed before use, but one vial from each box was selected at random, filled with lab distilled water, and analyzed as a control. Between April 18, 1989 and April 27, 1990, 392 such control vials were analyzed. One of those vials analyzed on October 20, 1989 proved to contain 20 parts per trillion of fluorescence on the TDFF. That sample was analyzed on the PEFS and tested positive.

If compared to all of the vial blanks, the one random detection in the control vials corresponds to an occurrence rate of about one in 400 samples. If the one random detection is compared to those blank vials analyzed during the time interval when the random detections were observed in the well samples -- roughly June 1, 1989 through the end of December 1989 -- then the occurrence rate is about one in 200. Given only one random detection in the control vials, however, one should be very cautious with these statistics.

5.1.5.7 HPLC Identification of the Dyes

Shortly after the random detections began, the need for an additional level of analytical confirmation/identification of the dye in the continuous pulses and the random detections was identified. The PEFS can distinguish rhodamine dyes from a number of other materials that produce a fluorescence response in the TDFF, but the PEFS can not distinguish Rhodamine WT from Rhodamine B. To date, the only analytical technique found to have the specificity and sensitivity to separate Rhodamine WT from Rhodamine B in our samples is HPLC. Twin City Testing Corporation provides a proprietary HPLC analysis that has proven to have the ability to clearly distinguish Rhodamine WT from Rhodamine B and other similar fluorescent materials, if the concentration of dye in the sample exceeds the detection limits. Given the roughly 25 ml samples that remain after the PEFS scan, the HPLC technique has a variable detection limit around 30 to 60 ppt of Rhodamine WT.

(The Rhodamine WT standards prepared for HPLC analyses are from the batch of dye introduced into the ground on May 10, 1989 and indicate that the Rhodamine B content of the Dye Trace Rhodamine WT is less than 0.1 percent. These standards were prepared from aliquots of the original dye which had been stored for three months. The lack of any detectable

Rhodamine B in the Rhodamine WT standards eliminates any significant possibility that chemical degradation of Rhodamine WT to Rhodamine B is a source of Rhodamine B. This observation is completely consistent with the expert opinion of a chemist specializing in these fluorescent compounds.)

Unfortunately, as is shown in Figure 2 of Appendix M, the bulk of the random detections are less than the detection limit of the HPLC technique. Random detections could be confirmed in only those samples with the highest dye concentration. These samples may not be representative of the bulk of the phenomenon. Table 5 of Appendix M is a summary of the HPLC results obtained to date.

Two of the continuous-pulse monitoring well samples, 304 and 307, have been analyzed by HPLC. Those two samples contained Rhodamine WT and did not contain Rhodamine B. The concentration of dye in the continuous pulse from private well 108 is not yet up to the detection limit of the HPLC technique. Two samples from the continuous pulse in well 151 have been analyzed by HPLC. The first sample, collected on 11/02/89, appeared to be a normal part of the continuous pulse. That sample contained Rhodamine WT and did not contain Rhodamine B. The second sample from 151, collected on 11/05/89, appeared to contain a random detection on top of the continuous pulse. That sample contained both Rhodamine WT and Rhodamine B.

Eight of the random detection samples from private wells contained Rhodamine B and did not contain Rhodamine WT. Nine of the random detection well samples analyzed by HPLC contained neither Rhodamine WT nor Rhodamine B above the method detection limit.

Two samples of the leachate from the Oronoco Landfill waste cells have been subjected to HPLC analyses. The sample from Demolition Cell #1 contained neither Rhodamine WT nor Rhodamine B. The sample of leachate from Mixed Solid Waste Cell #2 contained large concentrations of both Rhodamine WT and Rhodamine B and several other large fluorescent peaks.

The pattern of the HPLC data obtained to date is straight forward. The continuous pulses of dye observed in the monitoring wells and 151 are Rhodamine WT and do not contain Rhodamine B. The random detection samples that are large enough to measure contain Rhodamine B and do not contain Rhodamine WT.

5.1.5.8 Consumer Products Containing Rhodamine WT and/or Rhodamine B

When the random detection phenomenon became apparent, a variety of common red or pink materials were subjected to PEFS analyses. Table 6 of Appendix M summarizes the results. Seed corn, commercial sewer tracing dye, recreational vehicle antifreeze fluid, liquid soldering flux, and Lumicolor purple pens appear to contain rhodamine dyes. The HPLC results demonstrate that the colorant used on seed corn was Rhodamine B. That

information checks with the data supplied by seed corn companies. We do not yet know if the other products which tested positive contain Rhodamine WT, Rhodamine B, both, and/or some other rhodamine dye. The interferences listed at the bottom of Table 6 are indeterminate. The only interference sample tested by HPLC, the sample from Mixed Solid Waste Cell #2, contained both Rhodamine WT and Rhodamine B as well as several other large fluorescent peaks.

5.1.5.9 Air Deposition Measurements

A series of measurements were made in February 1990 to see if any red fluorescent material was contaminating the sample collection and analysis system from air deposition. Five sets of three vials filled with distilled water were prepared. One of these sets was placed in the OCH Laboratory, another in the Dye Trace office in the Waste-to-Energy Facility, and a set was placed in each of three private residences where random detections had been observed. Two of the vials in each set were opened. The third was left closed. The vial were left in place for one week. All three vials from each set were then analyzed through the normal sample analysis protocol. The results are summarized below.

Air Experiment

Sample	Batch #	TDFF result (in ppb)
OCH Lab -- closed	1269	0.000
OCH Lab -- open #1	1269	0.000
OCH Lab -- open #2	1269	0.000
Dye Trace Office -- closed	1269	0.000
Dye Trace Office -- open #1	1269	0.000
Dye Trace Office -- open #2	1269	0.000
Well #182 -- closed	1269	0.000
Well #182 -- open #1	1269	0.000
Well #182 -- open #2	1269	0.000
Well # 154 -- closed	1269	0.000
Well # 154 -- open #1	1269	0.000
Well # 154 -- open #2	1269	0.000
Well # 148 -- closed	1269	0.000
Well # 148 -- open #1	1269	0.000
Well # 148 -- open #2	1269	0.000

No evidence of air transport of fluorescent red material was observed during the period sampled.

5.1.5.10 Surface Wipes Measurements

At the same places as the Air Deposition Measurements were made, a check was made to see if any of the surfaces were contaminated with water-soluble red fluorescent materials. A sterile gauze pad was wet with distilled water and the surface at each sampling location was wiped clean. The contents of the pads were then squeezed into two vials at each site. One vial was left unfiltered and the other vial was filtered through a 0.45 micron non-pyrogenic filter. The vials were then analyzed through the normal sample analysis protocol. The results are shown below.

Surface Wipes Measurements

Sample	Date collected	Batch #	TDFF result (in ppb)	PEFS
OCH Lab -- straight	3/12/90	1329	0.071	-
OCH Lab -- filtered	3/12/90	1329	0.020	i
Dye Trace Office -- straight	3/09/90	1329	0.223	-
Dye Trace Office -- filtered	3/09/90	1329	0.038	i
Well # 182 -- straight	3/11/90	1329	0.203	-
Well # 182 -- filtered	3/11/90	1329	0.020	i
Well # 154 -- straight	3/11/90	1329	0.041	-
Well # 154 -- filtered	3/11/90	1329	0.010	i
Well # 148 -- straight	3/11/90	1329	0.041	-
Well # 148 -- filtered	3/11/90	1329	0.015	i

Although up to 0.223 ppb of fluorescence was observed in the unfiltered samples, the filtered samples yielded fluorescence ranging from 0.010 to 0.038 ppb. All of the filtered samples yielded interference spectra on the scanning fluorescence spectrophotometer. No evidence of significant contamination of surfaces was observed.

5.1.6 Sampling Protocol Change

When the "Random Dye Detections -- Oronoco Dye Trace Study: An Interim Data Summary and Interpretation" Report (Appendix M) was issued in June 1990, one change was introduced to the sample collection protocol. At the public meeting of March 14, 1990 and in subsequent correspondence, the residents were asked to triple rinse their sample vials and caps before collecting their samples.

At the beginning of the study, triple rinsing of vials was discussed. It was not included in the initial sampling protocol because there was some concern that excess improper handling of vials might result in increased potential for sample contamination. However, after the onset of the random detection phenomenon, this protocol was adopted.

As noted in 5.1.2 above, the random detection phenomenon had essentially disappeared by spring 1990 and did not recur in the summer and fall of 1990. It is not known if the sampling protocol change prevented its recurrence or if the unknown cause of the 1989 problems was not present.

5.2 Special Studies

5.2.1 Background Sampling

As is discussed in 3.5 and 3.6 above, background sampling of the monitoring wells, 1XX and 2XX residential wells, the springs, and the stream sites began on or after April 11, 1989. In many, but not all cases, a month of daily background samples was accumulated before the first dye introduction on May 10, 1989. The results of this background sampling are included in the Phase I graphs in Appendices D, E, F and G (also see 5.3, 5.4, 5.5 and 5.6 below).

One note of explanation is necessary, particularly for the Phase I residential well graphs. The operator training and initial set up of the TDFF produced blank vial background readings in the 0.000 to about 0.020 ppb range. The nominal average of these readings was about 0.010 $\pm$ 0.010 ppb. On June 1, 1989, between the analysis of batches 129 and 130, the baseline and other operating parameters of the TDFF were recalibrated to produce readings of 0.000 ppb for blank vials which contained no dye. The TDFF was recalibrated at several subsequent times but was always set to produce 0.000 ppb readings for blank vials. It is, therefore, very important to note that TDFF readings of 0.010 $\pm$ 0.010 ppb in batches numbered <130 are equivalent to readings of 0.000 ppb in batches numbered >130. The initially high values seen in most of the Phase I residential well graphs are the result of the instrument settings.

In order to remove this artificial discontinuity in some of the Phase I graphs, the initial samples for the monitoring wells and several of the residential wells were reanalyzed. The apparently high values in the background samples largely disappeared. Compare the initial values seen in most of the 1XX and 2XX residential well Phase I graphs with those seen in wells 106 and 112, for example. The time, effort and expense required to reanalyze all of the residential well background samples to remove the discontinuity from all of the Phase I graphs was judged to be unnecessary. However, the sample(s) from each sampling point with the highest TDFF value(s) collected during this time period were reanalyzed on the PEFS to confirm the absence of dye.

There was no evidence of any significant background fluorescence in any of the private wells during the background sampling period. Evidence of the random detection phenomenon occurred in only one private well during the background sampling period (Well 217 on 5/19/89). However, it was not identified as a random detection until August 1989 when that sample was reanalyzed on the PEFS.

5.2.2 Rhodamine WT Degradation Study

In July 1989 a special study was initiated to measure the long-term stability of Rhodamine WT in the Dye Trace Study water samples. The goal was to compare the relative stability of Rhodamine WT under three storage conditions: ambient temperature in light, ambient temperature in dark, and refrigerated in the dark. Water was collected from residential well 176, monitoring well 309, and springs 407 and 416. A quantity of the elutant used on the charcoal bugs also was prepared. These five solutions were split; one half was spiked with Rhodamine WT to yield concentrations in the 2 to 5 ppb range, while the un-spiked half served as a control. Sub-samples were then split from the spiked and un-spiked stock solutions. All of the samples were prepared and analyzed in duplicate. The results of these measurements are shown in Appendix O.

Rhodamine WT appeared to be reasonably stable in the residential well water, monitoring well water, and spring water. The duplicate samples of water from residential well 176, monitoring well 309, and spring 407 revealed no significant degradation of the dye over more than a year from July 21, 1989 through December 27, 1990. The data also revealed no significant difference between the light or dark samples or the room temperature or refrigerated samples. The observed fluctuations were probably more related to the long term stability of the filter fluorometer and its standards than to any changes in the samples. These data indicated that any of the water samples obtained to date in the Dye Trace could be reanalyzed if necessary to resolve questions about the original analyses.

Rhodamine WT in the bug elutant was much less stable. Both the ambient temperature light and dark samples degraded with a half-life of about a month, with no obvious difference between the light and dark samples. The refrigerated elutant samples appeared to degrade distinctly slower, with a half-life of about four to five months. Even the refrigerated bug elutant samples degraded much faster than any of the water samples.

Based on these findings, the following protocols were established:

1. The bug elutant should be refrigerated until analyzed and analyzed as rapidly as possible after elution. If unrefrigerated eluted samples were not analyzed within a week, or refrigerated eluted samples within a month, any Rhodamine WT in the sample would have significantly degraded. Storage of the bug elutants for more than a couple of months probably accomplishes nothing, even when refrigerated.

2. Valid data could be obtained from the water samples which had been stored at room temperature since the beginning of the Dye Trace. Any questions about the early samples should be resolved as rapidly as possible, however.

3. The protocol of storing the Mayo positives in refrigerators was not significantly improving the shelf life of the samples. However, if adequate refrigerated storage existed, the protocol could be continued without harm.

5.2.3 Fluorescein Backgrounds

As part of the decision about which dye to use for the second dye input (see section 3.1.2 above), sample vials from selected locations were analyzed on the TDFF for fluorescein. Since fluorescein photo-degrades and because these samples had not been carefully maintained in the dark, the resulting numbers are only lower limits of any fluorescein present. There was no reason, however, to believe that fluorescein was actually present in any of these samples, and the data were actually a measure of the fluorescence in these samples in the green portion of the spectrum.

The sample vials collected as part of the multiple sampling per day from wells # 106, 132, and 185 (see section 5.1.5.2 above) were selected for fluorescein analyses as were vials from springs 410 and 411. The results of these measurements are listed in graphical and tabular form in Appendix N and are briefly summarized below.

Mean Fluorescein Backgrounds in Selected Samples

Sample	date collected	mean fluorescence (in ppb)
Well # 106	5/28/89 - 12/04/89	0.016 ± 0.010
Well # 132	6/01/89 - 12/03/89	0.003 ± 0.005
Well # 185	5/29/89 - 12/09/89	0.025 ± 0.021
Spring 410	5/25/89 - 12/05/89	0.230 ± 0.420
Spring 411	5/15/89 - 12.08/89	0.230 ± 0.210

The background fluorescence in the green portion of the spectrum is, in general, higher and more variable than the background fluorescence in the red portion of the spectrum. The spring samples gave higher and more variable backgrounds than did the well samples.

5.2.4 Analysis of Rochester Municipal Wells for Rhodamine WT

In response to a request by the participants in the Dye Trace Study, samples of the Rochester Municipal wells were collected and analyzed through the normal sample analysis protocol to see if they contained any Rhodamine WT from the Dye Trace. The results of that survey are presented below.

Rochester Municipal Wells Rhodamine WT Survey

Well ID	MGS #	Date collected	Time	Batch #	TDFF result (in ppb)	PEFS
11	220666	6/11/90		1630	0.002	-
12	220833	6/11/90		1630	0.000	-
13	222525	6/11/90	1218	1630	0.000	-
15	225528	6/11/90		1630	0.000	-
16	220827	6/11/90		1630	0.000	-
17	220822	6/12/90	932	1630	0.000	-
18	222527	6/11/90		1630	0.000	-
19	220681	6/11/90		1630	0.000	-
20	220662	6/11/90		1630	0.000	-
21	220625	6/12/90	1015	1630	0.000	-
22	220818	6/11/90	850	1630	0.000	-
23	220660	6/11/90		1630	0.000	-
24	220819	6/12/90	915	1630	0.000	-
25	220675	6/11/90		1630	0.000	-
27	224212	6/11/90	1205	1630	0.000	-
28	180567	6/11/90		1630	0.000	-
29	161425	6/11/90		1630	0.002	-
320	147661	6/12/90	1057	1630	0.000	-
330	220627	6/12/90		1630	0.000	-
SLP3		6/12/90	835	1630	0.020	i
SLP4		6/12/90	835	1630	0.005	-

No evidence of Rhodamine WT was detected in these samples collected on June 11/12, 1990.

5.2.5 Dye Stabilization Tests in Monitoring Wells

In April 1989, Donohue staff performed stabilization tests on the landfill monitoring wells to determine the necessary purge times for the individual wells (see Appendix D.2). These stabilization tests were based on the normal temperature, conductivity and pH stabilization criteria. Once dye began to emerge from several of the monitoring wells, it was possible to check to see if the stabilization times established on the basis of field parameters were valid for the Dye Trace.

On August 31, 1989, dye stabilization tests were made on monitoring wells 303, 304 and 307. The pump in each well was activated and the flow was sampled at 15 second to one minute intervals. The samples were then analyzed using the TDFF protocol at the U of M. The results of these individual analyses are also in Appendix D.2.

Figure 18 is a composite figure summarizing the results of the stabilization tests on all three wells. The initial samples at both 303 and 307 were higher than the stable value. The concentration in each well then dropped and then came back up to the stable value. Well 303 stabilized in about one minute and 45 seconds (the established purge time was three minutes). Well 307 stabilized in about six minutes (the established purge time was ten minutes).

Well 304 was one of the four low-yielding monitoring wells which normally pumped dry during the purging operation. In these situations the established protocol was to wait varying numbers of minutes for the well to refill with water and then to continue the purge. For Well 304 the protocol was to pump the well dry, wait five minutes and then restart the pump and collect a sample (see Appendix D.2). By sampling in 10 to 30 second intervals it was possible to obtain five or six samples before Well 304 pumped dry in each case. Five cycles were sampled in sequence, with five minute waits between each cycle. The dye concentration in all of the samples was essentially the same.

In summary, repetitive sampling of three of the monitoring wells indicated that the purge times established using field parameters were adequate to assure stable dye concentration readings.

5.3 Monitoring Wells

The Phase I and Phase II graphs for the monitoring wells are in Appendix D. The summary results for the monitoring wells are shown in Figures 19 through 29. Note that the scale of the vertical dye concentration axis varies from Figure to Figure. The vertical axis of Figure 21 is a logarithmic scale. The rest of the vertical scales and all of the horizontal scales are linear. These graphs of dye concentration versus time will be referred to as breakthrough curves.

Rhodamine WT dye was detected in monitoring wells 303, 305, 304, 307, 309 and 302. The shapes of the breakthrough curves were very different between the monitoring wells. The pattern of dye movement revealed by the breakthrough curves was complex both in space and in time.

Dye reached the closest shallow monitoring well, 303, first (see Figure 21). The average of these background samples was 0.012 $\pm$ 0.008 ppb. Between April 11 and the morning of May 10, 1989, 30 daily background samples were collected from monitoring well 303. The Rhodamine WT dye was washed into the bedrock at about 12:15 p.m. on May 10. The next sample was collected from monitoring well 303 at 8:51

the following morning, May 11. That sample contained 8.4 ppb of Rhodamine WT. Only twenty and a half hours after it was introduced, the concentration of dye was already over 700 times the background level. Monitoring well 303 is about 670 feet southeast of the Phase I dye introduction point.

During 1989, the dye concentration in monitoring well 303 peaked at 18 ppb on May 12 and then decreased steadily to 0.32 ppb on May 16. On May 17 the dye concentration peaked a second time at 2.1 ppb and then began a long slow decline that lasted through June, July and most of August. On August 30, the dye concentration in monitoring well 303 began to increase to a third peak of 4.3 ppb on September 4. The dye concentration then declined steadily through the fall of 1989 and the winter of 1990. On March 12, 1990, the dye concentration began to rise. It reached a fourth peak of 2.5 ppb on March 16 and subsequently declined. A complex fifth peak was seen on April 25 through May 2, 1990, and a sixth peak occurred on July 9, 1990. The dye concentration has been dropping since the sixth peak. As of late November 1990, eighteen months after the dye was introduced, the dye concentration in monitoring well 303 was still more than ten times the April/May 1989 background level.

Dye reached the second closest shallow monitoring well, 305, four days after it was introduced into the quarry (see Figure 23). Monitoring well 305 is about 1350 feet northeast of the quarry or about twice as far as monitoring well 303. Starting on May 14, the dye concentration in monitoring well 305 rose in three days to values between about 0.4 and 0.8 ppb. The dye concentration remained in this range until late June 1989 when it abruptly dropped to values <0.1 ppb for the first three weeks in July. The values again rose to concentrations of 0.2 to 0.3 ppb in mid-August, dropped to values <0.1 ppb in eary September, and then rose again to values in the 0.5 to 0.8 ppb range in a broad peak which lasted from late September through the end of November 1989. The concentration decreased through December 1989 and January 1990. By February 16, 1990, monitoring well 305's dye concentration was down to a few times background levels. The dye concentration then rose in March and April, declined back almost to background in early May 1990 and then began again to rise through the summer and fall of 1990. As of late November 1990, monitoring well 305 was producing dye concentrations around 0.6 ppb, nearly as high as measurements in the first peak during May and June of 1989.

The breakthrough curves for the shallow monitoring wells 303 and 305 were distinctly different, both qualitatively and quantitatively. No dye has been detected in the other three shallow monitoring wells, 306, 308 and 310.

Two deep monitoring wells, 304 and 307, simultaneously began to record dye one week after it was introduced into the quarry. Monitoring well 304 is the closest deep monitoring well to the quarry and is about

650 feet southeast of the dye input point, adjacent to monitoring well 303. Monitoring well 307 is about 2,850 feet east of the dye input point (over four times further away) and is on the opposite side of the landfill from well 304. On May 17 the dye concentration in both monitoring wells began to rise. The concentration reached a peak of 0.96 ppb in well 307 on June 30 and a peak of 0.83 ppb in well 304 on July 3 (which was the next sampling event). Dye concentrations declined through early September 1989 in both wells, rose to second peaks in early October 1989, decreased through the fall and winter of 1990, rose again through spring 1990 to broad peaks in June and July, and then began a slow decline. As of late November 1990, the dye concentrations in monitoring wells 304 and 307 were decreasing but were still about 50 times their April/May 1989 background levels. The breakthrough curves for monitoring wells 304 and 307 were very similar (compare Figures 22 and 25).

A third deep monitoring well, 309, began to record dye on June 23, 1989, 44 days after dye was introduced into the quarry (see Figure 27). Monitoring well 309 is located 2,830 feet almost due east of the Phase I dye introduction point. The breakthrough curve for monitoring well 309 does not resemble that for the two shallow monitoring wells 303 and 305 or the deep monitoring wells 304 and 307. The dye concentration in 309 rose slowly throughout the summer and fall of 1989. By November and December 1989 the dye concentration in 309 had reached values of 0.08 to 0.10 ppb and has remained in that range through November 1990.

On March 16, 1990, deep monitoring well 302 recorded its first sample with Rhodamine WT, over 10 months after the dye was introduced (see Figure 20). Monitoring well 302 is located 2,111 feet east-southeast of the Phase I dye introduction point. The March 16, 1990 monitoring well sampling event happened to be the day duplicate samples were collected from well 302 as part of the ongoing QA/QC plan. Both samples contained 0.039 ppb. The concentrations rose to 0.059 ppb and then dropped back to background levels by the end of March 1990. On July 9, 1990, a second pulse of dye began to emerge at 302. That second pulse peaked at 0.89 ppb on July 23, 1990. The second pulse also quickly decreased and by September 1990, dye concentrations in monitoring well 302 were back down around 0.010 ppb. The breakthrough curve for 302 looks nothing like the breakthrough curves for the other five positive monitoring wells.

Dye has not been detected in monitoring wells 301, 306, 308, 310, or 311. The summary data from these monitoring wells is shown in Figures 19, 24, 26, 28, and 29.

Figure 30 is a histogram of the rainfall data from the landfill at the same horizontal scale as Figures 19 through 29. By overlaying Figure 30 onto Figures 19 through 29 the response of the monitoring wells to precipitation/infiltration events can be correlated. The dye concentra-

tion in five of the six positive monitoring wells appeared to increase in response to precipitation/infiltration events and then to decrease in dry periods. The dye concentration in the sixth, 309, did not appear to respond to precipitation/infiltration events.

Table 2 below summarizes the responses of the monitoring wells to precipitation/infiltration events. The precipitation/runoff events are arranged roughly in decreasing order of size. The most significant precipitation/infiltration event recorded by the Dye Trace was the 1990 spring thaw.

The winter of 1989/1990 was unusually dry and there was a very small snow pack. The spring thaw began on April 9 when the average daily temperature (as well as the overnight low) was above freezing. The peak of the thaw was on April 12 when the high for the day was 67°F at the Rochester Airport and the average temperature was 57°F. On April 14 and 15, 1.97 inches of warm precipitation fell at the landfill. This combination of warm rain on top of melting snow produced a response in five of the monitor wells, 302, 303, 304, 305, and 307. This is not unusual. The spring thaw is often the largest and most significant annual recharge event for the ground waters of southeastern Minnesota.

The second most significant event, which produced dye increases in all of the positive wells except 302, was the 2.50-inch rainfall on August 31, 1989. This was the second largest rainfall that occurred during the Dye Trace. Even large August rainfall events often produced little or no recharge due to evaporation/transpiration losses. (Note that the fourth largest rainfall, the 2.16 inch event on August 19, 1990, produced no responses in the monitoring wells.) However, the August 31, 1989 event was preceded by 2.12 inches of rain on August 27 and 28, 1989, which apparently served to saturate the ground and enhance the recharge from the August 31 storm.

The largest single rainfall during the Dye Trace, 3.58 inches on July 7, 1990, produced responses in three monitoring wells, in shallow monitoring wells 303 and 305 and in monitoring well 302. The third largest rainfall, 2.30 inches on April 24, 1990, also produced responses in three monitoring wells, 303, 304, and 305.

The May 10, 1990 rainfall, 1.58 inches, produced responses in 303 and 305. The August 27-28, 1990 storm produced a response in monitoring well 303 in addition to "priming" the ground for the August 31, 1990 storm. A 1.75-inch rainfall on June 26, 1989 and a 1.23-inch rainfall on July 18, 1989 produced responses in monitoring well 305.

The most cryptic rise in dye concentration is the small, but distinct rise on February 21, 1990 in well 305. There is no obvious precipitation event that correlates with this rise. The Climatological Data from the Rochester Airport indicates that the average temperatures on February 21 and for several days preceding the 21st were below freezing. This rise in 305 does not look like a thaw event.

The monitoring wells show varying time lags between the precipitation/infiltration event and the response in the well. Monitoring well 303, the shallow well closest to the Phase I dye input point, consistently yielded the shortest response times. In most cases the dye increased in the first sample collected after the rainfall. The response time in well 303 to the dye from the Phase I input point appears to be one day or less.

Monitoring well 304 responded in seven to eleven days. Monitoring well 305 responded in one to three weeks. Monitoring well 307 responded in about two weeks. Two rainfall events produced one to two day responses in monitoring well 302. However, other rainfall events which produced responses in other monitoring wells had no effect on monitoring well 302.

The continuous dye pulses seen in the monitoring wells do not resemble the random detection phenomenon. The association in time and space with the first dye input was so strong that it was generally assumed that the TDFF data were adequate to confirm the presence of Rhodamine WT. Every monitoring well positive sample was not, therefore, subject to PEFS scans. In general, when monitoring well samples which tested positive on the TDFF were analyzed on the PEFS, those samples scanned positive, as expected. The first several positive samples from each monitoring well were scanned but samples were only scanned occasionally thereafter.

Only a few samples from the monitoring wells were submitted for HPLC confirmation. Those samples were largely viewed as QA/QC "knowns" to check the HPLC results (see Appendix I). HPLC results were obtained for four TDFF positive samples from monitoring wells 302 (two samples), 304, and 307. The HPLC data indicated the presence of Rhodamine WT and the absence of Rhodamine B in all four samples.

The second dye pulse in monitoring well 302 was much larger than the first pulse and it emerged after the March 30, 1990, Phase II dye introduction. It is possible that this second, large pulse of dye in 302 was due to the second dye introduction. However, several lines of evidence are consistent with the hypothesis that this second pulse was from the Phase I introduction. The second pulse was similar in shape and duration to the first pulse. The second pulse correlated with the large July 7, 1990 precipitation/infiltration event which also produced responses in monitoring wells 303 and 305. The responses in the latter two wells appears to be from Phase I, not from Phase II, dye. There was no hint of

a response to Phase II dye in monitoring wells 310 and 311, which are between well 302 and the Phase II dye input point. In the absence of any other indication of Phase II dye, the simplest assumption is that both pulses seen in monitoring well 302 were due to Phase I dye. A fundamental ambiguity remains, however, because Rhodamine WT was used in both dye inputs.

5.4 Residential Wells

The Phase I and Phase II graphs for the residential wells are in Appendix G in numerical order by Dye Trace number.

Continuous pulses of Rhodamine WT dye were detected in only two residential wells, first in well 151 and then in well 108. Figure 31 is a summary of the TDFF data from residential well 151. Background sampling of well 151 began on April 29, 1989. Eight of the daily samples collected through May 22, 1989, yielded non-zero TDFF readings. Values >0.005 ppb were scanned and yielded negative or interference PEFS results. The TDFF values were then 0.000 ppb until July 3, 1989, when a random detection of 0.020 ppb (which was a PEFS position scan) occurred at 151. The TDFF values returned to 0.000 ppb for three weeks. On July 26, 1989, the TDFF values began to rise. The samples on July 26 and 27 were PEFS traces and then subsequent samples were PEFS positives. (After about a month of positive PEFS scans from the 151 samples, only periodic samples were subjected to PEFS analysis.) The dye concentration slowly increased during fall 1989 and winter and spring 1990. The dye concentration leveled off at about 0.80 ppb during late spring and summer 1990. In August 1990, the values decreased steadily to about 0.040 ppb and then leveled off, where they remained as of November, 1990.

On top of this relatively smooth dye pulse, three discernible events occurred. Two random detections occurred on September 3 and November 5, 1989. On November 17, 1989, the well owner shock chlorinated his well. A decrease in dye concentration immediately followed this event and lasted through November 22, 1989.

Three samples from well 151 and a field blank from 151 have been subjected to HPLC analyses (see Appendix I). Samples collected on November 2, 1989 and May 3, 1990 contained Rhodamine WT and no Rhodamine B. The November 5, 1989 sample, which was one of the two random detections on top of the smooth pulse samples, yielded both Rhodamine B and Rhodamine WT. The field blank collected at the same time as the May 3, 1990 samples contained neither Rhodamine WT nor Rhodamine B.

Figure 32 is a summary of the TDFF data from residential well 108. Background sampling of 108 began on April 11, 1989. During the background sampling, six samples were analyzed that yielded TDFF results of 0.010 to 0.018 ppb. All six of these samples yielded interference or negative PEFS scans. Two random detections occurred in 108 in the middle of the summer

of 1989, a 0.008 ppb PEFS positive on July 31 and a 0.040 ppb PEFS positive on August 28. In September and October, 1989, the samples from 108 started irregularly showing tiny amounts of TDFF fluorescence but all of the values above 0.005 ppb tested negative on the PEFS. Between November 5 and November 10 samples yielding TDFF values of 0.007 to 0.009 ppb and PEFS traces were collected. The residents of 108 then moved out and no samples were collected for three weeks.

New owners resumed sampling of 108 on December 2, 1989. The December 3 sample yielded a TDFF value of 0.028 ppb and a PEFS positive. The samples for the rest of December 1989 and January 1990 were in the 0.010 to 0.020 range on the TDFF and yielded trace or positive PEFS scans. The 108 samples have remained in the 0.020 $\pm$ 0.005 range through the rest of the Dye Trace.

Replicate samples of 108, collected on May 3, 1990, have been analyzed by HPLC (see Table 4 in Appendix I). The May 3, 1990 sample yielded a TDFF value of 0.020 ppb and the HPLC analyses indicated Rhodamine WT in the 10-50 ppt range with no detectable Rhodamine B, <10 ppt.

Residential wells 151 and 108 are old Prairie du Chien wells. Documented well logs or construction details are non-existent for both wells. Information supplied by the owner indicates that Well 151 was drilled in 1965, is 165 feet deep, and is cased. The length of casing is unknown and it is not clear that the well was grouted. The elevation of the top of the well is about 1045 feet which places the bottom of the well at about the 880 foot level. Well 151 is 1.21 miles (6,369 feet) northeast of the Phase I dye introduction point.

Information supplied by the former owner indicates that residential well 108 is 189 feet deep and cased. The date the well was drilled, the length of the casing, or if it is grouted are unknown. The elevation of the top of the well is about 1060 feet which places the bottom of the well at about the 870 foot level. Residential well 108 is 0.40 miles (2,089 feet) north of well 151 and is 1.50 miles (7,919 feet) northeast of the Phase I dye introduction point.

Wells 151 and 108 clearly document the movement of Phase I dye in the ground water of the Prairie du Chien Aquifer north-northeast from the landfill. Except for the monitoring wells, no other clear indication of Phase I dye has been detected to date.

Phase II dye has not been confirmed in any residential wells. Based on the Phase I results, the Phase II dye is expected to show up in the Prairie du Chien wells. The distances and directions of the Prairie du Chien wells closest to the Phase II dye introduction point are:

Well #	Distance feet (miles)	Direction	Phase II Dye
310/311	1,478 (0.28)	northwest	no
302	2,221 (0.42)	northwest	maybe
308/309	2,347 (0.44)	north-northwest	no
306/307	2,737 (0.52)	north-northwest	no
135	3,280 (0.62)	north	?
151	6,713 (1.27)	north	no
230	4,036 (0.76)	north-northeast	?
179	1,710 (0.32)	northeast	?
178	4,151 (0.79)	east-southeast	no
216	3,025 (0.57)	southeast	no
111	1,626 (0.31)	south-southeast	no
119	2,214 (0.42)	southwest	no

The only hints of Phase II dye are the second pulse in monitoring well 302 (discussed above) and the results from wells 179,135, and 230.

Residential well 179 is one of the closest wells to the Phase II dye introduction point and, according to the water table map, is downgradient. Well 179 is a Prairie du Chien well reported by its owner to be 200 feet deep. Well 179 is perhaps the most obvious place for Phase II dye to be detected.

Figure 33 summarizes the data from well 179. Background sampling at well 179 began on April 12, 1989. The initial data in Figure 33 illustrate the baseline shift described in section 5.2.1 above. The samples collected between April 12 and May 19 were analyzed in batch numbers below 129 and yielded values in the 0.005 to 0.020 ppb range. The three highest values were later scanned on the PEFS and yielded negative scans.

The well 179 samples collected between May 20 and October 13, 1989 had TDFF values $\leq$ 0.003 ppb and most were 0.000 ppb, except for three random detections. Random detections were observed in July, August and September 1989. All three samples tested positive on the PEFS but the individual samples were too dilute, 0.019 to 0.020 ppb, for HPLC confirmation. The residents of the house served by well 179 closed the house for the winter and left Minnesota in mid-October 1989.

The owners of well 179 returned to Minnesota in the spring of 1990 and began resampling the well on April 18, 1990. After a month of 0.000 ppb readings, some sort of "event" occurred in well 179 in late May 1990. Three successive samples yielded TDFF values of 0.020 ppb followed by a four day decline back down to 0.000 readings. The five highest TDFF readings in this May 1990 event all yielded interference scans when subjected to PEFS analysis. These samples were not concentrated enough for HPLC analysis.

The June 1990 samples from well 179 yielded only 0.000 ppb TDFF values. On July 7, 1990, the TDFF readings abruptly jumped to 0.030 ppb. July 7, 1990 was the date of the largest precipitation event observed during the Dye Trace (see Table 2 in section 5.3 above.) The TDFF values climbed to 0.038 ppb, held at 0.018 ppb for about two weeks and then dropped to around 0.010 ppb. The TDFF values continue fluctuating around 0.010 ppb to the present.

The initial TDFF values <0.030 ppb all yielded interference PEFS scans. The later TDFF values around 0.018 ppb all yielded trace PEFS scans as have many of the current TDFF values around 0.010 ppb. None of the well 179 samples through the end of Phase II have yielded a positive PEFS scan.

The four samples which yielded the highest TDFF readings, July 8 through 11, 1990, were combined and submitted for HPLC confirmation. The results of that analysis are shown in Table 5 of Appendix I. The results are ambiguous. The sample contained a trace of Rhodamine WT and no detectable Rhodamine B. Unfortunately, this fifth set of HPLC analyses had higher than average Rhodamine WT blanks and the meaning of this result is not clear. These well 179 samples may or may not have contained Rhodamine WT.

Private well 135 is about 0.62 miles north, down the surface valley from the Phase II dye introduction point. According to its owner the well is 135 feet deep and is a Prairie du Chien well. Well 135 is used primarily to provide stock water and is not operated in the winter months.

Figure 34 summarizes the data from well 135. Sampling of well 135 began on April 22, 1989. Well 135 recorded five random detections between June 12 and August 5, 1989. The fourth of these random detections, on July 20, 1989, with a TDFF value of 0.165 ppb, was one of the most concentrated random detections observed in the Dye Trace. The July 20, 1989 sample scanned positive on the PEFS. This sample was submitted for HPLC confirmation and those results are listed in Table 2 of Appendix I. The July 20, 1989, sample contained no detectable Rhodamine WT, <0.040 ppb, but did contain a trace of Rhodamine B, 0.040 to 0.060 ppb. On October 28, 1989, the owner of 135 stopped sampling the well for the winter.

The first 1990 sample from well 135 was obtained on April 25, 1990, and regular sampling began on May 18, 1990. Through May, June and July, 1990, the TDFF values from well 135 were 0.000 ppb. The August 9, 1990 sample yielded a TDFF value of 0.009 ppb which gave a negative PEFS scan. The next two samples, August 13 and 16, yielded TDFF values of 0.015 ppb and trace PEFS scans. The rest of the Phase II samples from well 135 yielded TDFF values between 0.001 and 0.010 ppb. Those samples which were subjected to PEFS analysis were all negative scans.

The August 13 and 16 samples were not concentrated enough to allow HPLC analysis. The 0.015 ppb TDFF values are too low to allow any definitive judgements to be made.

Residential well 230 is an old Prairie du Chien well about three quarters of a mile northeast of the Phase II dye introduction in the Reiter Sinkhole. Well 230 was not in routine use and sampling of it did not start until July 4, 1990. Figure 35 summarizes the available data from well 230. The initial samples gave TDFF values of 0.000· ppb but the July 7 sample gave a TDFF value of 0.010 ppb which gave a negative PEFS scan. The July 8 sample gave a TDFF value of 0.022 ppb and yielded a positive PEFS scan. The next three samples, July 9, 10 and 11, yielded TDFF values of 0.079 ppb and trace PEFS scans. The samples then dropped abruptly back to TDFF values of 0.000 ppb.

The July 8 through 11 samples were combined and submitted for HPLC confirmation. The results of this analysis are listed in Table 5 of Appendix I. The well 230 composite sample contained a trace amount of Rhodamine WT and no detectable Rhodamine B. As noted in the discussion of well 170 above, the fifth group of HPLC analyses had a higher than normal blank for Rhodamine WT, so the trace level of Rhodamine WT in the composite well 230 sample was ambiguous.

5.5 Springs

The recent literature on monitoring in karst terrains has uniformly emphasized the importance of local springs in monitoring scheme (Quinlan and Ewers, 1984, 1985; Quinlan and Alexander, 1987; Quinlan, Ewers and Fields, 1988; Field, 1989; Quinlan, 1989.) Section 3.5.1 outlines the efforts to locate the local springs, the sampling protocols adopted, and the evolution of the spring sampling program throughout the Dye Trace. Both direct water samples and charcoal bugs were used to sample the springs.

Based on the available potentiometric information, the spring complex (416, 416.5, 423 and 423.5) northwest of the landfill was initially thought to be the most likely place for Phase I dye to emerge. As the pattern of continuous dye detections in the monitoring wells and the two residential wells became evident, springs 412 and 411 (and 411.5) northeast of the landfill became the more reasonable places for dye to emerge. Springs 412 and 411 remain the more obvious candidates for the dye to ultimately emerge.

5.5.1 Direct Water Samples

The Phase I graph showing the results from the direct water samples from spring 411 is shown as Figure 36. The Phase I and II graphs for the rest of the sampled springs are in Appendix E.1. No continuous pulses of Rhodamine WT dye were observed in any of the springs.

Most of the springs displayed an ambient level of fluorescence in the 0.010 to 0.050 ppb range. Almost all of the springs recorded numerous spikes of fluorescence that reached the 0.200 to 0.300 ppb range. These spikes yielded interference or negative PEFS scans and therefore were not due to the presence of Rhodamine WT. Nor were they random detections because they were often several samples long and yielded no positive PEFS scans.

Two exceptions to the general pattern of interference spikes in the springs occurred in spring 411. The June 26 and July 16, 1989 samples from 411 yielded positive PEFS scans. In both cases, the positives were only one sample long, which fits the random detection pattern seen in the well samples. These two PEFS positives were scattered among even larger interference spikes. Both samples were too low in concentration for effective HPLC confirmation. These two samples appear to be the only manifestation of the random detection phenomenon in the springs. The simplest hypothesis is again that these two isolated samples have nothing to do with the Dye Trace.

5.5.2 Bugs

The Phase I and II graphs showing the results of the spring bugs are in Appendix E.2. No evidence of Rhodamine WT was observed in the spring bug samples.

The background or ambient TDFF fluorescence readings in the elutant from the spring bugs was very high and extremely variable compared to the analyses of the direct water samples. The TDFF fluorescence levels observed in the bugs ranged over a factor of 500, from <0.010 ppb to > 5 ppb. The samples that were subjected to PEFS analysis yielded interference, or (occasionally) negative scans. No pattern is readily apparent in these highly variable data. In this dye trace, the low levels of dye present in the aquifer rendered this technique useless.

5.6 Streams

Section 3.5.2 explains the rational for the seven stream sampling stations and their location is shown in Figure 10. Stations 401 through 404 were sited down the length of the Middle Fork of the Zumbro River. Stations 407 through 405 were sited down the length of the South Fork of the Zumbro River.

5.6.1 Direct Water Samples

Graphs of the results obtained from the direct water samples from the stream stations are shown in Appendix F.1. No Rhodamine WT dye was detected in the stream stations.

The background fluorescence in the stream station water samples, while higher than the large springs and well samples, was reasonably constant. The mean and standard deviation of the background fluorescence from the stream station water samples is:

Middle Fork Zumbro River		South Fork Zumbro River	
Station	bkg. fluor.	Station	bkg. fluor.
401	0.056 ± 0.019	407	0.038 ± 0.012
402	0.055 ± 0.019	406	0.037 ± 0.013
403	0.054 ± 0.017	405	0.034 ± 0.010
404	0.054 ± 0.021		

("bkg. fluor." is in ppb.)

The background fluorescent material seems to be more abundant in the Middle Fork than in the South Fork.

Those few TDFF results that were checked with PEFS scans were all interferences with no evidence of a peak at the rhodamine position. None of the stream samples were analyzed by HPLC.

5.6.2 Bugs

Graphs of the results obtained from the bug samples from the stream stations are shown in Appendix F.2. No Rhodamine WT dye was detected in the bugs from the stream stations.

The background fluorescence in the stream station bugs was very high and variable. The background fluorescence in the bugs was about 100 times the background fluorescence in the direct water samples. Presumably this was due to the adsorptive concentration, by the charcoal, of the fluorescent materials (probably a range of organic chemicals) from the streams.

The most striking pattern evident in the stream bug data was an abrupt drop in the TDFF readings in the summer of 1989. All of the stream bugs initially gave TDFF readings in the 1.5 to 5 ppb range. Each of the stream bug stations then shifted abruptly to values varying between about 0.2 and 2 ppb. This transition occurred at different times in the different bugs. Whatever caused this shift does not appear to be related to any event relevant to the Dye Trace.

Those bug samples that were subjected to PEFS analysis all yielded interference scans with no evidence of rhodamine dyes. None of the bug samples were subjected to HPLC analyses.

5.7 QA/QC Summary

5.7.1 Calibration Standards

Calibration standards were used to calibrate the TDFF and PEFS instruments each time a batch of samples was analyzed (Donohue, 1990b). The necessary calibration standards were prepared in the Hydrogeochemistry Laboratory at the University of Minnesota. Sets of standards were prepared with concentrations of Rhodamine WT spanning the range of concentrations

encountered in this Study. During each dye introduction, samples of the concentrated dye were collected in amber glass bottles and stored. The standards were prepared using serial gravimetric dilution starting with the dye as received from Crompton & Knowles. The dye, as received, was assumed to be a 20 weight per cent solution because, to our knowledge, no primary standard Rhodamine WT material was commercially available.

The Rhodamine WT solutions were gravimetrically diluted with a 1% solution of analytical grade ammonium hydroxide in deionized water. The deionized water was boiled for 15 minutes, to kill any bacteria in the water, immediately before mixing with the ammonium hydroxide.

The calibration standards for the TDFF were placed in eight-dram glass vials, marked and sealed to prevent evaporation losses or contamination from the water baths. Typically, four standards covering a range in concentrations were analyzed before and after each batch of 40 samples. These eight measurements were used to calculate eight correction factors which, in turn, were averaged to calculate a mean correction factor for each batch (Donohue, 1989c). Individual sets of these calibration standards could be used many times due to the non-destructive nature of TDFF analyses.

A set of calibration standards would typically yield stable correction factors for a couple of months and then the standards would begin to degrade. When the ongoing QA/QC checks indicated that the calibration standards were beginning to degrade, new groups of standards were prepared from the original concentrated dye. The calibration standards made after April 1990 were prepared from dye from the second dye introduction. Calibration standards prepared before April 1990 used dye from the first dye introduction. No significant difference was evident between the sets prepared from different dye batches.

Tables summarizing mean correction factor and standard deviation data are presented in Appendix H.1.

Two calibration standards were prepared for the PEFS. These standards were also prepared by serial gravimetric dilutions of the as-received dye using 1% ammonium hydroxide solutions in boiled deionized water. The PEFS analyses were destructive in that each analysis required the sample to be placed in a quartz cuvette. The cuvettes were cleaned after each analysis and the sample discarded. Each analysis consumed about five milliliters of sample. Therefore, the two PEFS standard solutions were prepared in quantities of about one liter and stored in amber glass bottles. No significant degradation of these standards has yet been detected.

5.7.2 Duplicate Samples

5.7.2.1 Laboratory Duplicates

Beginning with the Phase I introduction of dye, the first sample analyzed in each batch of forty samples was analyzed again at the end of the analysis to determine the ability of the analyst to generate reproduceable results. A comparison of the results was made through an RPD calculation (Donohue, 1990b, QAPP Section 4.3.1). The allowable RPDs were 20% for the monitoring wells, 10% for the residential wells, and 30% for the spring and stream samples.

This information is presented in Appendix H.2. This table identifies the number of the analysis batch, the date of analysis, the TDFF value of the first sample analyzed (DUP1), that sample's reanalyzed value (DUP2), the calculated RPD result and the absolute numerical difference between the two analyses. Batches without sample duplicate analysis have no data represented in the four right hand columns.

The absolute difference calculation was added to provide better guidelines for evaluating analysis quality when samples had TDFF values at or below 0.015 ppb. Since a small difference between the duplicate analyses at lower concentrations would result in a high RPD, the RPD calculation was not a useful QA/QC limit for results below 0.015 ppb.

Of the nearly 1800 batches analyzed, only 18 had duplicates with RPDs exceeding 10%. Of those 18 exceedences, half were for samples with equal to or less than 0.015 ppb. Of the remaining nine,2 samples were from springs and the RPD met the 30% RPD guideline, while one monitoring well sample met the 20% guideline. The remaining six outliers (batches 118, 119, 243, 922, 1013 and 1493) were not judged significantly out-of-line to warrant reanalysis of the batch. No reanalysis of sample batches occurred as a result of laboratory duplicate data.

5.7.2.2 Positive Duplicates

When positive dye detections occurred, two positive samples per week were randomly selected and reanalyzed on the filter fluorometer to evaluate the accuracy of analysis (Donohue, 1990b, QAPP section 4.3.1).

These results are presented in tables in Appendix H.3. Of the 151 positive samples reanalyzed, 21 sample RPDs did not fall within the limits described in Section 5.7.2.1, above. No reanalysis of the original samples was performed.

Early in the study, positive duplicates were analyzed for samples that were later determined to be random detections. When the random detection phenomenon was understood, the practice of reanalyzing random detection positive dye samples was ended. After that point, only samples identified as positives by the PEFS analysis were randomly selected for positive duplicate analysis.

5.7.2.3 Monitoring Well Duplicates

Each week, two monitoring wells were randomly selected for duplicate sample collection. The frequency of duplicate sample collection was the same as regular sample collection.

The tables presenting these results are found in Appendix H.4. Eight of over 700 duplicate monitoring well analyses resulted in RPD values in excess of the 20% limit. They were MW303 (5/30/89, 6/3/89), MW304 (6/9/89, 8/21/89), MW305 (5/23/89, 5/24/89), MW307 (7/17/89) and MW309 (8/2/89). Those samples were not rerun.

5.7.2.4 Spring and Stream Duplicates

Each week, one per ten spring or stream sites was randomly chosen for duplicate collection. Duplicate bug and water samples were collected for each chosen site according to the same schedule as regular sample collection.

Results are presented in Appendix H.5.a and H.5.b. No attempt was made to compare the RPD values for spring and stream direct water and bug samples due to the highly variable levels of background fluorescence in the springs, streams and charcoal packets.

5.7.3 Laboratory Blanks

One blank made from laboratory distilled water was analyzed at the beginning and end of each batch of forty samples to assure the fluorometer was zeroing properly. All blanks had zero values.

5.7.4 Control Standards

One control standard, of known concentration, per eighty field samples was selected for filter fluorometer analysis to assure sample accuracy. (Donohue, 1989b). Control standard sets of individual samples were replaced when signs of degradation were seen. Over the course of the study, three sets of forty control standards were used. The table below lists the duration of use for each set.

Set	Date Started	Date Ended
A	5/11/89	10/1/89
B	10/2/89	6/21/90
C	6/22/90	present

Percent recovery values for control standards can be seen in Appendix H.6.

The use of control standards proved to be the prefereable tool for evaluating an analyst's performance. In general, when the percent recovery of control standards was not within the 90 to 100 percent range, the batch was reanalyzed. This happened in 17 cases (batches: 58, 62, 70, 110, 113, 169, 189, 229, 263, 265, 277, 306, 330, 394, 962, 1477 and 1542).

If, however, the percent recovery was within five percent of those limits and the fluorescence values were <0.010 ppb, the batch was not reanalyzed. This happened in 42 cases (batches: 84, 97, 228, 427, 483, 531,533, 535, 543, 571, 586, 588, 595, 607, 619, 675, 726, 731, 732, 742, 743, 769, 934, 956, 1072, 1129, 1130, 1132, 1141, 1223, 1224, 1233, 1234, 1264, 1310, 1360, 1363, 1369, 1411, 1548, 1567, and 1612).

In some cases, a percent recovery value significantly out-of-bounds served as an indication that an individual control standard was dying (batches: 550, 596, 1080, 1114, and 1610). The use of that standard was then discontinued.

In other cases, misreading of the TDFF scales resulted in unacceptable values (batches: 722, 727, 759, and 798).

Ten instances of out-of-bound values were due to the mislabeling of control standard vials when they were removed from analytical batches for later use (batches: 895, 902, 907, 930, 968, 1000, 1010, 1012, 1023, and 1033).

In batches 1654 to 1761, twenty-three out-of-bound values were calculated. The analyst, coming near the end of his contract, was becoming inefficient. It was unnecessary to reanalyze any of these batches.

Two batches, 1411 and 1476, had out-of-bound values for which there was no accounting.

5.7.5 Materials Blanks

5.7.5.1 Vial Blanks

Before distribution to samplers, one vial from each gross (144 vials) of new sample vials was filled with distilled, deionized water. It was analyzed on the filter fluorometer for the presence of fluorescence caused by the vial materials. During the study, only one vial blank showed fluorescence.

Results are presented in Appendix H.7.a.

5.7.5.2 Charcoal Blanks

See Section 3.6.1.3.

5.7.6 Field Blanks

See Section 3.5.4.7.

5.8 VOC Testing

No VOCs were present in the water supplies of residential wells 108 and 151 at the time of testing. Detections of other compounds from samples taken in conjunction with the VOC testing program did occur. Below is a table listing detections which occurred during sampling events initiated as part of the Dye Trace Study. Complete laboratory results may be found in Appendix P.

ID	Sampling Date	Parameter	Results
151	10/19/89	VOCs	none detected
		total metals	0.01 mg/L Cu
			0.04 mg/L Fe
			0.13 mg/L Zn
151	10/25/89	anions	6.6 mg/L NO_3-N
			18.9 mg/L Cl
			18.1 mg/L SO_4
		coliform bacteria	present 1/100 ml
151	12/12/89	coliform bacteria	not present
108	12/27/89	anions	5.2 mg/L NO_3-N
			7.2 mg/L Cl
			18.2 mg/L SO_4
		coliform bacteria	not present
108	1/19/90	VOCs	none detected
108	7/3/90	VOCs	none detected
151	7/3/90	VOCs	none detected
108	9/5/90	total metals	0.7 ug/L Cr
151	9/5/90	total metals	2.2 ug/L Cr
			0.02 mg/L Cu
			0.04 mg/L Fe
			0.11 mg/L Zn
108	11/19/90	VOCs	none detected
		total metals	0.6 ug/L Cr
151	11/19/90	VOCs	none detected
		total metals	0.6 ug/L Cr
			0.01 mg/L Cu
			0.12 mg/L Zn

5.9 Anion Testing

5.9.1 Private Wells

Some of the wells included in the Anion Survey are very old. Many of the wells have no written record of their depth, aquifer utilized, or type of construction. The wells contain pumps and are in use.

To obtain detailed, accurate well information, the wells would have to be turned off, the pumps removed, and the wells logged. This was not feasible. The information listed in Table 1 of Appendix L was compiled from the available logs and from the residents' memories. Significant uncertainty was associated with some of the geologic information in Table 1 of Appendix L. Those wells with a six numerical digit "MGS #" in Table 1 of Appendix L had the most reliable well construction information.

Figure 2 of Appendix L is a scatter plot showing all of the nitrate-nitrogen and chloride data obtained in this survey. There is a strong difference between the nitrate-nitrogen and chloride contents of the waters in the Prairie du Chien and Jordan Aquifers in the Study Area. The wells in the Prairie du Chien Aquifer contain much higher nitrate-nitrogen and chloride contents than do the wells in the Jordan Aquifer. The data from the Prairie du Chien wells (and from the Quaternary wells) plot all across Figure 2 while the data from most of the Jordan wells plot down near zero.

Figure 3 of Appendix L is a histogram of the nitrate-nitrogen contents of the Prairie du Chien and Jordan wells. The nitrate-nitrogen contents of the Prairie du Chien wells range up to almost 20 ppm. Ten of the 43 Prairie du Chien wells (23%) contain water with nitrate-nitrogen contents above the 10 ppm Maximum Contaminant Level, 30 wells (70%) contain between 1.0 and 10 ppm, and only 3 wells (7%) contain below 1.0 ppm. In contrast, 95% of the Jordan wells contain less than 1 ppm of nitrate-nitrogen.

Figure 4 of Appendix L is a histogram of the nitrate-nitrogen content of the Jordan wells alone. (Note the enormous scale change between Figures 3 and 4. Figure 4 is an expansion of the bottom 1/20th of the smallest histogram interval in Figure 3.) Of the 63 Jordan wells analyzed, eight (13%) contain no detectable nitrate-nitrogen [<0.005 ppm]; 47 (75%) contain between 0.005 and 0.10 ppm; six (10%) contain 0.10 to 1.0 ppm; and only two (3%) contain more than one ppm. Comparisions to the corresponding Prairie du Chien nitrate-nitrogen data are shown in Figure 5 as pie charts.

Figure 6 of Appendix L is a histogram of the chloride contents of the Prairie du Chien and Jordan wells. The chloride contents of the Prairie du Chien wells range up to more than 40 ppm and only 3 of the wells contain less than two ppm. In contrast, most of the chloride contents of

the Jordan wells are below two ppm. Figure 7 is a histogram of the chloride contents of the Jordan wells alone. Only seven (11%) of the Jordan wells contain more than 1.3 ppm of chloride, only one well contains <0.5 ppm, and 55 wells (87%) contain between 0.5 and 1.3 ppm.

Wells 150 and 620 (identified as Jordan Aquifer wells in Table 1 and Figures 2, 3, and 6 of Appendix L) produce water that contains more than one ppm nitrate-nitrogen. These same two wells contain the two highest chloride levels observed in Jordan Aquifer wells. The water in these wells is much more characteristic of the Prairie du Chien Aquifer rather than the Jordan Aquifer. It appears that these wells are actually producing water from the Prairie du Chien Aquifer. Six more of the Jordan wells (wells # 174, 651, 655, 704, 718 and 754) are producing water with nitrate contents between 0.1 and 1.0 ppm. Four of these six wells appear to have elevated chloride levels. These six wells may be producing water from the Prairie du Chien Aquifer, or they may be producing a mixture of waters from the two aquifers. The situation here is less clear-cut.

The opposite situation is also evident. Three of the wells identified as Prairie du Chien wells (wells # 154, 106, and 115) are producing water with <0.2 ppm nitrate-nitrogen and <0.9 ppm chloride. These wells appear to be producing Jordan Aquifer water.

Jordan wells apparently producing Prairie du Chien water could be due to 1) misinformation on the well depth and construction; 2) defective casing through the Prairie du Chien; or 3) natural features which allow rapid movement of surface water into the deeper aquifer. Prairie du Chien wells apparently producing Jordan water can only be due to misinformation on the well depth and/or construction.

Given 1) the strong possibility of mixed data sets from misidentified wells; 2) the problem of "less than" values in some cases, and 3) the strongly asymmetric data distributions, arithmetic averages of the chloride and nitrate-nitrogen data from the two aquifers would probably be biased and misleading. The median values of such distributions are more statistically robust estimates of the "averages" of the distributions. The median values of nitrate-nitrogen and chloride values of the Prairie du Chien and Jordan private wells are listed in Table 2 of Appendix L. The median Prairie du Chien well in this survey contains about 300 times as much nitrate-nitrogen and about 14.5 as much chloride as does the median Jordan well.

The elevated levels of nitrate-nitrogen and chloride in the Prairie du Chien Aquifer wells relative to the Jordan Aquifer wells are apparently due to a wide range of human activities in the Study Area. Essentially all of the Prairie du Chien Aquifer is affected to some degree by recent surface contaminants. The Jordan Aquifer, in contrast, is still hydrogeologically isolated from these surface contaminants.

In contrast to the nitrate-nitrogen and chloride data, the sulfate and fluoride data from the Prairie du Chien and Jordan private wells are very similar. Figure 8 of Appendix L is a histogram of the sulfate data from the two aquifers. These distributions appear to be more normal and so arithmetic averages are appropriate. The average sulfate contents of the Prairie du Chien and Jordan wells are 21.2 $\pm$ 6.3 ppm and 20.0 $\pm$ 3.8 ppm, respectively. The averages of the two distributions are within one standard deviation of each other.

Figure 9 of Appendix L is a histogram of the fluoride data from the Prairie du Chien and Jordan Aquifers. The arithmetic averages of these two distributions are 0.124 $\pm$ 0.056 ppm and 0.166 $\pm$ 0.045 ppm, respectively. These distributions are essentially the same. The sulfate and fluoride data show no impact from surface activities.

Figure 10 of Appendix L is a histogram of the bromide contents of the private well samples. The bromide levels in all of the wells are very low and in many cases the levels are below the analytical detection limit which is about 0.030 ppm. Figure 11 is a scatter plot comparing the bromide and chloride data from the private wells. Most of the wells with detectable bromide are the Prairie du Chien wells with the higher chloride contents. The bromide data are too low to be of much use in defining the system's hydrogeology. Due to these very low levels, no bromide averages or means are shown in Table 2 of Appendix L.

None of the private wells contain phosphate levels above the detection limit, 0.050 ppm. It is very unusual to detect any significant levels of phosphates in ground water. Calcium phosphate is so insoluble that if phosphate does enter the ground water it is very quickly removed by precipitation. Due to these very low levels, no phosphate averages or means are shown in Table 2 of Appendix L.

The only two private wells in which continuous pulses of Rhodamine WT dye from the Dye Trace Study have been detected (108 and 151) are Prairie du Chien wells. The anion levels in these two wells are near the median values for all of the Prairie du Chien wells. The anion data from the private wells does not reveal any strong evidence of contamination from the landfill -- either collectively or in any individual well.

5.9.2 Springs

Water samples for anion analyses were collected by county personnel from 10 springs. The spring samples were collected during a period of active precipitation and high surface run-off and the presence of surface water run-off may have affected some of the results.

The data from these analyses are listed in Table 1 of Appendix L. The spring data are shown as "S"s in Figure 2. All of the springs emerge from the Prairie du Chien Formation and their anion results plot within the field defined by the Prairie du Chien wells in Figure 2. The anion data split the springs into two reasonably well-defined groups.

Four of the springs have lower nitrate, chloride, sulfate, and fluoride contents than do the other six springs. These four springs (411.5, 412, 418, and 422) are designated Group I springs. The average anion contents of the Group I springs are listed in Table 2 of Appendix L. Five of the springs have higher nitrate, chloride, sulfate, and fluoride contents than do the other five springs. These five springs (416, 416.5, 419, 423, and 423.5) are designated Group II springs. The average anion contents of Group II springs are listed in Table 2. Spring 410 appears to be an intermediate case. In Figure 1, it plots near the Group II springs but its sulfate and fluoride contents are much nearer the Group I spring values.

The Group II springs appear to be draining primarily the Prairie du Chien Aquifer. Group II consists of four springs (416, 416.5, 423, and 423.5) located close together in the northwest part of the Study Area and spring 419 in the southeast part of the Study Area. The Group I springs appear to be producing a mixture of Prairie du Chien and Jordan Aquifer water. The significance, if any, of these difference in anion contents is not clear. If dye is ever detected in either group of springs the difference may prove to be useful.

The anion data from the springs do not reveal any strong evidence of contamination from the landfill.

5.9.3 Monitoring Wells

The anion data from the monitoring wells are listed in Table 1 of Appendix L and the chloride and nitrate-nitrogen results are shown in Figure 2. Eight of the 10 Prairie du Chien monitoring wells (302, 303, 304, 305, 307, 308, 309, and 311) contain levels of all six anions that are consistent with the range of concentrations seen in the Prairie du Chien Aquifer private wells and springs. The Jordan monitoring well (301) contains levels of all six anions consistent with the levels seen in the Jordan Aquifer private wells. The remaining two Prairie du Chien wells are distinctly different.

Monitoring well 306 contained more than twice as much chloride, 166 ppm, as the next highest Prairie du Chien well. This is sixteen times the chloride content of the median Prairie du Chien well. Monitoring well 306 also contained the only significant level of phosphate seen in this survey. The phosphate level in well 306, 2.36 ppm, is about 50 times higher than the upper limit on the phosphate concentrations in all of the other wells and springs.

The anion data are consistent with the available historic data from the monitoring wells (Braun, 198b, 1989c). Figure 37 compares the chloride data from 1984 through 1988 with that obtained in the anion scan sampling in April 1990 for monitoring wells 306 and 307. Three quarterly samplings from monitoring well 306 and 307 between May 1985 and January 1986 yielded chloride values very near the median value of 10 ppm seen in the Prairie

du Chien wells in the area. In April and June 1986, the chloride values in 306 increased by over a factor of 1000, indicating a major groundwater contamination event from the landfill. With one exception, all of the subsequent chloride readings from 306 have been at least 10 times their 1985 ambient levels. Evidence of that event, or subsequent releases, continues to be present in monitoring well 306. In contrast, the chloride values in monitoring well 307 remained constant in the 10 to 20 ppm ambient range.

Monitoring well 310 contained more than twice as much sulfate, 90.7 ppm, as any other well. Sulfate is a recognized leachate indicator. The anion data from monitoring well 310 indicate the presence of leachate contamination.

Monitoring wells 306, 308 and 310 are the shallow, water-table monitoring wells along the east side of the landfill. Dye was not detected in these wells. Apparently, as dye moved eastward it also moved deeper into the aquifer beneath these wells (see Figure 39).

6.0 CONCLUSIONS

6.1 Random Detection Phenomenon versus Continuous Dye Pulses

The random detection phenomenon proved to be the major scientific, as well as socio-political, problem of the Oronoco Dye Trace Study. An understanding of the phenomenon was essential for the scientific and socio-political credibility of this project. The observations described in 5.1 above can be summarized as:

1) The majority of the random detections contained extremely small concentrations of dye.

2) The random detections occurred in the summer and fall of 1989. During the late summer of 1989, the occurrence rate approached 1 in every 200-300 samples analyzed. The random detections disappeared in the winter of 1990 and did not reappear in the summer and fall of 1990.

3) The phenomenon appeared at random locations within the Study Area, a control area located 20+ km away from the dye introduction site, and in a vial blank.

   The random detections were observed in all sampled aquifers, including aquifers separated by significant aquitards from the aquifer into which the dye was introduced.

5) The random detections were only "one sample long."

6) In those cases where random detections were observed in samples collected in duplicate, the random detection was always observed in only one of the two samples.

7) If the random detection phenomenon was due to dye that was coming from the aquifer or from the plumbing systems, the filters would remove it -- as was shown by the filtered and unfiltered pairs from 108 and 151. The even split of random detections between the filtered and unfiltered pairs collected from wells without continuous dye pulses, therefore, indicated that the phenomenon was not in the aquifer but was present in sample vials or acquired by the samples after the water left the homeowners' faucets.

8) HPLC analyses confirmed that the dye in the continuous pulses was Rhodamine WT. Only the largest of the random detections contained enough dye for HPLC analyses. Those random detections which yielded HPLC results above the method's detection limit contained Rhodamine B -- not Rhodamine WT.

9) Several consumer products used in the Dye Trace Study Area contain Rhodamine B and/or other rhodamine dyes.

The observations are consistent and indicate that:

1) The random detection phenomenon was not in the aquifer but was introduced into the sample vials at the factory or at some point(s) after the water left the water-supply faucets.

2) The dye producing the random detections was not the Rhodamine WT that is being used in the Dye Trace. The dye most likely causing the random detection phenomenon was Rhodamine B. The source of this Rhodamine B is unknown.

3) The random detections contained no evidence concerning potential groundwater flow paths from the vicinity of the landfill to individual wells.

4) The random detection phenomenon consumed large amounts of financial, technical, and socio-political resources with essentially zero contribution to the goals of the dye trace.

6.2 Dye Movement

Section 2.4.1 lists the five goals of the Dye Trace Study. The first three: determination of the local direction and velocities of groundwater flow, evaluation of the effectiveness of the existing monitoring wells, and the identification of nearby residential wells most likely to intercept potential landfill contamination are directly addressed by the results of the Phase I dye movement.

Phase I dye reached six monitoring wells, 303, 305, 304, 307, 309, and 302, and two private wells, 151 and 108. Phase I dye has not yet been confirmed in any of the other five existing monitoring wells, stream stations, springs, or approximately 200 other residential wells. All of the wells with continuous dye pulses are producing water from the Prairie du Chien Aquifer.

Phase II dye has not yet been confirmed anywhere. There is no evidence that dye from either dye input has reached the Jordan Aquifer.

6.2.1 Direction of Phase I Dye Travel

The breakthrough curves for the eight positive wells (Figures 20, 21, 22, 23, 25, 27, 31 and 32) reveal a pattern of dye movement that is complex in space and time. Phase I dye movement is being profoundly affected by some type of storage in the hydrogeologic system beneath the landfill and down-gradient from the Phase I dye input point. All of the positive wells, with the possible exception of monitoring well 302, continue to yield dye over a year and a half after it went into the subsurface. This storage probably involves a karst subcutaneous zone (Williams, 1983) in the unsaturated zone within the Prairie du Chien Aquifer. This storage could also involve occlusion of joints or fractures by infilling glacial sediments, potential storage by impoundments, isolation within crevices, and adsorption/desorption phenomena.

The breakthrough curves of the positive wells do not display the shapes characteristic of groundwater flow dominated by conduit flow. The Prairie du Chien Aquifer in the landfill vicinity is behaving neither as a well-developed, conduit-flow karst aquifer nor as a well-behaved porous-media aquifer. The Prairie du Chien Aquifer in the Dye Trace Study area appears to be an intermediate case.

The following discussion of the dye movement will be divided into "landfill scale" and "residential well scale" components. The landfill scale component will include the landfill monitoring wells which are within a few thousand feet or less of the Phase I dye input point. The residential well component will include all of the other monitoring points which are one-half mile to several miles from the dye input point.

Figures 38 and 39 are plan-view and cross-section maps that, taken together, summarize the currently preferred interpretation of the Phase I dye movements. Figures 38 and 39 represent a working hypothesis which describes the groundwater movement under and around the landfill. The hypothesis or interpretation represented by these Figures is consistent with all of the available information. The hypothesis is not unique. It is incomplete due to the limits of the available information at several critical points (e.g. a lack of sufficient sampling points). This interpretation will be refined and revised as additional information becomes available. Other interpretations are possible.

The interpretation or hypothesis represented by Figures 38 and 39 is useful in that it represents specific predictions that can be tested by additional measurements and information. The location of the plume shown in Figures 38 and 39 is conservative in that it is the minimum necessary to explain the available information. The plume location is not a unique interpretation, however, particularly in those areas more than a few hundred feet from a positive well, and should not be taken as the established limits of the plume.

6.2.1.1 Landfill Scale Dye Movement

At the landfill scale, the leading edge of the dye first moved roughly east under the northern part of the landfill along or above the water table and reached shallow monitoring wells 303 and then 305. The shallow eastward movement was of limited extent because no dye has been detected in shallow monitoring wells 306, 308 or 310. There is no information on the extent of the dye's shallow movement to the north, west, or south in this initial spread along the water table due to the lack of monitoring points in those directions.

Next, the leading edge of the Phase I dye pulse moved deeper to the mid-levels of the Prairie du Chien Aquifer and simultaneously reached monitoring wells 304 and 307, on opposite sides of the landfill. The leading edge of this mid-level dye movement eventually reached monitoring well 309 and, much later, monitoring well 302. The limited extent of mid-

-level dye movement to the southeast and south is shown by the absence of dye in 311 and its sporadic appearance in 302. The limits of mid-level dye movement to the north and west of the landfill were not identified due to the absence of monitoring locations.

6.2.1.2 Residential Well Scale Dye Movement

The network of residential wells sampled in this study extended in all directions from the landfill. Dye has been confirmed at only two of those wells. Dye first appeared in well 151 and then in well 108. Both wells are mid-level Prairie du Chien wells and are north-northeast of the landfill. The dye pulses in these two wells clearly demonstrate that a component of the groundwater flows from the vicinity of the landfill to the north-northeast, in the Prairie du Chien, to these two wells. This flow direction is consistent with the available potentiometric surface information. These two wells are the most likely to intercept potential leakage from the landfill.

No confirmed evidence of flow in any other direction exists. Wells in all other directions were sampled and analyzed but dye was not detected.

6.2.2 Speed of Dye Movement

Given that the end of the long continuous pulses of dye have not yet been observed, the average speed of the dye through the system can not be calculated. However, the arrival of the leading edge of the dye pulse at each of the eight positive wells can be converted into dye travel speeds, with the additional assumption that the dye traveled in a straight line between the input point and the positive well. The path the dye actually followed is certainly longer than the straight line distance and the resulting calculated speeds are, therefore, only lower limits of the actual speeds. These are useful lower limits of the speeds at which potential pollutants could be expected to spread through the Prairie du Chien Aquifer in the vicinity of the landfill.

Speed of Phase I Dye Movement

Well #	Distance from Phase I Dye input (feet)	Travel Time (days)	Speed (miles/year)
303	670	0.85	54.5
305	1,349	4	23.3
304	653	7	6.5
307	2,851	7	28.2
309	2,830	44	4.5
302	2,111	310	0.47
151	6,369	77	5.7
108	7,919	207	2.7

This range of speeds, 0.47 to 54.5 miles/year, is intermediate between the flow speeds seen in well-developed conduit flow karst aquifers and in porous-media aquifers. The former often have flow speeds measured in miles per day, while the latter are often characterized by flows in the feet per year range. The flow speeds further emphasize the intermediate nature of the Prairie du Chien Aquifer.

6.2.3 Dilution and Dispersion in the Prairie du Chien

Quantitative dilution or dispersion calculations require that the flow relationships between the sampling points be known. If the dye were to emerge from one of the springs, for example, the concentration of dye in that spring could be compared to the input dye concentration. If there were enough positive wells to define a dye plume in three dimensions, then the concentration gradients along or across such a plume would allow dispersion parameters to be calculated. Unfortunately, the existing array of positive wells is too sparse to allow detailed dilution or dispersion calculations to be made. None of the springs have yielded positive results. There is no reason to assume that the reasonably smooth pulses from wells 309, 151, and 108 are related in any simple fashion to one another or that they reflect the maximum concentration of the dye plume in their vicinity. Therefore, the relative concentrations in these pulses cannot be converted into dilution or dispersion parameters.

The other positive monitoring wells are dominated by pulses of dye that are apparently washed out of storage from the subcutaneous zone of the karst system by recharge events. The documentation of these variations has important implications for future monitoring at this site. Any contaminants leaking from the landfill may be temporarily stored in the subcutaneous zone and then washed into the aquifers by subsequent recharge events. The resulting short-lived pulses of contaminants would appear at variable, phased intervals after recharge events.

6.2.4 Where is the Phase II Dye?

The 1000 pounds of Phase II dye were poured into the Reiter Sinkhole on March 30, 1991. As of February 1991, no confirmed detections of the Phase II dye have been made. The most promising case is well 179, but the levels have to date remained too low for unambiguous HPLC confirmation. If the fluorescence at well 179 is eventually confirmed, a 98 day travel time (taken from the July 7, 1991 peak) coupled with the 1,710 feet straight line distance from the Phase II dye input will correspond to a speed of 1.2 miles per year.

There are three basic classes of reasons that dye traces fail to detect dye: 1) the points where the dye emerges are not monitored, 2) the dye is diluted or attenuated below detection limits before it reaches the sampling points; and/or 3) the trace is terminated before the dye reaches the sampling points.

It does not seem probable that the Phase II dye has emerged undetected at some unsampled location. All of the potential springs were monitored and numerous wells in all directions from the dye input point were sampled. Every available Prairie du Chien and representative Jordan sampling locations were covered (as were a number of inconceivable locations). If, however, the unconfirmed well 179 data represent the very edge of a narrow dye plume moving roughly northeast (which is down the potentiometric surface), there are no other available Prairie du Chien wells to be sampled between well 179 and the river to the east and northeast to allow continued tracking of the dye movement.

The dilution and attenuation characteristics of each aquifer must be calibrated for Rhodamine WT. That calibration was accomplished by the Phase I dye input. Phase I dye was detected at a well 1.5 miles from the dye input point. This demonstrates that 20 pounds of Rhodamine WT can produce measurable responses in this aquifer. Phase II involved the input of ten times as much dye as did Phase I.

It does not seem probable that the Phase II dye was diluted or attenuated below detection limits. The prompt dilution of the Phase II dye by the 12,000 gallons of water poured into the sinkhole produced a mixture with a Rhodamine WT concentration of about 2,000,000 ppb. The surface area that drains into the Reiter Sinkhole is about 91 acres and the rainfall after the Phase II dye input would have produced about 3.9 million gallons of runoff using standard SCS surface runoff assumptions. Dilution by surface runoff diluted the Phase II dye to about 6,200 ppb. (Assuming that all of the rainfall ran into the sinkhole will only reduce this number to 730 ppb.) Phase I dye was unambiguously detected in well 108 at 0.020 ppb. Taking 0.020 ppb as a realistic practical detection limit, the rainfall dilution should have produced a solution that was over 300,000 times the Dye Trace detection limit for Rhodamine WT.

The improbability of dilution reducing the Phase II dye below the detection limit can be illustrated by another simple calculation. The 1,000 pounds of 20 weight percent solution of Phase II dye will produce 1.2 trillion (10^{12}) gallons of water with a Rhodamine WT concentration of 0.020 ppb. If the Prairie du Chien Aquifer is 300 feet thick and has an effective porosity of 0.2, each square mile of saturated Prairie du Chien contains about 12 billion (10^{9}) gallons of water. The Phase II dye will label the water in about 100 square miles of the Prairie du Chien Aquifer to above the Dye Trace detection limit.

The third potential reason, that the dye has not yet reached the available sampling points before sampling ceases, is the only remaining possibility. As noted above, the next available Prairie du Chien sampling points north or east of well 179 are springs 411, 418, and 422. Of these three, 411 is by far the largest. Spring 411 is about 1.7 miles from the Phase II dye input point. If the very preliminary speed of 1.2 miles per year to well 179 is correct, then Phase II dye could be expected to reach spring 411 about 1.4 years after it was input (i.e. late summer of 1991).

In summary, the simplest hypothesis that is consistent with all of the available information is that the Phase II dye is moving northeast at a velocity of about 1 to 2 miles per year. In the context of this hypothesis, well 179 caught only the very edge of the plume either because it is too shallow or along the side of the flow path. Sooner or later dye should be detectable. However, until that occurs this hypothesis cannot be confirmed or negated.

6.2.5 Effectiveness of Existing Monitoring Wells

The simplest interpretation of the positive results obtained from monitoring wells 302, 303, 304, 305, 307, and 309 yields a picture of dye moving eastward under the northern half of the landfill. This interpretation also indicates that the dye moved downward through the Prairie du Chien Aquifer from the subcutaneous zone, along the water table for a distance and then moved primarily along the mid-level of the aquifer. This interpretation is only possible if the monitoring wells are accurately recording the flow of groundwater under the site.

The monitoring wells are effective. They recorded the dye as it moved through the system and will therefore presumably record any pollutants from potential landfill leakage. Dye was detected in all of the wells that it passed. These wells were installed in the early 1980s using conventional monitoring well installation practices. The wells were not sited using any special techniques to optimize their locations. The only significant atypical feature of the monitoring wells is the relatively long, 40 foot, screens installed in the water-table wells. This extra length of screen allowed the wells to continue to function as the water table fluctuated.

Several of the monitoring wells, such as 304, yield only limited amounts of water before they pump dry. Monitoring well 304 yields a consistent pattern of dye movement. Apparently the relatively low yield is a function of the aquifer properties and not of the well construction and does not adversely impact the monitoring well's ability to function as designed.

The demonstration that conventional monitoring wells will successfully intercept materials moving through this karst aquifer system greatly simplifies the task of monitoring this site. These results should increase the public confidence in that this site can be monitored successfully.

6.3 Implications of Dye Movement

The implications of the Phase I dye movement can be summarized in terms of the five goals of the Dye Trace Study (Section 2.4.1).

I. To determine the local directions and velocities of groundwater flow beneath and adjacent to the landfill.

The Phase I positive wells document a pattern of groundwater flow from west to east under the northern portion of the landfill which contains the municipal waste and demolition waste cells that are the potential source of groundwater contamination. The groundwater leaves the site in a north northeast direction. The flow appears to be contained within the Prairie du Chien Aquifer.

The groundwater flow velocities revealed by the spread of the dye through the aquifer system range from miles per month, close to the source, to miles per year in the more distant parts of the flow system. These velocities are intermediate between fully developed conduit-flow karst systems, which often exhibit flow velocities of miles per day, and the velocities of groundwater flow in porous-media aquifers, which are typically measured in feet per year. The Prairie du Chien Aquifer in the vicinity of the landfill is an intermediate case between conduit-flow and porous media flow, perhaps due to the infilling of the karst aquifer with glacial sediments.

II. To determine if the existing network of landfill monitoring wells would intercept any potential groundwater contamination emanating from the site.

The consistent pattern of dye movement documents that the existing monitoring wells work. These conventional monitoring wells do sample material moving through the hydraulically significant flow paths of the aquifer. This result is surprising in view of the literature on monitoring in karst terrains. The success of conventional monitoring wells is apparently due to the intermediate nature of the flow beneath and adjacent to the landfill.

III. To identify the private wells among the surrounding residences most likely to be impacted by potential groundwater contamination emanating from the site.

The positive detection of dye at residential well 151 and 108 identify these two wells as the most likely wells to be impacted among the area wells sampled. Both are old wells which produce water from the Prairie du Chien Aquifer. The anion survey data indicates that all of the Prairie du Chien has been impacted to varying degrees by surface contaminants. The results of the Phase I dye movement indicates that Prairie du Chien wells and springs northeast of the landfill are the most likely water supplies to be impacted by potential groundwater contamination emanating from the landfill.

Having identified two private wells offsite that are most likely to be impacted by potential groundwater contamination emanating from the landfill, it is important that those two wells be maintained as sampling locations. A very significant amount of effort and resources has gone into identifying these two wells. The response of the well owners has been to investigate ways of acquiring alternative water supplies. Such

efforts can involve the loss of access to the existing wells. For example, the drilling of a new, deep well conventionally requires the abandonment of the existing well. Such procedures can be avoided if the need to preserve access to the existing wells is recognized.

IV. In general, to provide the information necessary to design a more effective Environmental Monitoring System for the site.

The proposed additions to the EMS are discussed below in Section 8.0. The dye movement highlighted the complexity of the system being monitored and significantly improved the information base on which a more effective EMS can be built.

V. To identify data gaps which could be addressed with additional hydrogeologic investigations as part of the subsequent Remedial Investigation and Feasibility Study of the site.

The pattern of dye movement has emphasized significant gaps in the characterization of the site. The dye movement has revealed that the Prairie du Chien Aquifer beneath and adjacent to the site is a complex aquifer with properties intermediate between porous-media and conduit-flow karst aquifers.

Poorly understood vertical gradients are present in the aquifer particularly along the east side of the landfill. The cause and implications of these gradients are important unanswered questions. Attempts to routinely model the water level data from the monitoring wells without an adequate understanding of these vertical gradients produces potentiometric maps at the site-scale which imply groundwater flows at right angles to that documented by the dye movement (see Figures 2 through 8 in Braun, 1991). These apparent contradictions in predicted versus measured flow directions are confusing to managers and regulators and reduce public confidence in the monitoring of the site.

The storage of potential contaminants in the subcutaneous zone of the vadose zone is evident in the dye movement results. This storage component complicates the monitoring of the site. The materials stored temporarily in the subcutaneous zone are released in two modes: in pulses after recharge events and more slowly as the storage zones drain. These pulses will be difficult to document with conventional quarterly monitoring protocols. The challenge will be to find sampling strategies that can catch the pulses within the confines of economic reality.

The protocols currently accepted for purging wells before representative samples are collected may not work with some of the critical monitoring wells. The protocols in question were designed for high to medium yielding porous-media aquifers and have had the unintended effect of preventing collection of samples from low yielding monitoring wells. The Dye Trace has demonstrated that representative results can be obtained from wells that pump dry in a few minutes. The sampling protocol should be revised for these low-yielding wells.

6.4 Implications for Wells at which No Dye was Detected

Negative data is the most difficult type of information to interpret. It must be remembered that the absence of proof is not proof of absence. The rigorous interpretation of the data for wells at which no dye was detected is simple:

> Under the hydrogeologic and technical conditions operating during this dye trace, groundwater flow connections from the dye input point to the negative wells were not demonstrated.

This explicitly does not mean that such connections do not potentially exist, only that they were not found under the conditions of this study.

The pattern of negative results are consistent with several lines of positive results. The positive dye detections document groundwater flow to the northeast in the mid-level of the Prairie du Chien Aquifer. The information on the potentiometric surface in the Prairie du Chien Aquifer presented in this report also indicates flow to the northeast. The anion information clearly shows that the waters in the Jordan Aquifer are isolated from the waters in the Prairie du Chien Aquifer. These positive results yield a consistent picture of groundwater flow to the northeast in the Prairie du Chien which should reassure individuals with wells in other directions and in the Jordan and deeper aquifers that their wells have a low probability of being impacted by potential contaminants emanating from the landfill.

While the absence of dye in a given well does not indicate that a groundwater flow connection exists between the landfill and that well, the negative result does not prove the absence of such a hypothetical connection. However, to an individual concerned about potential groundwater contamination from the landfill, the absence of dye in their well should be good news.

6.5 Implications of the Anion Survey

In southeastern Minnesota, the Prairie du Chien and Jordan Aquifers are conventionally treated as though they are a single hydrogeologic unit. The results of the anion survey indicate that, in the Study Area, the Jordan Aquifer is hydrogeologically isolated from the Prairie du Chien Aquifer. The Prairie du Chien Aquifer has been extensively impacted by surface contamination from a wide variety of human activities. That surface contamination is evident in elevated nitrate-nitrogen and chloride levels. The Jordan Aquifer, in contrast, seems to have escaped this surface contamination -- at least so far. The median Prairie du Chien well contains about 300 times more nitrate-nitrogen and about 14.5 times more chloride than does the median Jordan well.

The cause of the hydrogeochemistry isolation of the Jordan Aquifer from the Prairie du Chien Aquifer in the Study Area is unknown. The water quality differences, however, are supported by the strong vertical gradients in the water levels within the Prairie du Chien seen in the paired monitoring wells 306-307, 308-309, 310-311 and the water levels in the nearby private wells

219-220 and 135. There are at least two broad classes of hypotheses that can explain the hydrogeochemical isolation of the two aquifers: 1) dynamic or flow phenomenon and 2) some type of local aquitard within the Prairie du Chien Group.

Both hypotheses could be tested with additional work. Measurements of the in situ aquifer characteristics in the Prairie du Chien and Jordan Aquifers in the Study Area coupled with flow modeling could be used to evaluate the dynamic or flow hypotheses. Detailed gamma logging (perhaps coupled with other geophysical logging techniques) of several of the deeper wells at and immediately around the landfill might be able to document the existence of a local aquitard. Coupled pump tests of the monitoring wells could also be very diagnostic if such studies have not already been done.

Chloride and (to a lesser extent) nitrate-nitrogen are constituents in landfill leachate. However, given the wide distribution of the contamination in the Prairie du Chien Aquifer and the multitude of anthropogenic sources of these two chemicals in the Study Area, there is little evidence that the Oronoco Landfill is a significant source of any of the nitrate-nitrogen and chloride contamination observed in the residential wells and springs in this survey.

The springs in the Study Area emerge from the Prairie du Chien Formation. In some cases, their water geochemically resembles water seen in Prairie due Chein wells. In other cases, the water appears to be a mixture of Jordan and Prairie du Chien water. Although the springs contain elevated levels of nitrate-nitrogen and chloride, the landfill does not appear to be a major source of these contaminants.

In contrast to the springs and private wells, two of the monitoring wells contain evidence of leachate contamination from the landfill. Monitoring well 306 (14A) contains the highest chloride and phosphate levels observed in the survey. Monitoring well 310 (15A) contains the highest sulfate levels observed in the study. The levels of these three anions in 306 and 310 are 2 to about 50 times the levels observed in the private wells and springs. These elevated levels, particularly compared to the now extensive data from the other monitoring wells, private wells and springs, indicate that leachate from the landfill has reached the shallow water-table aquifer in the immediate vicinity of the Oronoco Landfill.

In view of the relative hydrogeochemical isolation of the Jordan Aquifer in the Study Area, emphasis should be placed on monitoring the contaminant levels in the Prairie du Chien Aquifer. The current monitoring well array has 1 Jordan well and 10 Prairie du Chien wells. Additional future monitoring should focus on the upper portion of the Prairie du Chien Aquifer.

7.0 POST-STUDY DYE MONITORING PLAN

Neither the fluctuations in size nor the length of the Dye Trace Study could have been predicted at the time the original proposal was being formulated. As results became apparent, needed changes were made. However, it was anticipated that, at some point, the efforts expended to continue the study would outweigh the value of the information obtained and the study would end. At that time, a post-study dye monitoring plan would be implemented solely for the sake of learning when the dye was no longer in the aquifer at detectable concentrations.

Based on the dye movement during the first phase of the study, dye was expected to become apparent during Phase II within a few months. After four months, with no apparent dye detections from the second introduction, the study size was reduced. Four months later, with still no apparent detections, the size of the study was further reduced.

This "maintenance mode" of sampling, involving only 54 sites sampled on a weekly basis, will be continued until it is reasonable to assume detection of the second pulse of dye will be unlikely. At that point, a post-study monitoring plan will be implemented. Although this plan has not yet been developed, it is anticipated to consist of a skeletal framework of sampling sites where dye is currently detected, sampled on a monthly or quarterly basis until dye is no longer apparent.

8.0 PROPOSED ENVIRONMENTAL MONITORING SYSTEM

The results of the Dye Trace, along with a review of the existing information on the landfill, has identified a number of information gaps that need to be filled with additional geotechnical work before the existing monitoring systems is modified.

The existing monitoring well system needs to be subjected to pump tests and slug tests while the water levels in all of the other monitoring wells are measured with continuous data acquisition systems. The relative responses of the various monitoring wells to each other during pump and slug tests may yield significant new information on the flow system beneath the landfill. The simultaneous arrival of the dye at monitoring wells 304 and 307 on opposite sides of the landfill and the subsequent similarity of their breakthrough curves illustrates the possibility that unexpected relationships may exist.

The source of the vertical head gradients along the east side of the site is a major unresolved problem. The phenomenon responsible for the head gradients may be a major factor in the site hydrogeology. The pump and slug tests may help to define the phenomenon. Gamma logging of the monitoring wells and nearby private wells is also a promising approach. If the head gradients are due to perching on some type of local aquitards within the Prairie du Chien, those features may be evident on the gamma logs. For instance, east of the landfill site there is a significant sandstone member, the New Richmond Sandstone, at the bottom of the Shakopee Formation in the middle of the Prairie du Chien Group. West of the landfill site, the New Richmond Sandstone is not identifiable (Austin, 1972, p. 467). It is possible that a local shaley facies of the New Richmond depositional environment may be a significant aquitard under the landfill site.

The size and extent of contaminant pulses in the existing monitoring wells needs to be evaluated. The current quarterly monitoring has documented a number of pulses of different chemical parameters moving through the system (e.g., Figure 37). The daily sampling for dye has documented rapid but variable responses of the monitoring wells to recharge events. It is important to determine if the leachate parameters are responding in a similar manner.

8.1 Sampling Points

All of the existing monitoring wells seem to be working and should be kept in the monitoring system. The two positive private residential wells, 151 and 108 should be added to the monitoring system. These are the only two off-site locations that have documented connections to the groundwater flow under the site.

The pattern of dye movement indicates that the dye left the landfill in the northeast corner of the site and that direction is consistent with the Study Area scale potentiometric maps. There are no existing monitoring wells along the east half of the north side of the waste cells. Several new monitoring wells need to be constructed to fill the gap in the northeast corner of the site between monitoring wells 305 and 306/307. Both shallow, water table wells and deeper mid-aquifer wells should be installed. The vertical extent of the dye plume is very poorly delineated with existing sampling points. There is a lack of monitoring of the Jordan Aquifer at the landfill site. At least one of the new monitoring wells in the northeast should be a Jordan well. Such a well will also allow a direct measurement of the extent of the vertical head gradient into the Jordan. The new monitoring wells will need to be evaluated with pump and slug tests and gamma logging. The site conditions necessitate that all of the new monitoring wells should be installed with at least 20 foot screens and the shallow, water table wells should have 40 to 50 foot screens.

There is a long distance between the northeast corner of the landfill site and private well 151. Additional monitoring wells are needed in this area to monitor contaminant migration potential. Such wells would most effectively be installed after the situation in the northeast corner of the landfill is evaluated via new monitoring wells. These off-site wells should be installed with long screens in the mid-levels of the Prairie du Chien. At least one more Jordan monitoring well is needed in this general area. Both the Jordan well and the Prairie du Chien wells will serve to fill an important gap in the potentiometric sampling network.

8.2 Sampling Frequency for EMS

A prominent feature in the breakthrough curves of the positive monitoring wells is the complex response to recharge events. Order-of-magnitude dye increases in a day or two were common. To the extent that the dye mimics the potential movement of landfill leachate, those contaminants may also exhibit such large, short-term fluctuations. The sampling frequency for the new EMS should be designed to intercept such pulses, if they exist.

It would be prohibitively expensive to conduct daily analyses for many important leachate parameters, VOCs for example, for any length of time. It is more economically feasible to investigate the recharge response rate of a simple leachate parameter such as chloride. If such simple conservative parameters exhibit large, short-term fluctuations, then the possibility of fluctuations in the more significant parameters should be investigated.

Samples which would be adequate for the first part of such an investigation already exist. The array of samples collected during the Dye Trace from monitoring well 306, for example, could be selectively analyzed for chloride. Analyzing the samples spanning the 1990 spring thaw and the July 7, 1990 storm would cover the two largest recharge events that have occurred during the Dye Trace. A few additional samples spaced throughout the sample set will probably suffice to establish any trends. If short-term fluctuations are

documented, the current permit-required quarterly sampling plan should be modified to establish sampling times likely to intercept the response from recharge events.

The recent karst literature (Quinlan and Alexander, 1987; Quinlan, 1989) emphasize the importance of collecting many samples from each location and then evaluating, based on hydrologic conditions, which small fraction of the collected samples to submit for expensive analyses. It is clear that routine quarterly sampling has little chance of catching a short-term fluctuation and no chance of confirming such a pulse. Designing an economically viable sampling protocol that is capable of documenting these short term pulses may prove to be the most difficult part of a new EMS.

List of References

S.L. Abidi (1982) Detection of diethylnitrosamine in nitrite-rich water following treatment with Rhodamine flow Tracers. Water Res., vol. 16, pp. 199-204.

S.L. Abidi (1987) Ph.D, National Fisheries Research Center, La Crosse, WI. Letter to E. Calvin Alexander, Jr. dated September 28, 1987.

T. Aley (1977) A model for relating land use and groundwater quality in southern Missouri. In: Dilamarter, R.R. and Csallany, S. C. (eds.) Hydrologic Problems in Karst Areas, Western Kentucky University, Bowling Green, KY, pp. 323-332.

T. Aley (1988) Complex radial flow of ground water in flat-lying residuum-mantled limestone in the Arkansas Ozarks. In: Environmental Problems in Karst Terrains and Their Solutions Conference (2nd, Nashville, TN), Proceedings, National Water Well Association, Dublin OH, pp. 159-170.

E.C. Alexander, Jr. and G.L. Maki (1988). Sinkholes and sinkhole probability (Sheet 7 of 9). Geologic atlas Olmsted County, Minnesota (County atlas series C-3). St. Paul, Minnesota.

E. Calvin Alexander, Jr., Scott C. Alexander, Howard Trussell, Barbara J. Huberty, Geri L. Maki and James F. Quinlan (1990a) The Oronoco Landfill dye trace I: The monsters that live below one part per billion. GEO^2. v. 17, nos. 2 & 3, p. 59.

E. Calvin Alexander, Jr., Scott C. Alexander, Barbara J. Huberty, Geri L. Maki and James F. Quinlan (1990b) The Oronoco Landfill dye trace II: Verification of the effectiveness of monitoring wells at a karst superfund site. 1990 Geological Society of America Annual Meeting, Dallas, Texas, Abstracts with Programs, p. A296.

G.S. Austin (1969) Paleozoic stratigraphic nomenclature for southeastern Minnesota. Minn. Geol. Survey Information Circular 6, St. Paul., 11 pp.

George S. Austin (1972) Paleozoic Lithostratigraphy of Southeastern Minnesota. In: (P.K. Sims and G.B. Morey, eds.) Geology of Minnesota: A Centennial Volume, Minn. Geological Survey, St. Paul, MN, pp. 459-473.

Braun Engineering Testing (1991) Annual monitoring report Oronoco SLF Olmsted County, Minnesota [for 1990], Report CMKX-91-0163, 8 pp. + 28 Figures + data tables.

Braun Engineering Testing. 1989b. Annual monitoring report Olmsted County Landfill SW-5 calendar years 1986 and 1987. 12 pp.

Braun Engineering Testing. 1989c. Annual monitoring report Olmsted County Landfill, SW-5 calendar year 1988. 10 pp.

Braun Engineering Testing. 1989e. Groundwater sampling and analysis Olmsted County sanitary landfill April 25, 1989. Minneapolis, MN. 2 pp.

Braun Engineering Testing. 1989f. Groundwater sampling and analysis Olmsted County sanitary landfill August 14, 1989. Minneapolis, MN. 2 pp.

Braun Engineering Testing. 1990. Groundwater sampling and analysis Olmsted County sanitary landfill October 30-31, 1989. Minneapolis, MN.

Donohue (1987) Olmsted County Sanitary Landfill: Background Data Evaluation and Preliminary Hydrogeologic Investigation Workplan. Report to Olmsted County dated April 28, 1987, 78 pp plus appendices - not published.

Donohue (1988) Olmsted County Sanitary Landfill: A Proposal for Conducting a Dye Trace Study. Report to Olmsted County dated December 19, 1988, 13 pp. plus appendices.

Donohue (1989a) Dye Trace Study Proposal Addendum. Letter to Mr. Roger Bjork, MPCA, dated March 31, 1989, 12 pp. plus attachments.

Donohue (1989b) Quality Assurance Project Plan (QAPP) For Olmsted County Dye Trace Investigation of Oronoco Sanitary Landfill. Report to Olmsted County dated March, 1989, 42 pp. plus appendices.

Donohue (1989c) Olmsted County Sanitary Landfill: Quality Assurance Project Plan (QAPP) for the Dye Trace Investigation. Report to Olmsted County dated May 8, 1989, 42 pp plus appendices.

Donohue (1990a) Dye Trace Workplan Addendum. Letter to Mr. Rodney Massey, MPCA, 4 pp. plus attachments.

Donohue (1990b) Quality Assurance Project Plan (QAPP) for Olmsted County's Dye Trace Investigation of the Oronoco Sanitary Landfill, May, 1989, Revised March 23, 1990. Report to Olmsted County, 33 pp. plus appendices.

Donohue (1990c) Quality Assurance Project Plan Addendum for Olmsted County's Dye Trace Investigation of the Oronoco Sanitary Landfill, March 26, 1990. Report to Olmsted County, 11 pp. plus appendices.

Malcolm S. Field (1989) The vulnerability of karst aquifers to chemical contamination. In: Moore, Zaporzec, Csallany & Varney (eds.), Recent advances in Ground-Water Hydrology, Proceedings, IAHS, Minneapolis, MN, pp. 130-142.

D. Ford and P. Williams (1989) Karst Geomorphology and Hydrology, Unwin Hyman, Boston, MA, 601 pp.

Michael B.J. Foster, Scott C. Alexander, E. Calvin Alexander, Jr. and Geology 5321 (1990) The October 1989 dual dye trace through the Mystery Cave system. A report to the Minn. Dept. Natural Resources, July, 1990, 29 pp.

Hickok and Associates. 1982. Rochester Sanitary Landfill; An Evaluation of Monitoring System. Wayzata, Minnesota. 51 pp.

Hickok and Associates. 1983a. Olmsted County Sanitary Landfill proposed landfill expansion area report of preliminary investigations. Wayzata, Minnesota. 30 pp.

Hickok and Associates, 1983b. Olmsted County Sanitary Landfill; addendum to report of preliminary investigations. Wayzata, Minnesota. 7 pp.

Hobbs, H.C. 1988. Surficial Geology (Sheet 3 of 9). Geologic atlas, Olmsted County, Minnesota (County Atlas Series C-3). Minnesota Geological Survey. St. Paul, MN.

Hogberg, R.K. 1973. Preliminary report on the geohydrology of the Locoshonas Landfill, Oronoco Township, Olmsted County, Minnesota. Minnesota Geological Survey, University of Minnesota. 10 pp.

Hogberg, R.K. and Todd H. Gilmer. 1976. Development of management methods and techniques to protect the ground water resources of Olmsted County, Minnesota (Minnesota Geological Survey Report of Investigations 15 - Preliminary Submittal). Minnesota Geological Survey, St. Paul, MN. 55 pp.

Roman Kanivetsky (1988) Bedrock Hydrogeology. Plate 5 in (N.H. Balaban, ed.) Geologic Atlas Olmsted County, Minnesota. County Atlas Series Atlas C-3, Minnesota Geological Survey, St. Paul, MN.

E. Mohring and E. Alexander (1986) Quantitative tracing of karst groundwater flow: Southeastern Minnesota, North Central U.S.A. Proceedings 5th International Symposium on Underground Water Tracing, Institute of Geology and Mineral Exploration, Athens, Greece, pp. 215-227.

J.H. Mossler (1987) Paleozoic lithostratigraphic nomenclature for Minnesota. Minn. Geol. Survey Report of Investigations 36, St. Paul, MN, 36 pp.

National Oceanic and Atmospheric Administration (NOAA). 1982. Climatography of the United States No. 84: daily normals of temperature, heating and cooling degree days and precipitation 1951-1980. Minnesota Rochester WSO. Asheville, NC.

NOAA, 1990. Rochester, Minnesota municipal airport local climatological data monthly summary January 1982-February 1990. Asheville, NC.

Olsen, B. 1988a. Bedrock geology (sheet 2 of 9). Geologic atlas Olmsted County, Minnesota (County Atlas Series C-3). Minnesota Geological Survey. St. Paul, MN.

Olsen, B. 1988b. Depth to bedrock and bedrock topography (sheet 4 of 9). Geologic atlas Olmsted County, Minnesota (County Atlas Series C-3). Minnesota Geological Survey. St. Paul, MN.

Arthur H. Perler (1988) Chief, Science and Technology Branch Criteria and Standards Division, USEPA, Washington, DC 20460. Letter dated August 2, 1988 to Janice Warnquist, Chemical Safety Manager, Crompton and Knowles Corporation, P.O. Box 341, Reading, PA 19603.

James F. Quinlan and E. Calvin Alexander, Jr. (1987) How often should samples be taken at relevant locations for reliable monitoring of pollutants from an agricultural, waste disposal, or spill site in a karst terrain? A first approximation. In: Karst Hydrogeology: Engineering and Environmental Applications, Barry F. Beck and William L., Wilson (eds.), Balkema, Boston, pp. 277-286.

J.F. Quinlan and R.O. Ewers (1984) Springs are more efficient and reliable than wells for monitoring ground-water quality in most limestone terrains--a consequence of transport processes occurring in conduits. In: International Conference on Ground-water Quality Research (2nd, Tulsa, OK), Proceedings. pp. 146-148.

James F. Quinlan and Ralph O. Ewers (1985) Groundwater flow in limestone terrains: Strategy Rationale and procedure for reliable, efficient monitoring of groundwater quality in karst areas. In: National Symposium and Exposition on Aquifer Restoration and Groundwater Monitoring (5th, Columbus, Ohio), National Water Well Association, pp. 197-234.

J.F. Quinlan, R.O. Ewers and M.S. Field (1988) How to use ground-water tracing to "prove" that leakage of harmful materials from a site in a karst terrain will not occur. In: Environmental Problems in Karst Terrains and Their Solutions Conference (2nd, Nashville, TN), Proceedings, National Water Well Association, Dublin, OH, pp. 289-301.

James F. Quinlan (1989) Ground-water monitoring in karst terrains; Recommended protocols and implicit assumptions. USEPA, Environmental Monitoring Systems Laboratory, Las Vegas, NV, EPA 600/X-89/050, 79 pp.

RMT, Inc., 1990; Evaluation Report, Olmsted County Landfill, Oronoco Township, Minnesota.

R.E. Sloan (1987) Middle and Late Ordovician lithostratigraphy and biostratigraphy of the Upper Mississippi valley. Minn. Geol. Survey Report of Investigations 35, St. Paul, MN, 64 pp.

P.L. Smart (1984) A review of the toxicity of twelve fluorescent dyes used for water tracing. NSS Bulletin, vol. 46, pp. 21-33.

P.L. Smart and I.M.S. Laidlaw (1977) An evaluation of some fluorescent dyes for water tracers. Water Resources Research, vol. 13, pp.15-33.

Martha J. Steele (1989) M.P.H., Senior Associate, Gradient Corporation, 44 Brattle Street, Cambridge, MA 02138. Letter dated November 20, 1989 to Peter Kornicki, Vice President, Crompton and Knowles Corporation, 3001 N. Graham St., Charlotte, NC 28233.

Thomas R. Steinheimer and Sharon M. Johnson (1986) Investigation of the possible formation of diethylnitrosamine resulting form the use of Rhodamine WT dye as a tracer in river waters. In: Seymour Subitzky (ed.) Selected Paper in the Hydrologic Sciences 1986. U.S. Geol. Survey Water Supply Paper 2290, pp. 31-49.

W. B. White (1988) Geomorphology and Hydrology of Karst Terrains, Oxford Univ. Press, New York, NY, 464 pp.

P.W. Williams (1983) The Role of the Subcutaneous Zone in Karst Hydrology. Jour. Hydrology, V. 35, pp 93-110.

H.E. Wright, Jr. (1972) Physiography of Minnesota, Rochester Till Plain. In: (P.K. Sims and G.B. Morey, eds.) Geology of Minnesota: A Centennial Volume, Minn. Geological Survey, St. Paul, MN, pp. 577-578.

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