Five-Year Review Report

First Five-Year Review Report

For

Monsanto Chemical Co. (Soda Springs Plant)

Caribou County, Idaho

September 2003

PREPARED BY:

U.S. EPA Region 10
Seattle, Washington

Approved by:

Michael F. Gearheard
Director
U.S. EPA Region 10
Office of Environmental Cleanup

Date:

30 Sept. 2003

First Five-Year Review Report
For
Monsanto Chemical Co. (Soda Springs Plant)
Caribou County, Idaho

Table of Contents

Figures

Appendices

List of Acronyms & Terms

Buffer Area	Portion of Monsanto site outside operating area (approximately 260 acres)
CERCLA	Comprehensive Environmental Response Compensation & Liability Act
Consent Decree	Legal document that implements ROD
COPCs	Constituent of Potential Concern (or COPC)
CWA	Clean Water Act
Decision Documents	ROD and Consent Decree
EPA	United States Environmental Protection Agency, Region 10
Golder	Golder Associates
IDEQ	Idaho Department of Environmental Quality
LBZ	Lower Basalt Zone
MCLs	Maximum Contaminant Levels (or MCL)
Monsanto site	Monsanto Chemical Co. (Soda Springs Plant)
MNA	Monitored Natural Attenuation
MWH	Montgomery Watson Harza
NCP	National Contingency Plan
NFA	No Further Action
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
Operating Area	Portion of Monsanto site inside fence where elemental phosphorous is produced (approximately 540 acres)
POC	Point of Compliance
RA Start	Date in WasteLAN remedial action initiated, October 15, 1998
RAOs	Remedial Action Objectives (or RAO)
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
UBZ	Upper Basalt Zone
WasteLAN	EPA Tracking Database

Executive Summary

Protectiveness Statement

The remedy at the Monsanto Chemical Co. (Soda Springs Plant) currently protects human health and the environment because all known groundwater and soil exposure pathways have been restricted through institutional controls or other means. However, in order for the remedy to be protective in the long-term, the following actions need to be taken: 1) the Lewis well and property needs to be evaluated for institutional controls; 2) Monsanto needs to submit a plan for upgrading their wind dispersal program and for evaluating in the short term those localized areas where increased ^{226}Ra soil concentrations have been observed; and, 3) the U.S. Environmental Protection Agency (EPA) needs to reevaluate during the next five-year review whether the monitored natural attenuation remedy underneath the operating area is proceeding as intended in the decision documents.

Remedies Selected By EPA in the 1997 Record of Decision

EPA selected four remedial actions for the Monsanto site, summarized as follows:

- Monitored natural attenuation with institutional controls for contaminated groundwater.
- Either institutional controls or soil excavation on buffer properties not owned or controlled by Monsanto, at the discretion of the property owners.
- No further action for operating-area source piles and materials. This remedy is subject to continued operations and ongoing five-year reviews**.**
- No further action for air, surface water, and Soda Creek sediments.

Technical Assessment Summary

Of the four remedial actions included in the Record of Decision, EPA has concluded that two of the remedies (institutional controls and no further action for air, surface water, and sediments) are functioning as intended in the decision documents. These remedies also remain valid in terms of exposure assumptions, toxicity data, cleanup levels, and remedial action objectives. In regards to the selected monitored natural attenuation (MNA) remedy for groundwater, EPA has learned that the MNA remedy underneath the operating area may take longer than was anticipated at the time of the Record of Decision. EPA has also decided that the Lewis well may need institutional controls. Otherwise, the MNA remedy for groundwater appears to be working as intended.

The one remedy EPA has concluded is not functioning as intended in the decision documents (no further action for on-site material piles), is summarized as follows ~

No Further Action (NFA) Remedy for On-Site Material Piles

EPA's conclusion that the NFA remedy for on-site material piles is not functioning as intended is based on three observations made during the five-year review, which are described in detail in the main body of the report. EPA has concluded in this instance that the remedial action objectives and related technical underpinnings of the remedy remain valid, though EPA has learned new information about management of material piles at the Monsanto site that has caused EPA to question the protectiveness of this portion of the remedy.

Five-Year Review Summary Form

SITE IDENTIFICATION
Site Name: **Monsanto Chemical Co. (Soda Springs Plant)**
EPA ID: **IDD081830994**
Region: **10** State: **ID** City/County: **Soda Springs, Caribou County**
SITE STATUS
NPL Status: **X Final** Deleted Other (Specify)
Remediation Status: **Construction Complete**
Multiple OUs? **No** Construction completion date: **09/20/2000**
Has site been put into reuse? Yes No **Not Applicable. Site is an operating facility.**
REVIEW STATUS
Lead agency: **X EPA** State Tribe Other Federal Agency
Author name: **Wallace Reid**
Author title: **Remedial Project Manager** Author affiliation: **EPA Region 10**
Review period: **09/27/2002 to 09/30/2003**
Date(s) of site inspection: **06/10/2003**
Type of review: **CERCLA Five Year Review**
Review Number: **X 1 (first)** 2 (second) 3 (third) Other (specify)
Triggering action: **RA Start**
Triggering action date 9from WasteLAN): **10/15/1998**
Due date (five years after triggering action date): **10/15/2003**

Five-Year Review Summary Form ~ continued

Issues:

- Groundwater samples from the Lewis well have revealed elevated cadmium and other hazardous constituent concentrations during the past five years, and the property where this well is located does not have institutional controls.

- MNA for groundwater underneath the operating area may take longer than anticipated during the RI/FS, though this observation needs to be reevaluated during the next five-year review.

- Wind dispersal is occurring from the Monsanto site, and this may be contributing to increasing off-site contamination.

- Three related technical matters that don't lead to EPA concerns about the protectiveness of the MNA remedy for groundwater, but are necessary details to be resolved with Monsanto based on this five year review are: 1) increasing molybdenum concentrations south of the operating area; 2) use of total nitrogen as nitrate for demonstrating compliance with the MCL; and, 3) annual sampling, analyses, and trend evaluation reporting of Soda Creek discharge concentrations at a level of detail similar to annual and five-year review groundwater reporting.

Recommendations and Follow-up Actions:

The five-year review team recommends that:

- EPA request Monsanto to submit a plan by February 1, 2004 pertaining to the Lewis well, examining the options for bringing the Lewis well under institutional controls, and for evaluating whether other such domestic wells may be present in the non-buffer area immediately south of the Monsanto site.

- EPA request Monsanto to submit a plan by February 1, 2004 to control wind dispersal from on-site material piles. This plan shall include a sampling program to investigate areas off-site where ^{226}Ra soil concentrations were found to have increased over the past five years. Monsanto shall conduct the sampling portion of this plan no later than sixty days following EPA approval, and Monsanto shall promptly report all sampling results to affected property owners.

- EPA request Monsanto to perform sampling and five-year review activities on a scale similar to the technical work performed in support of this review. Two exceptions shall be: 1) soil sampling off-site in areas where sampling density may be increased (as determined by results obtained during development of the wind dispersal control plan above); and, 2) Monsanto shall collect and analyze surface water discharges to Soda Creek for hazardous constituents at a level of detail consistent with ongoing groundwater data reporting.

- EPA request Monsanto to engage in technical dialogue with EPA and IDEQ to resolve three related groundwater technical matters described in the main body of the report.

Protectiveness Statement:

The remedy at the Monsanto Chemical Co. (Soda Springs Plant) currently protects human health and the environment because all known groundwater and soil exposure pathways have been restricted through institutional controls or other means. However, in order for the remedy to be protective in the long-term, the following actions need to be taken: 1) the Lewis well and property needs to be evaluated for institutional controls; 2) Monsanto needs to submit a plan for upgrading their wind dispersal program and for evaluating in the short term those localized areas where increased ^{226}Ra soil concentrations have been observed; and, 3) the EPA needs to reevaluate during the next five-year review whether the monitored natural attenuation remedy underneath the operating area is proceeding as intended in the decision documents.

Other Comments: None

Five-Year Review Report

I. Introduction

The purpose of this five-year review effort has been to determine whether the remedy implemented at the Monsanto Chemical Co. (Soda Springs Plant) [Monsanto site] remains protective of human health and the environment. The methods, findings, and conclusions of this five-year review are documented herein. Additionally, issues pertaining to possible remedy failures that could lead to potential exposures are itemized.

The United States Environmental Protection Agency Region 10 (EPA) is preparing this five-year review pursuant to the Comprehensive Response Compensation and Liability Act (CERCLA) § 121 and the National Contingency Plan (NCP). CERCLA § 121 states:

> ***If the President selects a remedial action that results in any hazardous substances, pollutants, or contaminants remaining at the site, the President shall review such remedial action no less often than each five years after the initiation of such remedial action to assure that human health and the environment are being protected by the remedial action being implemented. In addition, if upon such review it is the judgment of the President that action is appropriate at such site in accordance with section [104] or [106], the President shall take or require such action. The President shall report to the Congress a list of facilities for which such review is required, the results of all such reviews, and any actions taken as a result of such reviews.***

The agency interpreted this requirement further in the NCP; 40 CFR §300.430(f)(4)(ii), which states:

> ***If a remedial action is selected that results in hazardous substances, pollutants, or contaminants remaining at the site above levels that allow for unlimited use and unrestricted exposure, the lead agency shall review such action no less often than every five years after the initiation of the selected remedial action***

The EPA conducted a five-year review of the remedial actions implemented at the Monsanto site from September 2002 to September 2003. This report documents the results of this review. Monsanto retained independent contractors to perform investigations and to provide data as directed and approved by EPA in support of this five-year review. Montgomery Watson Harza (MWH) performed soil and sediment investigations and Golder Associates (Golder) performed groundwater monitoring.

The five-year review team consisted of Wallace Reid from EPA, Douglas Tanner, Margie English, and Clyde Cody from the Idaho Department of Environmental Quality (IDEQ), Robert Geddes of Monsanto, and various other Monsanto staff and contractors.

The entire project team, except Margie English from IDEQ, attended the site visit with EPA in Soda Springs on June 10th, 2003. IDEQ has also provided comments to EPA on a number of topics covered in this report, including interpretation of groundwater data. EPA also sent information about this five-year review effort to the general public in Soda Springs during June 2003 and offered to consider any comments the public might wish to make about the Monsanto site. A copy of EPA's notice to the public regarding the five-year review is included as Figure 1.

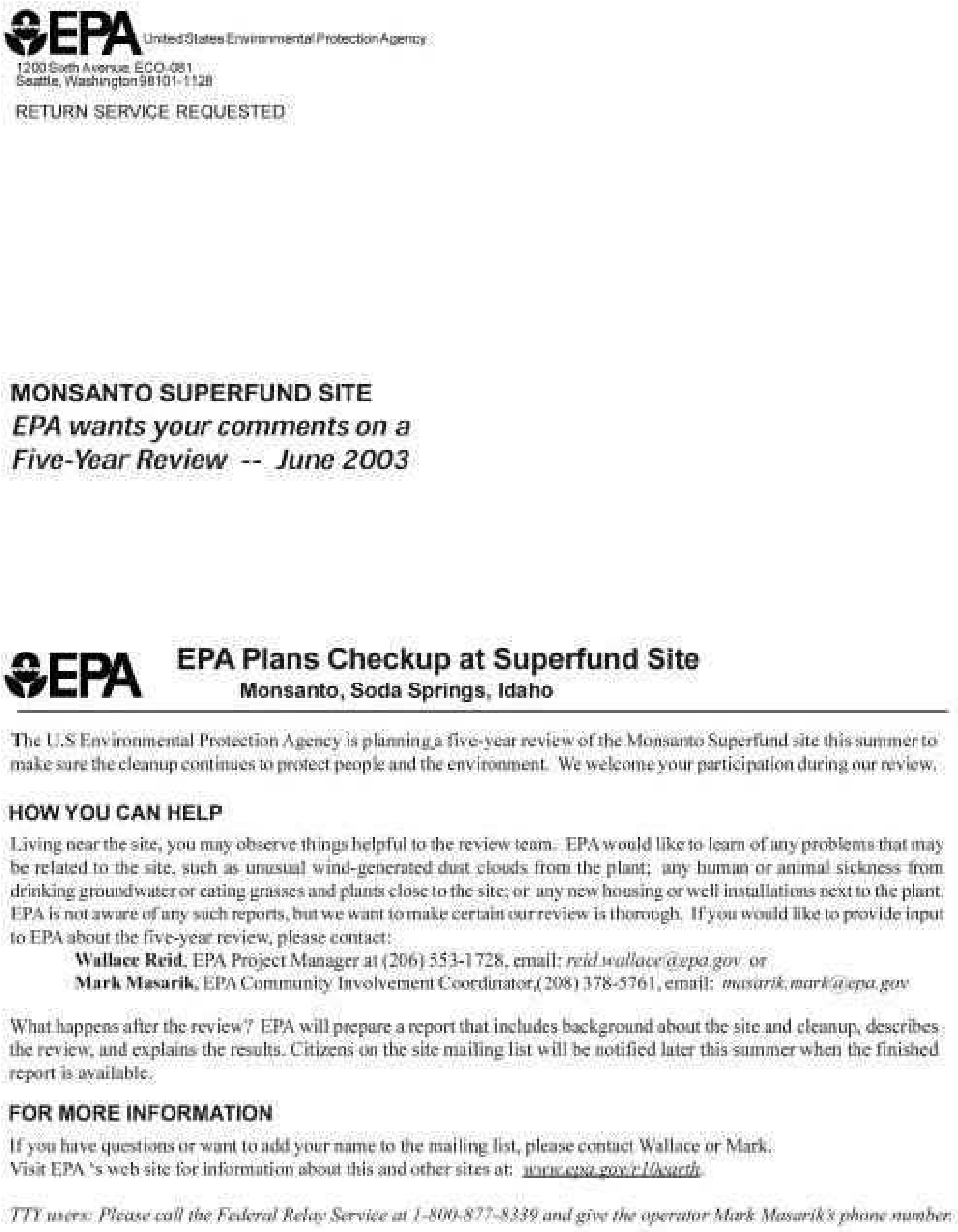
This is the first five-year review for the Monsanto site. The triggering action for this review is the date remedial activities were initiated, October 15th, 1998, as shown in EPA's WasteLAN database. Although the site has achieved construction completion status, the contaminants of potential concern (COPCs; used interchangeably in this report with the term "hazardous constituents") in both groundwater and soil remain elevated above background levels at some locations. This review was conducted to determine whether the remedy of institutional controls and monitored natural attenuation (MNA) remain protective.

Important language used for the first time in this five-year review and not used in the Monsanto decision documents (Record of Decision [ROD] and Consent Decree) are the terms: "operating area" and "buffer area". The term "operating area" is used in this five-year review to reference all Monsanto property inside the fence intended to secure operations of the currently operating Monsanto elemental phosphorous plant. The phrase "buffer area" is used in this five-year review to reference all Monsanto-owned and other properties outside the fence for which institutional controls have been recorded in Caribou County. The operating area and buffer area constitute the entire Monsanto site subject to this five-year.

II. Site Chronology

Event	**Date**
Confirmation of initial discovery of contamination	1985
Site added to the national priorities list (NPL)	August 30th, 1990
Administrative Order On Consent	March 19th, 1991
Remedial Investigation/Feasibility Study (RI/FS)	April 1996
Record of Decision Signed	April 1997
Consent Decree Signed	September 1997
Remedial Activities Initiated (RA Start)	October 15th, 1998
Construction Completion Date	September 20, 2000
First Five-Year Review Due Date	October 15, 2003

Figure 1
EPA Notice to Public Regarding Five-Year Review



EPA United States Environmental Protection Agency
1200 Sixth Avenue, ECO-081
Seattle, Washington 98101-1128

RETURN SERVICE REQUESTED

MONSANTO SUPERFUND SITE
EPA wants your comments on a
Five-Year Review -- June 2003

EPA Plans Checkup at Superfund Site
Monsanto, Soda Springs, Idaho

The U.S Environmental Protection Agency is planning a five-year review of the Monsanto Superfund site this summer to make sure the cleanup continues to protect people and the environment. We welcome your participation during our review.

HOW YOU CAN HELP

Living near the site, you may observe things helpful to the review team. EPA would like to learn of any problems that may be related to the site, such as unusual wind-generated dust clouds from the plant; any human or animal sickness from drinking groundwater or eating grasses and plants close to the site; or any new housing or well installations next to the plant. EPA is not aware of any such reports, but we want to make certain our review is thorough. If you would like to provide input to EPA about the five-year review, please contact:

Wallace Reid, EPA Project Manager at (206) 553-1728, email: *reid.wallace@epa.gov* or
Mark Masarik, EPA Community Involvement Coordinator,(208) 378-5761, email: *masarik.mark@epa.gov*

What happens after the review? EPA will prepare a report that includes background about the site and cleanup, describes the review, and explains the results. Citizens on the site mailing list will be notified later this summer when the finished report is available.

FOR MORE INFORMATION

If you have questions or want to add your name to the mailing list, please contact Wallace or Mark.
Visit EPA 's web site for information about this and other sites at: www.epa.gov/r10earth.

TTY users: Please call the Federal Relay Service at 1-800-877-8339 and give the operator Mark Masarik's phone number.

III. Background

A. Physical Characteristics

The Monsanto site is located in Caribou County, Idaho, approximately one mile north of the City of Soda Springs. [See Figure 2, Area Map.] Whereas most sites listed on the NPL consist primarily of contaminated properties containing little or no operating facilities, the Monsanto site in Soda Springs houses the only operating elemental phosphorus plant in the United States. The operating area (see Introduction or Acronyms for definitions of "operating area" and "buffer area") of the Monsanto site occupies approximately 540 acres. The size of the entire Monsanto site is approximately 800 acres, which includes the operating area as well as 260 acres of buffer area outside the fenced operating area. The buffer area, as well as the operating area inside the fence, contain institutional controls that were required as part of the decision documents. [See Figure 3, Vicinity Map.] The institutional controls are federally enforceable conditions pursuant to the decision documents, which bind Monsanto to maintain these institutional controls in perpetuity so long as elevated levels of hazardous constituents remain in place. Monsanto implements these institutional controls by recording property restrictions in Caribou County, including the decision documents and appropriate property easements. These property actions vary from parcel to parcel due primarily to the interests of private individuals who own portions of the buffer area; some of the buffer area is owned by Monsanto. The closest surface water body is Soda Creek, located 2,000 feet west of the operating area.

B. Land and Resource Use

The City of Soda Springs is located approximately one mile south of the Monsanto site with a population of about 3,300. Land use within the city limits is mostly residential with some commercial, agriculture, and light industrial zones. A light and heavy industrial zone extends from the north end of the City along State Highway 34 towards the Monsanto site.

The Monsanto site is located outside Soda Spring's city limits. The Monsanto workforce population is approximately 400. Land use within the fenced operating area is industrial. The Monsanto owned property includes agricultural land to the south and southwest of the operating area, and is surrounded by open agricultural and rangelands.

There are significant groundwater resources underneath the broad valley where both the Monsanto site and Soda Springs are located. The groundwater generally flows southward underneath the Monsanto site and then toward Soda Springs. However, even though Soda Springs is located hydraulically down-gradient of the Monsanto site, the Soda Springs population receives residential water supplies from either Formation Spring to the northeast or Ledger Creek Spring to the southeast. Both of these locations are unaffected by ground water flowing beneath the Monsanto site, and EPA reaffirmed as part of this five-year review that Soda Springs' water supplies are unaffected by the Monsanto site.

Figure 2
Area Map

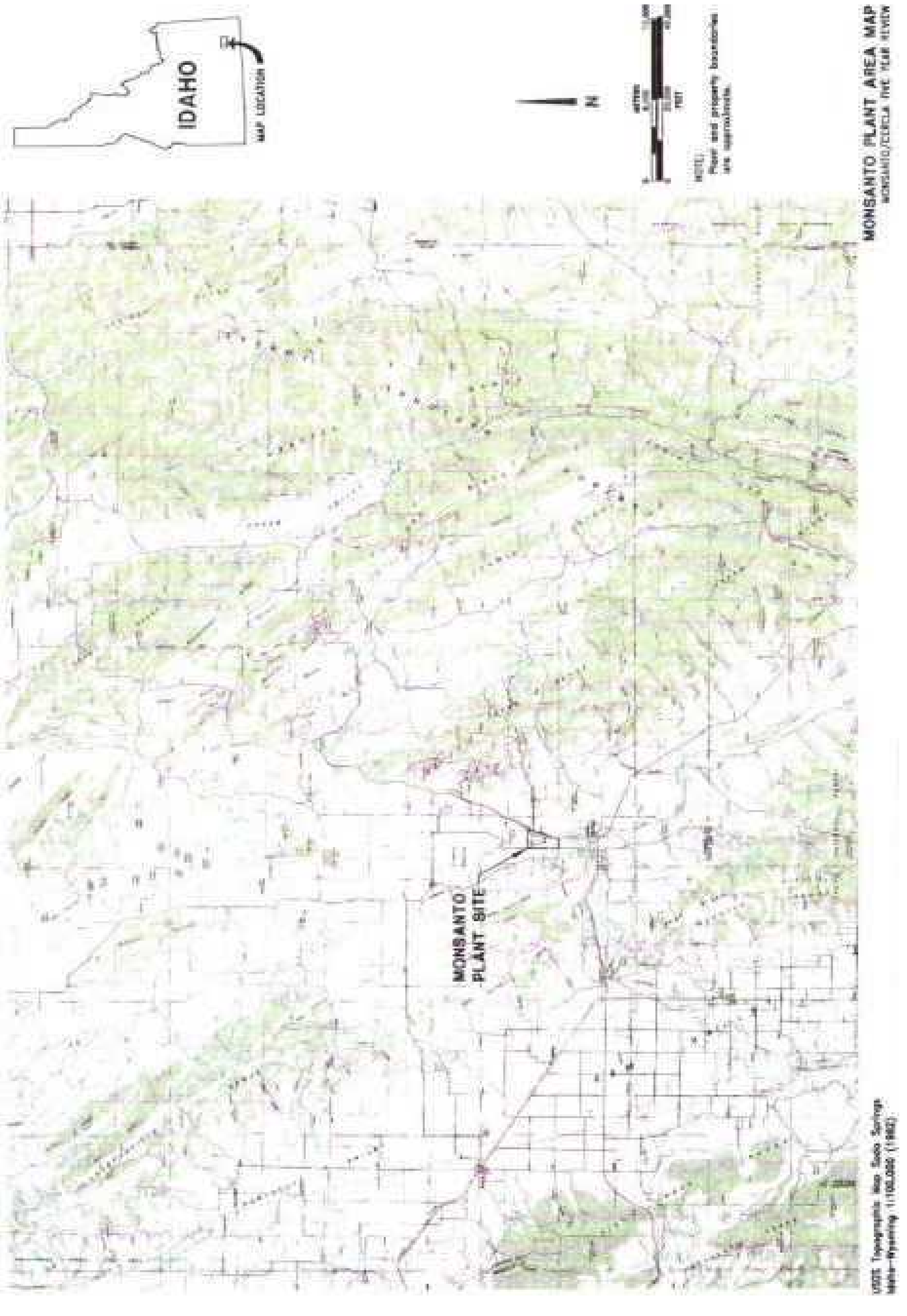
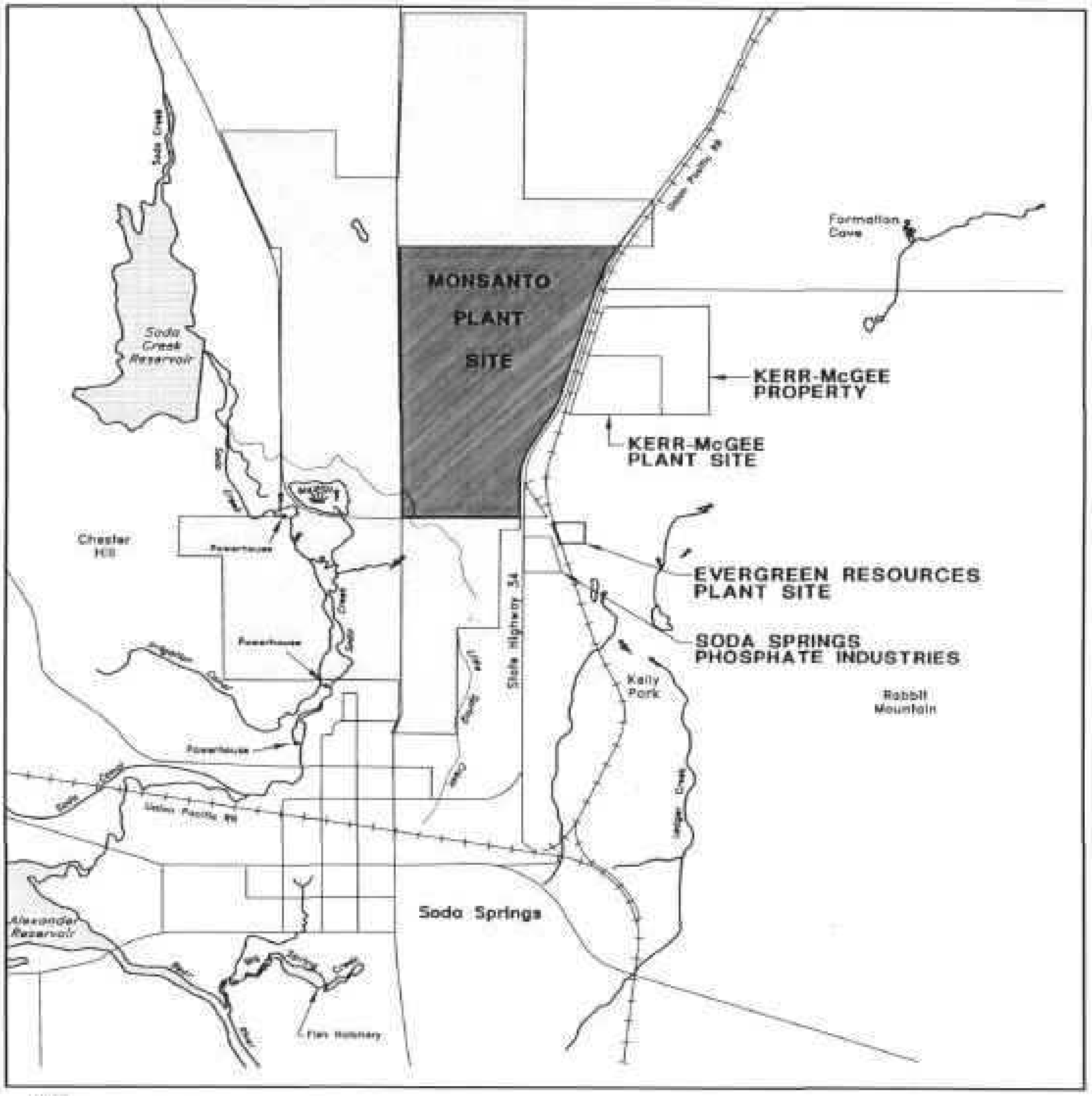


Figure 3
Vicinity Map



NOTE:
Plant and property boundaries are approximate.

SOURCE:
MONSANTO/PHASE II RI REPORT (GOLDER 1995)

LEGEND:

▨ MONSANTO PLANT SITE

☐ PROPERTY OWNED OR DEED RESTRICTION PURCHASED BY MONSANTO

MONSANTO PLANT VICINITY MAP
MONSANTO/CERCLA FIVE YEAR REVIEW

Groundwater hazardous constituent concentrations immediately south of the Monsanto operating area, but still within the buffer area, remain elevated above maximum contaminant levels (MCLs) for several hazardous constituents. This will be described in more detail herein. EPA is aware of one private groundwater well (Lewis well) south of the Monsanto buffer area that is elevated above MCLs, but has also observed a general trend of decreasing concentrations over the last five years in both the buffer area and the operating area. This trend predates the decision documents and may be attributed in some measure to operating changes Monsanto implemented after they learned groundwater contamination was found south of their site in the mid-1980s.

C. History of Contamination

Monsanto purchased the operating area property in 1952 in order to build the elemental phosphorus plant, which was located to take advantage of locally mined phosphate ore. Prior to EPA's CERCLA involvement, Monsanto hired Golder in 1984 to characterize groundwater impacts from past and current operations. This was approximately five years prior to EPA listing the Monsanto site on the NPL.

This pre-CERCLA investigation showed that groundwater under the Monsanto site contained elevated levels (above MCLs) of fluoride, cadmium, selenium, and vanadium. Monsanto determined from this work (without any EPA or IDEQ oversight) that their underflow solids pond, northwest pond, hydroclarifier, and intermediate processing steps in the elemental phosphorus production process were leaking into the subsurface and into groundwater, thereby creating the elevated hazardous constituent concentrations.

Kerr-McGee Chemical Corp. owned property (which they still own) and operated an industrial facility (now closed) in 1986, when the RI/FS for Monsanto was completed, immediately to the northeast of the Monsanto site. A separate plume unrelated to Monsanto (containing chloride, sulfate and vanadium) was also discovered by Golder. This plume originated on Kerr-McGee Chemical Corps. property to the east and extended onto the southeast portion of the Monsanto site. This plume still exists and is subject to investigation and follow-up by EPA pursuant to a separate action under CERCLA. The Kerr-McGee plume is distinguishable from the Monsanto plume by the distinct suite of hazardous constituents involved, so EPA's primary intent in this Monsanto five-year review is to acknowledge the Kerr-McGee plume for clarity, and to evaluate whether this plume interferes with the effectiveness of Monsanto's remedial activities. To date, EPA has not observed significant Monsanto issues pertaining to the Kerr-McGee plume. However, groundwater in the Lewis well south of the Monsanto buffer area contains elevated hazardous constituents from both the Kerr-McGee and Monsanto plumes, and this well is currently not protected by institutional controls. This matter is discussed later in this five-year review report.

D. Initial Response

Based on Monsanto's disclosure of groundwater impacts, EPA sampled in 1987 and found elevated levels of fluoride, cadmium, selenium, and sulfate in monitoring and production wells at the Monsanto site. Due largely to potential human health and environmental exposures from contaminated groundwater flowing south from the Monsanto site towards Soda Springs, and due also to documented environmental and likely human exposures to excess fluoride from at least one local well, EPA added the Site to the NPL on August 30, 1990.

E. Basis for Taking Action

Introduction

Between March 1991 and April 1996, Monsanto performed an RI/FS under EPA oversight. Investigations were performed for groundwater, soil, source materials, surface water, air, biota, and sediments. Constituents of potential concern were identified based on exceedances of EPA risk screening criteria. Sixty monitoring wells, eighteen spring locations, numerous off-plant soil-sampling locations, and sediment sampling locations from Soda Creek and Alexander Reservoir were sampled and chemically analyzed.

Issues of Potential Concern

A summary list of potential exposure concerns during the RI/FS included: 1) ^{226}Ra (radionuclide) exposures in the operating area, primarily to Monsanto employees; 2) potential residential exposures to metals and radionuclides in groundwater, soil, and air immediately outside the operating area if future residential development were not controlled; 3) potential elevated exposures inside the operating area if Monsanto or future property owners developed industrial processes other than the existing elemental phosphorous plant; 4) groundwater threats to the City of Soda Springs water supply; and, 5) surface water discharges to Soda Creek. The first three of these concerns at the conclusion of the RI/FS ended up being the primary drivers for development of remedial actions at the Monsanto site. The last two concerns were carried through the RI/FS, but EPA concluded in the decision documents that no remedial actions were necessary; these two issues are summarized below.

City of Soda Springs Water Supply

Groundwater generally flows southward underneath the Monsanto site and then toward Soda Springs. This was of great concern to EPA at the time the Monsanto site was listed on the NPL, but during the RI/FS EPA learned that groundwater supplies for Soda Creek are delivered from either Formation Spring to the northeast or Ledger Creek Spring to the southeast. Both of these locations are unaffected by ground water flowing beneath the Monsanto site.

Despite the finding that general water supplies to the City of Soda Springs were (and remain) unaffected by the Monsanto site, local groundwater immediately south of the operating area was (and still is) clearly impacted. Much of this area is now buffer area, since Monsanto has either purchased these properties or has purchased restrictive covenants to control further development. For example, Monsanto purchased the Harris properly immediately south of and adjacent to the operating area. Monsanto then closed the Harris well to prevent further consumptive uses, though it is still used for environmental monitoring. EPA is aware of only one private domestic well (the Lewis well) immediately south of the Monsanto site that is not restricted via institutional controls. This well appears to be affected by both the Monsanto and Kerr-McGee groundwater plumes, and it has over the past five years experienced concentrations of cadmium, fluoride, and other constituents that have exceeded MCLs. Monsanto and Kerr-McGee have cooperated to replace the Lewis home water supply with City of Soda Springs water. Therefore, the human consumption issues for the Lewis family have been resolved, but the long-term disposition of the Lewis well, the Lewis property, and surrounding private properties, remains unknown. Without institutional controls the Lewis well and property could transfer ownership without any notice to EPA or IDEQ, and use of the Lewis well could be altered without notice, which is of concern to EPA.

Surface Water Discharge to Soda Creek

The Monsanto elemental phosphorous plant pumps groundwater for production purposes and then discharges excess groundwater via a point source (pipeline) discharge to Soda Creek pursuant to a National Pollutant Discharge Elimination System (NPDES) permit. The NPDES permit was written to control thermal loading to Soda Creek, meaning that Monsanto must control the temperatures and total heat content they deliver to Soda Creek. Not included in the NPDES permit are any controls over other hazardous constituents that are also present in Monsanto's surface water discharge; these hazardous constituents are present in the discharge in part because they are present in groundwater that Monsanto pumps out of the ground for use in their plant. For example, discharge sample results over the past five years have documented excess (above MCL) concentrations of cadmium. This is not prohibited by the NPDES permit, and potential revision of the NPDES permit is outside the scope of this five-year review. Such review, if required, would be carried out by EPA's Clean Water Act (CWA) program in consultation with IDEQ. This five-year review report will be delivered to EPA's Clean Water Act program management for their consideration. Wallace Reid, EPA employee in the CERCLA program, did consult on at least two occasions during this five-year review with staff in EPA's CWA program. Mr. Reid learned that the Monsanto NPDES permit will not be subject to revision by EPA in the foreseeable future.

During the RI/FS EPA was concerned that contaminated surface water discharged to Soda Creek could end up being applied to crops or used for livestock. Thus, EPA decided at that time to test for hazardous constituent concentrations in surface water and sediment. Even though some COPCs were elevated in Soda Creek surface water and sediments relative to background concentrations, these concentrations were not sufficiently high for EPA to require remedial action. Both human-health and ecological exposures were considered in EPA's January 1995 baseline risk assessment, and in both cases the risks did not exceed EPA risk criteria for the Monsanto site. EPA therefore decided in the decision documents that no remedial activities were required to control discharges to Soda Creek, except annual monitoring and reevaluation of this decision during subsequent five-year reviews. EPA did obtain additional sediment samples from Soda Creek and Alexander Reservoir as part of this five-year review, and the results of these analyses are described later in this report.

Monsanto Site Risks Requiring Remedial Action

After completing the RI/FS, EPA decided the following potential Monsanto site exposures warranted remedial action:

1. Operating area (inside the fence) exposures to radionuclides from slag and source materials, which would primarily affect Monsanto employees;
2. Potential future exposures of people to metals and radionuclides in groundwater, soil, and air in any residential development that might be constructed on the immediate southern or northern fence-line areas immediately outside the Monsanto operating-area; and,
3. Potential increased Monsanto operating-area exposures of industrial employees to radionuclides if the Monsanto plant ever closed and were redeveloped for other industrial uses.

IV. Remedial Actions

A. Remedy Selection

The selected RAOs are detailed in the ROD and summarized below.

1. Prevent human ingestion of, inhalation of, or direct contact with groundwater at levels exceeding: cadmium 0.005 mg/L; fluoride 4 mg/L; manganese 0.015 mg/L; nitrate as N 44 mg/L; selenium 0.05 mg/L.
2. The ultimate goal of the remedy for groundwater is to eliminate groundwater contamination sources and to restore the shallow groundwater aquifer underlying the site to levels below applicable MCLs (no distinction between the operating area and buffer area is made in the ROD).

3. Prevent external exposure, ingestion, or inhalation exposure to ^{226}Ra soil concentrations exceeding 3.7pCi/g and a radiation effective dose equivalent of 15 mrem/year.

4. RAOs for the operating area material piles (identified in the ROD as solid waste piles) are not necessary due to wind dispersal controls implemented for these piles, and because Monsanto has an effective worker protection program; should these conditions change, RAOs to control off-plant dispersal of contaminants and to promote on-site worker protection would be required.

5. These RAOs are contingent on continued operation of the Monsanto elemental phosphorus plant. If Monsanto stops pumping production wells, converts the site to other industrial uses, or otherwise changes its operations in any substantial way, the RAOs will need to be reconsidered and/or amended by EPA. Any required changes to the remedy for the site based on amended RAOs would then also need to be considered at that time. During this five-year review Monsanto reiterated to EPA their intention to continue operation of the elemental phosphorous plant for the foreseeable future.

The selected remedies in the ROD to achieve the above RAOs are:

1. MNA with institutional controls for contaminated groundwater.

2. Either institutional controls or soil excavation on buffer properties not owned or controlled by Monsanto, at the discretion of the property owners.

3. No further action (NFA) for operating area source piles and materials. This remedy is subject to continued operations and ongoing five-year reviews.

4. No further action for air, surface water, and Soda Creek sediments.

B. Remedy Review

The CERCLA Five-Year Review requirements as determined by the ROD include the following:

1. Groundwater ~ review and assess groundwater and outfall monitoring data (which should be collected and evaluated at least annually).

2. Groundwater & Surface Water ~ compare groundwater and outfall quality and extent of contamination (plume(s)) to regulatory levels, remediation goals and groundwater modeling projections. Determine if/when remediation goals have been achieved, and if not, that institutional controls are still in place and effective.

3. Sediments ~ sediment samples should be collected to support the five-year review assessment of whether contaminant concentrations are remaining stable or declining as predicted.
4. Soils ~ soil sampling should be done no less often than every five years to: a) determine the concentrations of COPCs in soils; and, b) verify that source control is effectively preventing further spread of site contaminants and/or recontamination of soils.
5. Institutional Controls ~ review that institutional controls are in place for all soil grids surrounding the plant which contain ^{226}Ra concentrations greater than the remediation goal of 3.7 pCi/g, based on a statistically valid sampling program.
6. Operating Area ~ verify that operations continue to be in compliance with environmental and worker health and safety requirements so that potential releases and exposures remain adequately controlled and the remedy remains effective. Evaluate dust control efforts and land-use/institutional controls, and determine if closure has occurred or is planned.

C. System Operations/O&M

Although the ROD required no remedial construction activities except potential buffer area excavations as described above, Monsanto has reported to EPA several voluntary remedial construction activities from 1985 to the present. These activities were not performed under EPA or IDEQ oversight, and neither agency can confirm these details, but site operational changes do appear to have reduced the hazardous constituent loading to groundwater, as evidenced by decreasing concentrations in many site wells.

- In August, 1985, the old hydroclarifier, which was suspected as potentially affecting groundwater, was replaced with a unit that includes a synthetic liner, a leachate collection system, and a monitoring well network.
- In 1986, an old coke and quartzite dryer and wet scrubber was replaced with a more efficient dryer and dust collector, resulting in air emission reductions of over 95 percent. The coke and quartzite dust slurry ponds were remediated and capped.
- In 1986, four underground fuel storage tanks were replaced with aboveground tanks with concrete sumps. These underground tanks were removed to comply with new regulations. There was no indication that leaking had occurred.

- In September 1987, four parallel high-energy venturi scrubbers, separators, fans and stacks were installed to provide additional scrubbing of kiln exhaust. The parallel arrangement of equipment effectively reduced upset/breakdown emissions that would occur if only one or two fans existed. This project resulted in a reduction of particulate emissions of about 95% and contributes to a cumulative cleaning efficiency of 99.9 percent.

- In 1987, four wells (TW-3, TW-4, TW-5, and TW-6) which were discovered to be creating hydraulic communication between upper and lower aquifers due to poor construction were abandoned in accordance with regulatory guidelines.

- In 1983, the old underflow solids ponds suspected as sources of groundwater contamination were taken out of service. Much of the solids were subsequently excavated and recycled. In 1988, the upper layer of contaminated soil was removed, and the depression was back-filled with material excavated from the northwest pond (see below) and with clean material. The ponds were then filled with molten slag and sealed with a bentonite cap to isolate the remaining underflow solids from infiltration and prevent further migration of contaminants. Solids that remained in the pond are below the cap, but above the water table.

- In 1988, the northwest pond, also a suspected groundwater contamination source, was closed and excavated. Discolored soils were removed and deposited in the old underflow solids ponds. The base of the pond was sealed with bentonite. The area is currently permitted by IDEQ to received Plant sanitary solid waste and is being operated as a lined general waste landfill.

- In 1988, a new operating-area drinking water well (PW-4) was installed upgradient of known and suspected source areas to prevent degradation of the potable water supply. A new independent potable water distribution system was installed with the new well, thus preventing cross-connection of potable and raw process water.

- Between 1985 and 1989, several wells were installed around the hydroclarifier and used as recovery wells to intercept contaminated groundwater. The groundwater was pumped into the new hydroclarifier. Three wells were pumped intermittently at a rate of approximately 12 gallons per minute per well from *1985* to 1989.

- Since 1990, fugitive emissions from the baghouse dust disposal pile have been reduced through improved handling procedures and placing crushed slag on the surface of unused portions of the pile. Additional projects have significantly reduced fugitive air emissions from the conveyance of slag from the furnace.

- During 1992, emission controls were implemented in the nodule reclaim area. These controls included a stationary stacking tube and dust collectors at material transfer points to reduce fugitive dust emissions.
- Three separate “short-runner” projects have been implemented to significantly reduce fugitive air emissions from the conveyance of slag from the furnace to pots. Pots were moved and the shorter conveyance area fully enclosed. The No. 8 furnace project was completed during 1992. The short-runner upgrade to furnace No. 9 was implemented in 1993, and a similar upgrade for furnace No. 8 was completed in 1994.
- In 1993, sewage evaporation ponds were taken out of service and the Plant was connected to the City wastewater collection system. The ponds were closed in 1995.
- The one rural road was paved during spring 1995.
- The operating area is now free from regulated PCB containing equipment.

V. Progress Since the Last Review

This is the first five-year review.

VI. Five-Year Review Process

A. Administrative Components of the Five-Year Review Process

The team for this five-year review effort included representatives from EPA, IDEQ, and Monsanto. Team members were previously identified in the introduction to this report. EPA representatives in Boise also assisted in issuing a notice to the public that this five-year review effort was proceeding, and informed the public that EPA would welcome any comments pertaining to the Monsanto site in Soda Springs.

EPA requested and approved a Monsanto work plan during September 2002 to provide EPA with the technical data necessary to complete the analyses required for this report. Monsanto also submitted a draft Five-Year Report to assist EPA in this effort. EPA has used the technical data and information Monsanto provided under EPA's oversight, but all technical analyses, conclusions, and recommendations included in this report are solely those of EPA, in consultation with IDEQ.

B. Document Review

The RI/FS, ROD, Consent Decree, annual groundwater monitoring data, and appendices to this five-year review report were all reviewed in support of this five-year review effort.

C. Data Review

1. Sediment Investigation

Sediment samples were collected by Monsanto during October 2002 in accordance with the EPA approved "Work Plan and Sampling and Analysis Plan for CERCLA Five-Year Review". The sampling approximated previous sampling performed as part of the RI/FS in Soda Creek and the Alexander Reservoir. Samples collected during the five-year monitoring program were analyzed for arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and polonium-210 (^{210}Po). Appendix A, Alexander Reservoir and Soda Creek Sampling Results provides a complete presentation of the data collection and analyses. Appendix C, Monsanto Plant Sediment Data Validation and Quality Control Summary is provided in support of Appendix A. The results are summarized below.

2. Alexander Reservoir

The Table below summarizes the sediment analytical results from Alexander Reservoir. The entire suite of analytical results and discussion are provided in Appendix A and hereby incorporated into the official record for this five-year review. EPA has concluded from this data that monitored hazardous constituents in this portion of Alexander Reservoir are not increasing, and there is a general trend of decreasing concentrations. This conclusion is narrowly applicable to the location in Alexander

Reservoir where Bear Creek ("Control") and Soda Creek ("Affected") discharge into the Reservoir. Soda Creek is the water body into which Monsanto discharges their excess groundwater and surface water. The column "RI" refers to analytical results observed during the remedial investigation during the mid-1990s, and the column "M" refers to analytical results observed during this five-year review process. The results in the "RI" columns were used in EPA's risk assessments during the mid-1990s to determine that no remedial action was required to control Monsanto discharges to Soda Creek.

Sediment Quality Summary in Alexander Reservoir*

	Control RI	**Control M**	**Affected RI**	**Affected M**
$[\mathrm{As}]_{sed}$ mg/kg dw	**2.4**	**1.9**	**5.9**	**3.6**
$[\mathrm{Cd}]_{sed}$ mg/kg dw	**0.30**	**0.46**	**8.9**	**2.8**
$[\mathrm{Cu}]_{sed}$ mg/kg dw	**6.7**	**5.1**	**6.4**	**5.9**
$[\mathrm{Ni}]_{sed}$ mg/kg dw	**8.0**	**7.2**	**20**	**11**
$[\mathrm{Se}]_{sed}$ mg/kg dw	**0.70**	**0.29**	**2.3**	**0.66**
$[\mathrm{Ag}]_{sed}$ mg/kg dw	**0.040**	**0.077**	**0.10**	**0.087**
$[\mathrm{V}]_{sed}$ mg/kg dw	**19**	**7.8**	**25**	**11**
$[^{210}\mathrm{Po}]_{sed}$ mg/kg dw		**1.1**		**1.2**

* **Sample analytical results for this five-year review are average values, representing 9 sediment samples in the control area and 9 sediment samples in the affected area. The statistical average includes all samples collected in each area. All individual sediment results are presented in Appendix A.**

3. Soda Creek

The Table below summarizes the sediment analytical results from Soda Creek. The entire suite of analytical results and discussion are provided in Appendix A. EPA has concluded from this data that monitored hazardous constituents in this portion of Soda Creek are not increasing, and there is a general trend of decreasing concentrations. The column "RI" refers to analytical results observed during the remedial investigation during the mid-1990s, and the column "M" refers to analytical results observed during this five-year review process. "Control" in this context means upstream of the Monsanto outfall to Soda Creek and "Affected" means downstream from the outfall. The results in the "RI" columns were used in EPA's risk assessments during the mid-1990s to determine no remedial action was required to control Monsanto discharges to Soda Creek.

Sediment Quality Summary in Soda Creek

	Control RI	Control M	Affected RI	Affected M
$[As]_{sed}$ mg/kg dw	**6.2**	**24**	**33**	**9.2**
$[Cd]_{sed}$ mg/kg dw	**11**	**0.38**	**22**	**10**
$[Cu]_{sed}$ mg/kg dw	**2.7**	**6.4**	**18**	**5.1**
$[Ni]_{sed}$ mg/kg dw	**55**	**30**	**35**	**12**
$[Se]_{sed}$ mg/kg dw	**0.60**	**0.79**	**3.5**	**3.3**
$[Ag]_{sed}$ mg/kg dw	**0.10**	**0.14**	**1.6**	**0.11**
$[V]_{sed}$ mg/kg dw	**23**	**50**	**100**	**41**
$[^{210}Po]_{sed}$ mg/kg dw	**0.67**	**0.96**	**1.2**	**2.0**

*** Sample analytical results for this five-year review are average values, representing 7 sediment samples in the control area and 7 sediment samples in the affected area. The statistical average includes all samples collected in each area. All individual sediment results are presented in Appendix A.**

4. Soil Investigation

The soil investigation was conducted by Monsanto during October 2002 in accordance with the EPA approved "Work Plan and Sampling and Analysis Plan for CERCLA Five-Year Review". The sampling approximated previous sampling performed as part of the RI/FS. Samples collected during the five-year monitoring program were subject to analysis for ^{226}Ra, as this was the only hazardous constituent requiring remedial action for off-site soils at the time of the ROD. The summary data presented in this section is detailed in Appendix B, Monsanto Plant Soil Sampling Results, and supported by Appendix D, Monsanto Plant Soil Data Validation and Quality Control Summary Report.

The column "RI" refers to analytical results observed during the remedial investigation during the mid-1990s, and the column "M" refers to analytical results observed during this five-year review process. "Control" in this context means soil samples from locations EPA concluded were generally unaffected by the site, and "Affected" means soil samples from areas where elevated ^{226}Ra concentrations have been observed in the past. The results summarized by the "RI" columns were used in EPA's risk assessments during the mid-1990s to determine that remedial action was required in some areas to control potential exposures from elevated ^{226}Ra concentrations.

Soil Quality Summary Off-Site*

	Control RI	Control M	Affected RI	Affected M
[^{226}Ra]$_{soil}$ pCi/g dw	**1.6**	**1.2**	**1.8**	**1.6**

* **Sample analytical results for this five-year review are average values, representing 6 soil samples in the control area and 39 soil samples in the affected area. The statistical average includes all samples collected in each area. All individual sediment results are presented in Appendix A.**

EPA has noted Monsanto's interpretation that the summarized data above suggest ^{226}Ra soil concentrations have not increased over the past five years. However, regardless of whether this overall Monsanto claim is accurate or not, it fails to reveal that ^{226}Ra soil concentrations actually did increase in 16 of 39 off-site samples collected by Monsanto for this five-year review (approximately 40%). Four of these sixteen increases resulted in exceedances of the 3.7 pCi/g ROD objective in locations where exceedances had not been observed during the RI/FS. Two of these locations are outside the buffer area, where no institutional controls are in place. EPA recognizes that exceeding 3.7 pCi/g in any one sample off-site does not necessarily mean that an immediate exposure problem has been identified. EPA determined during the RI/FS that farming activities would be acceptable in areas where soil concentrations of ^{226}Ra 3.7 pCi/g were exceeded, but that such concentrations would not be acceptable for residential development. The two soil samples collected for this five-year review in which elevated ^{226}Ra soil concentrations were found outside of any institutional controls are from a local farm and an industrial rail yard. An EPA recommendation pertaining to this finding is included in this report.

A related EPA concern generated as a result of this five-year review effort is whether the selected NFA remedy for operating area material piles is further warranted. While EPA acknowledges Monsanto's conclusion that off-site ^{226}Ra sample results do not statistically demonstrate an increasing trend over the broad area under consideration, nonetheless the increased concentration in 40% of all samples collected suggests the possibility that wind dispersal of Monsanto's material piles is leading to unacceptable increases in hazardous constituent concentrations off-site. While the EPA review team was physically located at a sample location where the ^{226}Ra soil concentration had increased, on June 10th, 2003, a local storm event descended on the Monsanto site and our review team observed wind dispersal of materials from the operating area toward our location. An EPA recommendation pertaining to this finding is included in this report.

5. Site Inspection & Interviews

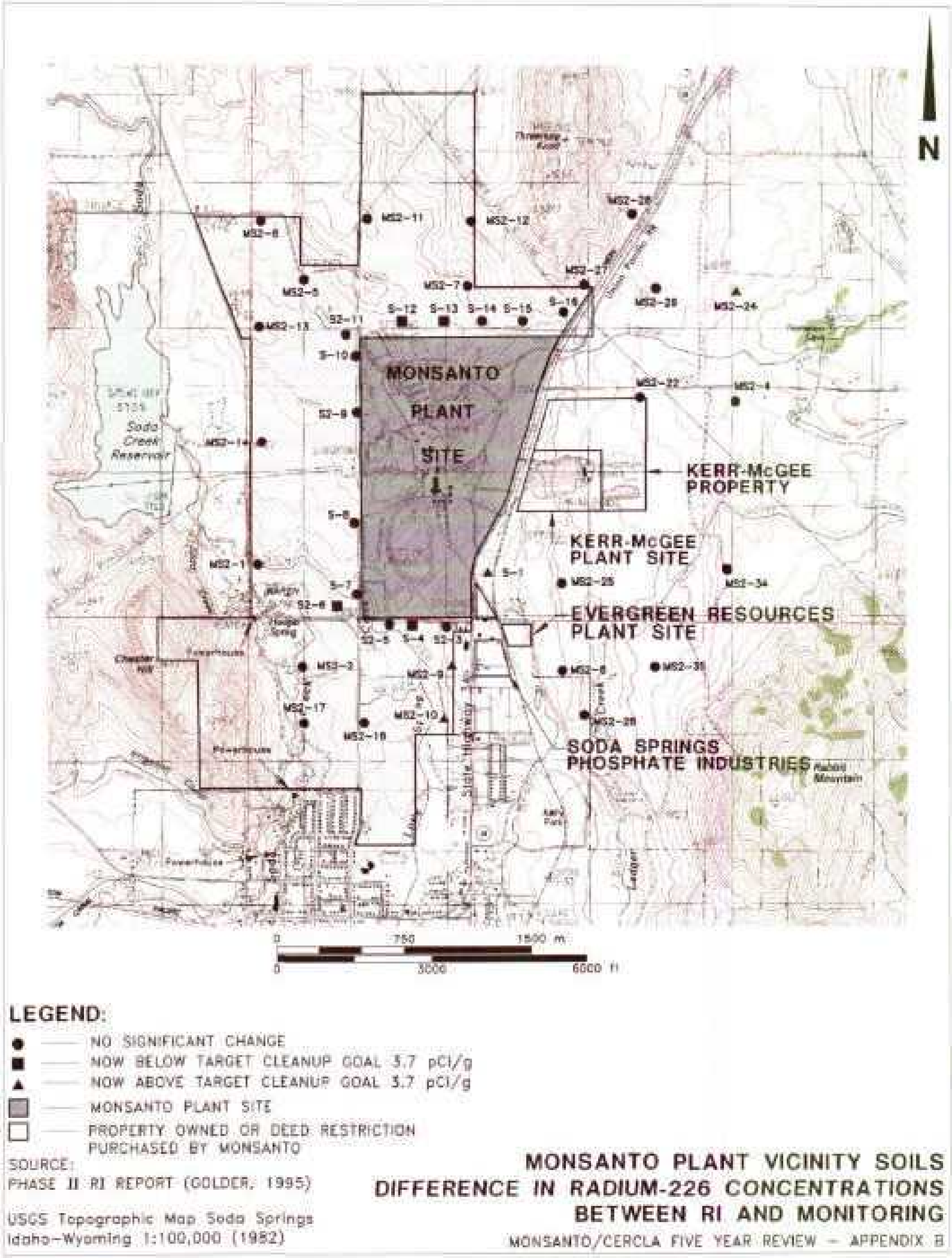
EPA and IDEQ inspected the Monsanto site on June 10th, 2003. Monsanto and their entire technical team participated in the inspection and were the primary interviewees for EPA and IDEQ inquiries. The site inspection occurred over an entire work day and included inspection of: 1) the Monsanto site operating area; 2) Monsanto site buffer area; 3) Alexander Reservoir; 4) Soda Creek, including Soda Creek's discharge location into Alexander Reservoir; and, 5) the soil sample location where an elevated ^{226}Ra concentration was observed.

6. Institutional Control Review

The ROD requires a review of land use and institutional controls for all soil grids surrounding the plant which contain ^{226}Ra concentrations greater than the remediation goal of 3.7 pCi/g based on a statistically valid sampling program. All of the affected property owners (those with soil concentrations exceeding 3.7 pCi/g at the time of the ROD) have elected institutional controls over the option of soil excavation and disposal. Monsanto purchased either the property or an environmental easement for all adjacent agricultural land showing elevated concentrations in the RI/FS, so potential ^{226}Ra exposures identified in the decision documents are controlled as of this five-year review.

Figure 4 shows an updated map of properties currently owned by Monsanto or other parties; parcels for which recorded (in Caribou County) deed restrictions are in place to limit residential uses and groundwater wells. Figure 4 also shows recent ^{226}Ra concentrations observed during this five-year review, which EPA has previously described herein.

Figure 4
Institutional Control Properties



7. Groundwater Investigation

The ROD established the points of compliance (POC) for annual and five-year review monitoring. Well TW-19 is listed as a POC, however, that well does not provide sufficient water. Well TW-20 is located in the same well pair as TW-19 and therefore replaces it as a point of compliance. The ROD also lists TW-29 as a POC. This well is located at the north end of the operating area where groundwater is unaffected by plant operations. This was a typographical error and TW-39 at the south plant fence line was the intended point of compliance. Reflecting these modifications, the POC wells subject to annual and five-year review monitoring are as follows:

- Production Wells: PW-01, 02 and 03
- South Plant Fence Line: TW-20, 34, 35 and 39
- Southern Plant Boundary: TW-53, 54**,** 55 and Hams well
- Soda Creek.

Well TW-34 is affected by naturally occurring manganese concentrations because it is completed in the transition zone between the upper basalt zone (UBZ) (fresh water) and lower basalt zone (LBZ). TW-34 is therefore not appropriate for monitoring the UBZ. The south plant fence line wells are located inside the southern plant fence line near Hooper Springs Road. The southern site wells are located outside the operating area but on Monsanto property in the southern buffer area. In May 2001, two locations were established in Soda Creek at locations upstream and downstream of the effluent discharge (non-contact cooling water) and surface water samples were collected during the 2001 and 2002 sampling rounds.

The ROD requires the following activities:

- Review and assess groundwater and outfall monitoring data (collected and evaluated at least annually), and

- Compare groundwater and outfall quality and extent of constituent plumes to regulatory levels, remediation goals, and groundwater modeling projections. Determine if/when remediation goals have been achieved, and, if not, that institutional controls are still in place and effectively preventing human exposure.

Groundwater POC & Institutional Controls

Based on the June 2002 sampling results, most POC wells are below remediation goals for the COPCs. For fluoride and nitrate, POC wells are below remediation goals. However, cadmium exceeds remediation goals at four POC wells (PW-01, TW-20, 39 and 54), manganese at TW-34, and selenium at six POC wells (PW-01, TW-20, 39, 53, 54 and Harris well).

With one exception, groundwater exceedances are located at points within Monsanto's operating area or buffer area, and EPA notes that concentrations overall are generally decreasing as was anticipated when the ROD was issued. EPA also concludes from the groundwater data that institutional controls necessary to prevent potential groundwater exposures in this southern portion of the Monsanto site are effective at this time, except for the Lewis well (described earlier in this report) which is the subject of an EPA recommendation included in this report.

Another technical matter the EPA review team will recommend for follow-up with Monsanto is the discovery of increasing molybdenum concentrations in groundwater samples collected from at least one southern boundary well (TW-53) and from the Harris well.

Groundwater Observations in the Operating Area

Appendix E provides a detailed presentation of groundwater results. In addition to the COPCs in the ROD, chloride, molybdenum and sulfate were analyzed. Furthermore, the following non-POC wells were monitored for the purposes of determining trends:

- Production well: PW-04
- Northwest Pond area wells: TW-16, 17 and 18;
- Old Underflow Solids Ponds Area Wells: TW-22, 24, 37 and 45;
- Hydroclarifier Area Wells: TW-40 and 44

Wells in the operating area have both increased and decreased in concentration for various COPCs over the past five years. The general trend appears to be decreasing concentrations, with some concentrations staying about the same. Increases in some COPC concentrations have been observed in the following wells, many of which are located near closed waste handling areas or refitted production units.

Fluoride:

Production Wells: PW-02, 03 and 04
Northwest Pond Wells: TW-18
Old Hydroclarifier Wells: TW-44

Manganese

NW Pond wells: TW-17

Selenium

Old Hydroclarifier wells: TW-40

Chloride

Old Hydroclarifier wells: TW-44

Groundwater Transport Modeling

A groundwater solute transport model was developed by Monsanto as part of the RIFS to predict the fate and transport of hazardous constituents in groundwater in the vicinity of the plant for a period of one hundred years. Three endpoints south of the plant were used, (the southern plant boundary, the estimated discharge point of the plume into Soda Creek, and the estimated discharge point of the plume into Bear River). The original RIFS model predicted that the constituent concentrations for cadmium would peak at the southern fenceline in 1994. The model was based on groundwater quality, data over a period of five years, and was revised during the five-year review process based on twelve years of available data. The revised model (Monsanto's model, but with new data) indicates that the cadmium peak will occur at the southern fenceline significantly later than originally anticipated. This information does not seriously raise concerns about meeting groundwater remedial action objectives in the Monsanto site buffer area as anticipated by EPA at the time of the ROD, but it suggests that remedial action objectives for groundwater may be more difficult to achieve underneath the Monsanto site operating area.

Groundwater Conclusion For This Five-Year Review

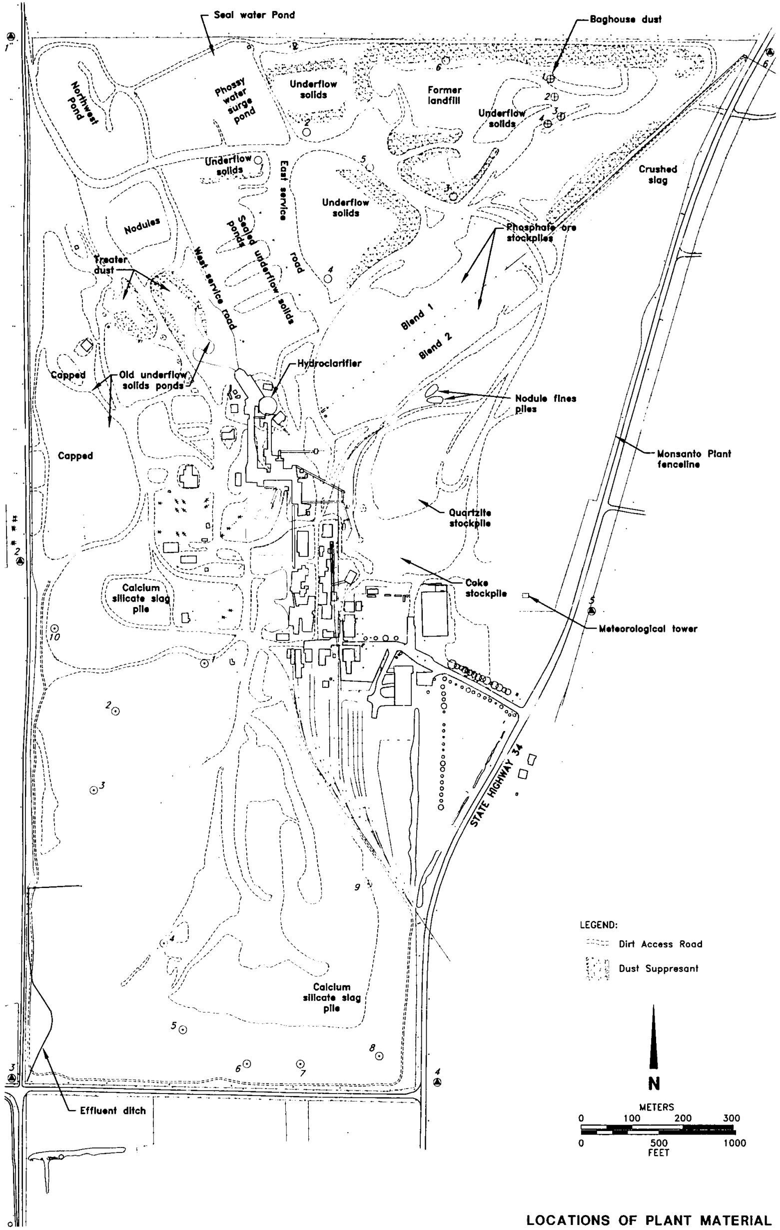
A review of the entire groundwater data set over the past five years (included in Appendix E and in the official record for the Monsanto site) reveals that COPC concentrations in groundwater in the buffer area south of the plant are generally decreasing. This also tends to be the case for wells in the operating area, but there are exceptions to this general trend. EPA has concluded from this that the monitored natural attenuation remedy for groundwater appears, as of this five-year review, to be working as intended in the buffer area and to be moving along somewhat more slowly underneath the operating area. EPA has included a recommendation pertaining to this finding later in the repot.

Three related technical matters that don't lead to EPA concerns about the protectiveness of the MNA remedy for groundwater but are necessary details to be resolved with Monsanto based on this five year review are: 1) increasing molybdenum concentrations south of the operating area; 2) use of total nitrogen as nitrate for demonstrating compliance with the MCL; and, 3) annual sampling, analyses, and trend evaluation reporting of Soda Creek discharge concentrations at a level of detail similar to annual and five-year review groundwater reporting. These technical matters are described in the RI/FS and decision documents, but have not been adequately addressed as of this five-year review in the official record. The EPA review team has included a recommendation in this report to sort out the details of these technical matters with Monsanto based on the findings of this five-year review. If Monsanto believes these maters have already been vetted with the regulatory agencies, they are welcome to point out any portion of the official record for EPA to review and evaluate.

8. Plant Compliance Review

The EPA review team inspected the operating area during the June 10th, 2003 five-year review site visit. We toured the material piles in the northeast quadrant of the operating area, and also noted significant wind dispersal from these piles later in the day. Figure 5 shows the current extent and locations of the material piles.

Figure 5 ~ Material Piles



SOURCE:
MONSANTO TOPOGRAPHIC MAP (April, 2003)

LOCATIONS OF PLANT MATERIAL
AND BY-PRODUCT STOCKPILE LOCATIONS
MONSANTO/CERCLA FIVE YEAR REVIEW

As already noted, EPA did observe wind dispersal from Monsanto's operating area (specifically from the underflow solids pile [shown on Figure 6 above]) during the June 10th, 2003 five-year review site inspection. This is a potential source of elevated ^{226}Ra off-site, so EPA has concluded that additional wind dispersal measures will be necessary to correct this problem and has determined that a higher density of off-site ^{226}Ra sampling will be necessary both in the short-term and during the next five-year review.

VII. Technical Assessment

Earlier in this report EPA summarized the four selected remedial actions for the Monsanto site as follows:

- Monitored natural attenuation with institutional controls for contaminated groundwater.
- Either institutional controls or soil excavation on buffer properties not owned or controlled by Monsanto, at the discretion of the property owners.
- No further action for operating-area source piles and materials. This remedy is subject to continued operations and ongoing five-year reviews**.**
- No further action for air, surface water, and Soda Creek sediments.

The five-year technical assessment that follows is completed as four distinct analyses, one for each selected remedy. For each selected remedy, EPA has answered yes or no to the following three questions, and has supplemented each response with supporting data, information, or references:

Question A: Is the remedy functioning as intended by the decision documents?

Question B: Are the exposure assumptions, toxicity data, cleanup levels, and remedial action objectives (RAOs) used at the time of remedy selection still valid?

Question C: Has any other information come to light that could call into question the protectiveness of the remedy?

A. Monitored Natural Attenuation for Groundwater

Question A: Yes
Question B: Yes
Question C: Yes

The ROD was written with the idea in mind that it is possible for elevated hazardous constituent concentrations below the operating area of the Monsanto plant to naturally decrease over time to acceptable (below MCL) concentrations. EPA has concluded based on five years of data collection and Monsanto's own modeling predictions, that achieving below-MCL concentrations everywhere underneath Monsanto's operating area is still possible but may occur over a longer timeframe than anticipated at the time of the ROD. In contrast, MNA progress in the buffer area surrounding the Monsanto site, particularly the southern buffer area, appears to be working as intended in the decision documents.

New information EPA has relied on to question the protectiveness of the remedy is the most recent transport modeling which shows contaminant concentrations decreasing for cadmium at a much slower rate than calculated during the RI/FS. This information does not demonstrate the remedy is ineffective, but is cause for continued annual groundwater monitoring and greater scrutiny by EPA during the next five-year review.

An additional new piece of information since the ROD relating to protectiveness of the remedy is elevated cadmium concentrations in the Lewis well (which is no longer used for potable water supplies). This well is outside current site institutional controls and it is unclear as of this five-year review what the ultimate status of the Lewis well will be.

B. Institutional Controls

Question A: Yes
Question B: Yes
Question C: No

EPA has concluded the institutional control remedy is working as intended. This may change in the future if additional elevated off-site ^{226}Ra soil concentrations are discovered, or if additional domestic wells are discovered in the buffer area, such as the Lewis well. Except for the Lewis well, no additional properties were discovered during this five-year review that may require Monsanto to implement new institutional controls. Several elevated off-site ^{226}Ra samples have been described herein, and EPA has included a recommendation in this report to respond appropriately to this finding.

C. No Further Action for On-Site Source Piles & Materials

Question A: No
Question B: Yes
Question C: Yes

EPA has considered three facts in determining that the NFA remedy for on-site materials is not working as intended. First, EPA observed significant wind dispersal from the underflow solids pile during our June 10th, 2003 inspection. Second, EPA is aware the underflow solids pile fails the Toxicity Characteristic Leaching Procedure (TCLP) test for certain hazardous constituents [from on-site interview with Bob Geddes, and EPA RCRA inspector Sylvia Burges], which would in most cases mean the material must be managed as a hazardous waste pursuant to RCRA. However, Monsanto has declared the underflow solids are exempt from the hazardous waste definition pursuant to the Bevill Amendment to RCRA. Either way, EPA is concerned that wind dispersal may lead to off-site contamination, which is the subject of the ROD and this five-year review. Third, several data points obtained during this five year review indicate that ^{226}Ra soil concentrations have increased in some localized areas over the past five years. Furthermore, the underflow solids likely contain ^{226}Ra, since it is a naturally occurring element in the local ores used in elemental phosphorous production, so it may be the source of increased ^{226}Ra concentrations off-site.

Based on this finding, EPA has included a recommendation herein for Monsanto to submit a plan to control wind dispersal of material piles. EPA has also requested herein that the wind dispersal plan include off-site soil sampling to occur within sixty days of plan approval by EPA, and that all affected off-site property owners be notified about all sample results on their properties.

D. No Further Action for Air, Surface Water and Soda Creek Sediments

Question A: Yes
Question B: Yes
Question C: No

As for the institutional control remedy, EPA has concluded based on this five-year review effort that the remedy decisions relative to air, surface water, and sediments were proper and remain protective as of this five-year review.

E. Technical Assessment Summary

In summary, of the four remedial actions included in the ROD, EPA has concluded that two of the remedies (institutional controls, and NFA for air, surface water, and sediments) are functioning as intended in the decision documents. These remedies also remain valid in terms of exposure assumptions, toxicity data, cleanup levels, and RAOs. In regards to the selected MNA remedy for groundwater, EPA has learned that the MNA remedy underneath the operating area may take longer than anticipated at the time of the ROD, and has noted further that the Lewis well may need institutional controls, but that otherwise the MNA remedy for groundwater appears to be working as intended.

The one remedy EPA has concluded is not functioning as intended in the decision documents (NFA for on-site material piles), is summarized as follows:

NFA Remedy for On-Site Material Piles

EPA's conclusion that the NFA remedy for on-site material piles is not functioning as intended is based on three observations made during the five-year review, all of which are already described in the previous section. EPA has concluded in this instance that the RAOs and related technical underpinnings of the remedy remain valid, though EPA has learned new information about management of material piles at the Monsanto site that have caused EPA to question the protectiveness of the remedy. For example, if wind dispersal continues as the review team observed on Jun 10th, 2003, off-site soil concentrations may continue increasing in localized areas, leading to more institutional controls and more potential off-site exposures.

VIII. Issues

The issues listed below have been articulated in detail elsewhere in this report, so for brevity they are simply repeated here as summary statements:

- Groundwater samples from the Lewis well have revealed elevated cadmium and other hazardous constituent concentrations during the past five years, and the property where this well is located does not have institutional controls.
- MNA for groundwater underneath the operating area may take longer than anticipated during the RI/FS, though this observation needs to be reevaluated during the next five-year review.

- Wind dispersal is occurring from the Monsanto site, and this may be contributing to increasing off-site contamination. EPA has determined this component of the Monsanto site remedy is not working as intended in the decision document.
- Three related technical matters that don't lead to EPA concerns about the protectiveness of the MNA remedy for groundwater but are necessary details to be resolved with Monsanto based on this five year review are: 1) increasing molybdenum concentrations south of the operating area; 2) use of total nitrogen as nitrate for demonstrating compliance with the MCL; and, 3) annual sampling, analyses, and trend evaluation reporting of Soda Creek discharge concentrations at a level of detail similar to annual and five-year review groundwater reporting.

Issues	**Affects Current Protectiveness (Y/N)**	**Affects Future Protectiveness (Y/N)**
1. Lack of institutional controls on Lewis well & property	N	Y
2. Monitored natural attenuation for groundwater may take longer underneath the operating area than anticipated at the time of the ROD	N	Y
3.Wind dispersal from Monsanto material piles may be contributing to ^{226}Ra soil concentration increases observed in localized areas off-site	N	Y
4.Three technical matters need resolution: 1) increasing molybdenum concentrations in the southern buffer area; 2) using total nitrogen as nitrate for MCL compliance; and, 3) sampling, analyzing and reporting Soda Creek discharge data at a level of detail similar to groundwater reporting	N	N

IX. Recommendations and Follow-up Actions

The five-year review team recommends that:

- EPA request Monsanto to submit a plan by February 1, 2004 pertaining to the Lewis well, examining the options for brining the Lewis well under institutional controls, and for evaluating whether other such domestic wells may be present in the non-buffer area immediately south of the Monsanto site.

- EPA request Monsanto to submit a plan by February 1, 2004 to control wind dispersal from on-site material piles. This plan shall include a sampling program to investigate areas off-site where ^{226}Ra soil concentrations were found to have increased over the past five years. Monsanto shall conduct the sampling portion of this plan no later than sixty days following EPA approval, and Monsanto shall promptly report all sampling results to local property owners.

- EPA request Monsanto to perform sampling and the next five-year review activities on a scale similar to the technical work performed in support of this review. Two exceptions shall be: 1) soil sampling off-site in areas where sampling density may be increased (as determined by results obtained during development of the wind dispersal control plan above); and, 2) Monsanto shall collect and analyze surface water discharges to Soda Creek for COPCs, report these finding to EPA annually, and as part of the next five-year review, and provide trend analyses of this discharge data at a level of detail consistent with ongoing groundwater data reporting.

- EPA request Monsanto to engage in a technical dialogue with EPA and IDEQ to resolve three related groundwater technical matters already described in this report.

					Affects Protectiveness (Y/N)	
Issue	**Recommendations and Follow-Up Actions**	**Party Responsible**	**Oversight Agency**	**Milestone Dates**	**Current**	**Future**
1.	Submit plan pertaining to institutional controls for Lewis well and nearby properties	Monsanto	EPA	2/1/2004	N	Y
2.	Reevaluate MNA for groundwater underneath operating area	EPA	EPA and IDEQ	Sep 2008	N	Y
3.	Submit plan pertaining to wind dispersal and off-site soil sampling	Monsanto	EPA	2/1/2004	N	Y
3.	Perform next five-year review technical work with some modifications	Monsanto	EPA	Sep 2008	N	Y
4.	Resolve three technical matters	Monsanto	EPA	2/1/2004	N	N

X. Protectiveness Statement

The remedy at the Monsanto Chemical Co. (Soda Springs Plant) currently protects human health and the environment because all known groundwater and soil exposure pathways have been restricted through institutional controls or other means. However, in order for the remedy to be protective in the long-term, the following actions need to be taken: 1) the Lewis well and property needs to be evaluated for institutional controls; 2) Monsanto needs to submit a plan for upgrading their wind dispersal program and for evaluating in the short term those localized areas where increased ^{226}Ra soil concentrations have been observed; and, 3) the U.S. Environmental Protection Agency (EPA) needs to reevaluate during the next five-year review whether the monitored natural attenuation remedy underneath the operating area is proceeding as intended in the decision documents.

XI. Next Review

The next five-year review for the Monsanto site is required by September 2008, five years from the date of this review.

MONSANTO

Monsanto Elemental Phosphorus Plant
CERCLA Five-Year Review
FINAL
APPENDIX A
Alexander Reservoir and Soda Creek Sediment Sampling Results

May 2003

Prepared by

MWH
MONTGOMERY WATSON HARZA

2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005

TABLE OF CONTENTS

TABLES

FIGURES

1.0 INTRODUCTION

Sediment samples were collected as part of the Phase II (1992-1995) Remedial Investigation (RI) and five-year monitoring program (in 2002) in the Alexander Reservoir at the inlets of Soda Creek and Bear River using a mini-ponar dredge at nine locations in each inlet. Samples were also collected along the upstream and downstream reaches of Soda Creek during Phase I (1991-1992) & II investigations and as part of the five-year monitoring program. These samples were collected in an effort to determine what, if any, impacts the Monsanto Phosphoria plant has on Soda Creek and Alexander Reservoir. Soda Creek is over six miles in length, and flows along the western side of the plant in a general north-to-south direction, and discharges into the Alexander Reservoir. Monsanto utilizes an NPDES-permitted outfall for cooling water that discharges into Soda Creek. Samples collected during the five-year monitoring program were subject to analysis with a reduced analyte list that included arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and polonium-210 (^{210}Po). The reduction in analytes from the Phase I & II investigations was approved by the USEPA and is found in the Record-of-Decision (ROD) (USEPA, 1997).

2.0 METHODOLOGY

Data collected from the RI and five-year monitoring program events were grouped into control and affected categories for evaluation. Data collected in Alexander Reservoir during the RI spatially matched the monitoring data collected by MWH in 2002. The analyte lists were also equivalent, save for ^{210}Po, which was analyzed for in the reservoir during monitoring, but not during the RI. The same stations were sampled during the monitoring as during the RI.

In Soda Creek, data were not collected in the exact same locations from the RI as during the monitoring. However, samples were collected at locations sufficiently close so as to provide a reliable comparison. Similarly, the analyte lists were comparable between the RI investigations and the 2002 monitoring. Soda Creek samples were classified as control (upstream) or affected (downstream) depending on their location in relation to the Monsanto plant outfall.

Supplemental Phase II RI data collected for Soda Creek at the time Alexander Reservoir was sampled (in 1994) are ignored here. The supplemental sediment quality data for the creek are reported as mg/kg clay in Golder Associates, 1997, and are thus not comparable to previously collected data or to that collected during the 2002 sampling.

Sediment collection in the reservoir and the creek followed the appropriate field sampling plan (MWH, 2002).

Statistical analysis was conducted nonparametrically with a Kruskal-Wallis analysis of variance accompanied, when significant, by a Fisher's least significant difference test to determine specific differences while controlling experiment-wise error (Georgia Institute of Technology, vol. II, chap. 6). All tests were performed at an experiment-wise Type I error rate (i.e., false alarm rate) of 0.05. For ^{210}Po in the reservoir, a Mann-Whitney test is used and there is no need for the Fisher's LSD test, because polonium-210 was not an analyte for reservoir sediments during the RI; thus, only two samples (monitoring control and monitoring affected), not four (RI control, monitoring control, RI affected, monitoring affected), are being compared.

Nonparametric methods are used because of heterogeneity of variance between control and affected areas that is not eliminated with a simple transformation.

These tests are outlined below for clarity.

> Kruskal and Wallis... extended the Mann-Whitney method to be applicable to two or more independent samples. The typical situation is to test the null hypothesis that all medians of the populations represented by k random samples are identical against the alternative that at least two of the population medians are different.
>
> The experimental design that is usually a precursor to applying this test is called the completely randomized design. This design allocates the treatments to the

experimental units purely on a chance basis. The usual parametric method of analyzing such data is called a one-way analysis of variance or sometimes is referred to as a single-factor between-subjects analysis of variance. This parametric method assumes normal distributions in using the F test analysis of variance on the data. Where the normality assumption is unjustified, the Kruskal-Wallis test can be used.

ASSUMPTIONS OF KRUSKAL-WALLIS ONE-WAY ANALYSIS OF VARIANCE BY RANKS TEST FOR SEVERAL INDEPENDENT SAMPLES

1. Each sample is a random sample from the population it represents.

2. All of the samples are independent of each other.

3. If there is a difference in any of the k population distribution functions F ($_{x1}$), F (x_2), ..., F (x_k), it is a difference in the location of the distributions. For example, if F (x_1) is not identical with F (x_2), then F (x_1) is identical with F (x_2 + c), where c is some constant.

4. The measurement scale is at least ordinal.

INPUTS FOR KRUSKAL-WALLIS ONE-WAY ANALYSIS OF VARIANCE BY RANKS TEST FOR SEVERAL INDEPENDENT SAMPLES

The data consist of several random samples k of possibly different sizes. Describe the ith sample of size n_i by X_{i1}, X_{i2}, . . . , X_{ini}, The data can be arranged in k columns, each column containing a sample denoted by $X_{i,j}$ where i = 1 to k and j = 1 to n_i for each i sample.

Table 8: Input Table for Kruskal-Wallis One-Way Analysis of Variance

sample 1	sample 2	. . .	sample k
$X_{1,1}$	$X_{2,1}$	. . .	$X_{k,1}$
$X_{1,2}$	$X_{2,2}$	. . .	$X_{k,2}$
. . .	. . .	. . .	. . .
$X_{1,n1}$	$X_{2,n2}$	. . .	$X_{k,nk}$

The total number of all observations is denoted by N

$$N = \sum_{i=1}^{k} n_i$$

total number of observations from all samples

Rank the observations X_{ij} in ascending order and replace each observation by its rank R (X_{ij}), with the smallest observation having rank 1 and the largest observation having rank N. Let R_i be the sum of the ranks assigned to the ith sample. Compute R_i for each sample.

$$R_i = \sum^{n_i} R(X_{ij}) \qquad i = 1, 2, \ldots, k$$

If several values are tied, assign each the average of the ranks that would have been assigned to them had there been no ties.

HYPOTHESES OF KRUSKAL-WALLIS ONE-WAY ANALYSIS OF VARIANCE BY RANKS TEST FOR SEVERAL INDEPENDENT SAMPLES

Because the Kruskal-Wallis test is sensitive against differences among means, it is convenient to think of it as a test for equality of treatment means. The expected value E (X) is the mean.

Ho: $E(X_1) = E(X_2) = \ldots = E(X_k)$ all of the k population means are equal

Ha: At least one of the k population means is not equal to at least one of the other population means

The hypothesis shown here is for testing means as used in Montgomery (1997) as an alternative to the standard parametric analysis of variance test. Sheskin (1997) and Conover (1999) state the null hypothesis in terms of all of the k population distribution functions being identical. This difference has no practical effect in the application of this test. The researcher is directed to the goodness-of-fit tests described elsewhere in this Chapter for tests regarding the equality of distribution functions.

TEST STATISTIC FOR KRUSKAL-WALLIS ONE-WAY ANALYSIS OF VARIANCE BY RANKS TEST FOR SEVERAL INDEPENDENT SAMPLES

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

When there are ties, the test statistic T is

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

S^2 is the variance of the ranks

$$T = \frac{12}{N(N+1)} \sum_{i=1}^{k} \frac{R_i^2}{n_i} - 3(N+1)$$

If there are no ties, $S^2 = N(N + 1)/12$ and the test statistic simplifies to

When the number of ties is moderate, this simpler equation may be used with little difference in the result when compared to the more complex equation need for ties.

INTREPRETATION OF OUTPUT (DECISION RULE) OF KRUSKAL-WALLIS ONE-WAY ANALYSIS OF VARIANCE BY RANKS TEST FOR SEVERAL INDEPENDENT SAMPLES

The tables required for the exact distribution of T would be quite extensive considering that every combination of sample sizes for a given k would be needed, multiplied by however many samples k would be included. Fortunately, if n_i are reasonably large, say $n_i \geq 5$, then under the null hypothesis T is distributed approximately as chi-square with k - 1 degrees of freedom, C_{k-1}. For k =3, sample sizes less than or equal to 5, and no ties, consult tables in Conover (1999).

Reject the null hypothesis Ho at level a if T is greater than its $1 - \alpha$ quantile. This $1 - \alpha$ quantile can be approximated by the chi-square Table C-2 with k-1 degrees of freedom. Otherwise, accept Ho if T is less than or equal to the $1 - \alpha$ quantile indicating the means of all the samples are equal in value. The p-value is approximated by the probability of the chi-square random variable with k - 1 degrees of freedom exceeding the observed value of T.

Mann-Whitney Test - Hypothesis About Population Means for Two Independent Samples

The Mann-Whitney test, sometimes referred to as the Mann-Whitney U test, is also called the Wilcoxon test. There are actually two versions of the test that were independently developed by Mann and Whitney in 1947 and Wilcoxon in 1949. They employ different equations and use different tables, but yield comparable results. One typical situation for using this test is when the researcher wants to test if two samples have been drawn from different populations. Another typical situation is when one sample was drawn, randomly divided into two sub-samples, and then each sub-sample receives a different treatment.

The Mann-Whitney test is often used instead of the t-test for two independent samples when the assumptions for the t-test may be violated, either the normality assumption or the homogeneity of variance assumption. If a distribution function is not a normal distribution function, the probability theory is usually not available when the test statistic is based on actual data. By contrast, the probability theory based on ranks, as used here, is relatively simple. Additionally, according to Conover (1999), comparisons of the relative efficiency between the Mann-Whitney test and the two-sample t-test is never too bad while the reverse is not true. Thus the Mann-Whitney test is the safer test to use.

One can intuitively understand the statistics involved in this test. First combine the two samples into a single sample and order them. Then rank the combined sample without regard to which sample each value came from. A test statistic could be the sum of the ranks assigned to one of the samples. If the sum is too small or too great, this gives an indication that the values from its population tend to smaller or larger than the values from the other sample. Therefore, the null hypothesis that there is no difference between the two populations can be rejected, if the ranks of one sample tend to be larger than the ranks of the other sample.

ASSUMPTIONS OF MANN-WHITNEY TEST FOR TWO INDEPENDENT SAMPLES

1) Each sample is a random sample from the population it represents.

2) The two samples are independent of each other.

3) If there is a difference in the two population distribution functions F (x) and G (y), it is a difference in the location of the distributions. In other words, if F (x) is not identical with G (y), then F (x) is identical with G (y + c), where c is some constant.

4) The measurement scale is at least ordinal.

INPUTS FOR MANN-WHITNEY TEST FOR TWO INDEPENDENT SAMPLES

Let $X_1, X_2, \ldots, X_n$ represent a random sample of size n from population 1 and let $Y_1, Y_2, \ldots, Y_m$ represent a random sample of size m from population 2. Let $n + m = N$. Assign ranks 1 to N to all the observations from smallest to largest, without regard from which population they came from. Let $R(X_i)$ and $R(Y_j)$ represent the ranks assigned to X_i and Y_j for all i and j. If several values are tied, assign each the average of the ranks that would have been assigned to them had there been no ties.

HYPOTHESES OF MANN-WHITNEY TEST FOR TWO INDEPENDENT SAMPLES

The Mann-Whitney test is unbiased and consistent when the four listed assumptions are met. The inclusion of assumption 3 allows the hypotheses to be stated in terms of the means. The expected value E (X) is the mean.

A. Two-sided test
   H_o: E (X) = E (Y)
   H_a: E (X) ¹ E (Y)

B. Upper-sided test
   H_o: E (X) ³ E (Y)
   H_a: E (X) < E (Y)

C. Lower-sided test
   H_o: E (X) £ E (Y)
   H_a: E (X) > E (Y)

The hypotheses shown here are for testing means. Different hypotheses are also discussed in most texts (e.g., Conover (1999) and Sheskin (1997)) that test to see if the two samples come from identical distributions. This does not require assumption 3. Elsewhere in this chapter, the Kolmogorov-Smirnov type goodness-of-fit tests are described which also test if two (or more) samples are drawn from the same distribution. For this reason, the identical distribution hypotheses of the Mann-Whitney test are not discussed here.

TEST STATISTIC FOR MANN-WHITNEY TEST FOR TWO INDEPENDENT SAMPLES

$$T = \sum_{i=1}^{n} R(X_i)$$

The test statistic T can be used when there are no ties or few ties. It is simply the sum of the ranks assigned to the sample from population one.
If there are many ties, the test statistic T1 is obtained which simply subtracts the mean from T and divides by the standard deviation

$$T_1 = \frac{T - mean}{std\ deviation} = \frac{T - n\dfrac{N-1}{2}}{\sqrt{\dfrac{nm}{N(N-1)}\sum_{i=1}^{N} \cdot R_i^2 - \dfrac{nm(N-1)^2}{4(N-1)}}}$$

where ΣR_i^2 is the sum of the squares of all N of the ranks or average ranks actually used in both samples.

$$\omega_p = n(n+m+1) - \omega_{1-p}$$

Lower quantiles ω_{p-1} of the exact distribution of T are given for n and m values of 20 or less in Table C-6. Upper quantiles ω_p are found by the relationship

$$T' = n(N+1) - T$$

Perhaps more convenient is the use T' which can be used with the lower quartiles in Table C-6 whenever an upper-tail test is desired.

When there are many ties in the data, T_1 is used which is approximately a standard normal random variable. Therefore, the quantiles for T_1 are found in Table C-1, which is the standard normal table.

$$w_p \cong \frac{n(N+1)}{2} + z_p\sqrt{\frac{nm(N+}{12}}$$

When n or m is greater than 20 (and there are still no ties), the approximate quantiles are found by the normal approximation given by
for quantiles when n or m is greater than 20, where z_p is the p^{th} quantile of a standard normal random variable obtained from Table C-1.

INTERPRETATION OF OUTPUT (DECISION RULE) OF MANN-WHITNEY TEST FOR TWO INDEPENDENT SAMPLES

For the two-sided test, reject the null hypothesis H_o at level α if T (or T_1) is less than its /2 quantile or greater than its 1 - $\alpha/2$ quantile from Table C-6 for T (or from the Standard Normal Table C-1for T_1). Otherwise, accept H_o if T (or T_1) is between, or equal to one of, the quantiles indicating the means of the two samples are equal.
For the upper-tailed test, large values of T indicate that H_1 is true. Reject the null hypothesis H_o at level α if T (or T_1) is greater than its α quantile from Table C-6 for T (or from the Standard Normal Table C-1 for T_1). It may be easier to find T' = n (N+1) - T and reject H_o if T' is less than its α from Table C-6. Otherwise, accept H_o if T (or T_1) is less than or equal to its α quantile indicating the mean of population 1 is less than or equal to the mean of population 2.
For the lower-tailed test, small values of T indicate that H_1 is true. Reject the null hypothesis H_o at level α if T (or T_1) is less than its α quantile from Table C-6 for T (or from the Standard Normal Table C-1 for T_1). Otherwise, accept H_o if T (or T_1) is greater than or equal to its α quantile indicating the mean of population 1 is greater than or equal to the mean of population 2. If the n or m is larger than 20, use
When n or m is greater than 20 (and no ties), the quantiles used in the above decisions are obtained directly from the equation given previously for this condition.

Results for the statistical evaluation outlined above, which were performed on each analyte are presented at the end of this appendix. Results from the data interpretation are presented in the following sections.

3.0 STATISTICAL RESULTS

3.1 SEDIMENT RESULTS

Sediment analytical results from Alexander Reservoir and Soda Creek are presented below.

3.1.1 Alexander Reservoir Sediments

Sediment sample medians collected in Alexander Reservoir are presented below. The data presented are from the RI conducted by Golder Associates, and the five-year monitoring conducted by MWH. In the tables below, sample median concentrations that are indistinguishable from one another are shown with their medians highlighted on the same row. Any differences are denoted by displaying medians on different rows. 'RI' results are from remedial investigation sampling events, and 'M' results are data collected during the five-year monitoring program.

For each analyte a graphical display of the data plotted against distance from the mouth of the Bear River (for control data) or the mouth of Soda Creek (for affected data). These plots are provided for visual interpretation.

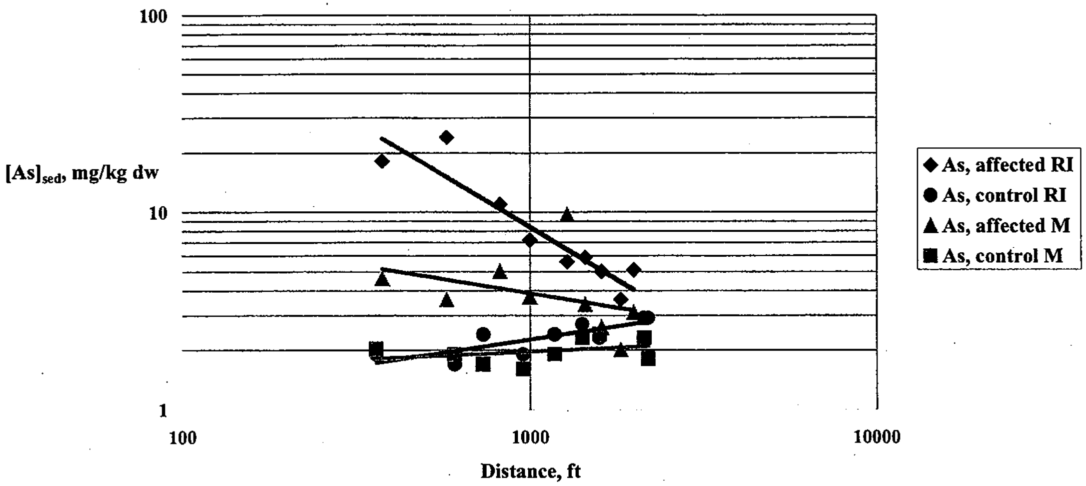
3.1.1.1 Arsenic

The medians of the arsenic data are presented in Table 3-1, *Alexander Reservoir Arsenic Comparisons*. The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically there is no difference between the controls in either the RI or M results. These results also show that affected area concentrations are elevated, but have decreased over time. The graphical plot in Figure 3-1 confirms the statistical analysis.

TABLE 3-1
ALEXANDER RESERVOIR ARSENIC COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[As]_{sed}$ mg/kg dw			■	
				■
	■	■		

Figure 3-1. Alexander Reservoir Sediment Quality Arsenic



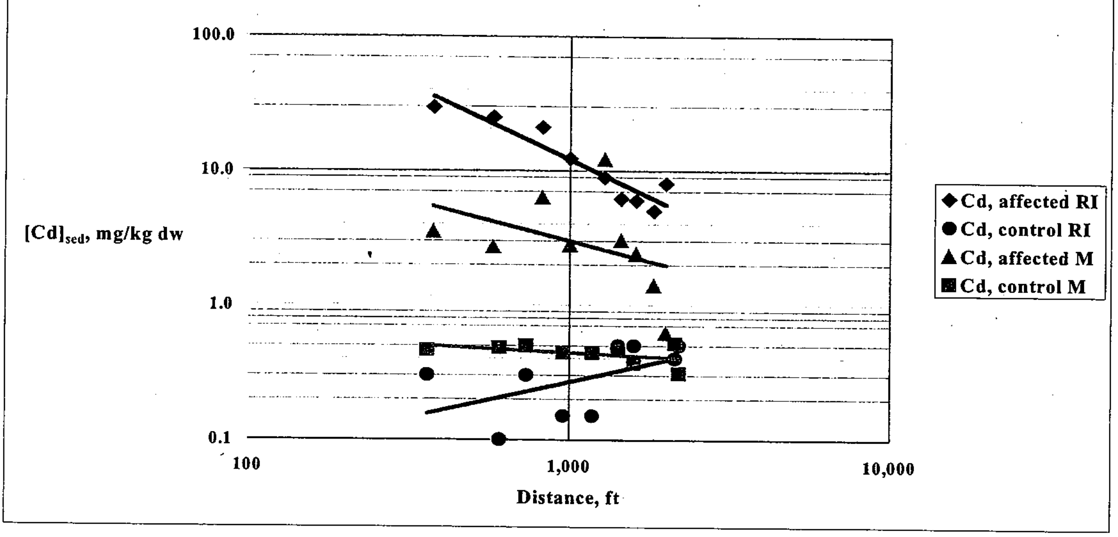
3.1.1.2 Cadmium

The medians of the cadmium data are presented in Table 3-2, *Alexander Reservoir Cadmium Comparisons*. The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically there is no difference between the controls in either the RI or M results. These results also show that affected area concentrations are elevated, but have decreased over time. The graphical plot in Figure 3-2 confirms the statistical analysis.

TABLE 3-2
ALEXANDER RESERVOIR CADMIUM COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[Cd]_{sed}$ mg/kg dw			■	
				■
	■	■		

Figure 3-2. Alexander Reservoir Sediment Quality Cadmium



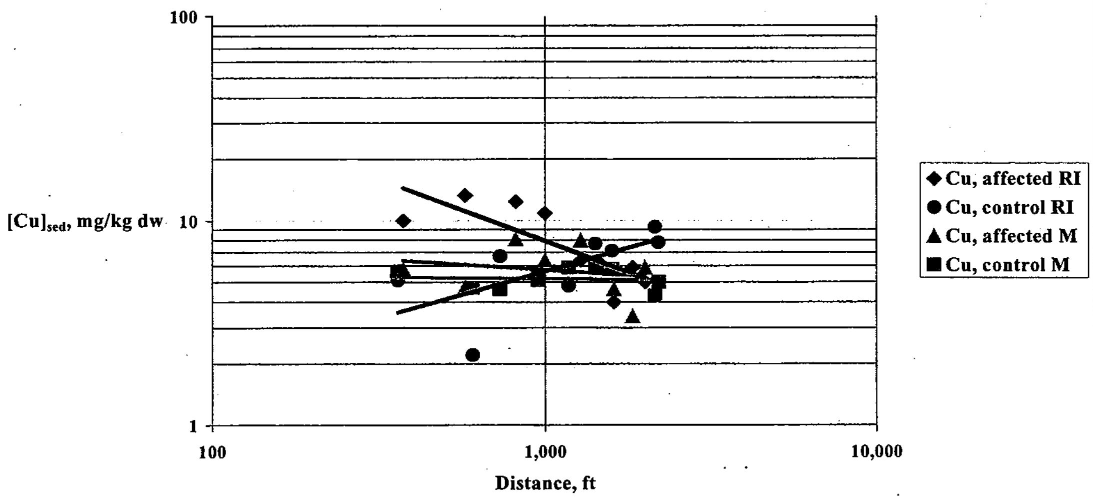
3.1.1.3 Copper

The medians of the copper data are presented in Table 3-3, *Alexander Reservoir Copper Comparisons*. The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically there is no difference among the controls or the affected samples in either the RI or M results. The graphical plot in Figure 3-3 confirms the statistical analysis.

TABLE 3-3
ALEXANDER RESERVOIR COPPER COMPARISONS

	RI	M	RI	M
$[Cu]_{sed}$ mg/kg dw	**Control**		**Affected**	
	[redacted]		[redacted]	[redacted]
	[redacted]	[redacted]		[redacted]

Figure 3-3. Alexander Reservoir Sediment Quality Copper



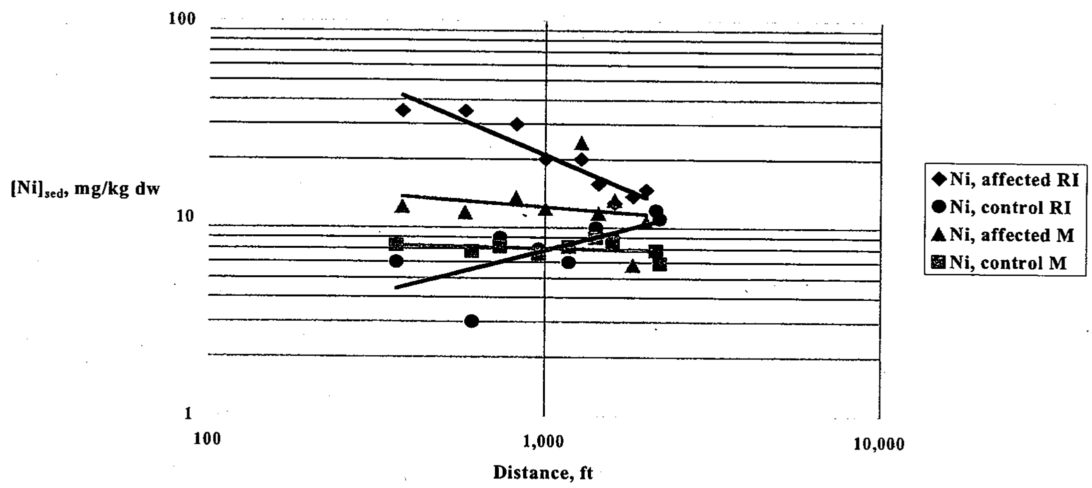
3.1.1.4 Nickel

The medians of the nickel data are presented in Table 3-4, *Alexander Reservoir Nickel Comparisons.* The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically there is no difference among the controls in either the RI or M results. These results also show that affected area concentrations are elevated, but have decreased over time. The graphical plot in Figure 3-4 confirms the statistical analysis.

TABLE 3-4
ALEXANDER RESERVOIR NICKEL COMPARISONS

	RI	M	RI	M
	Control		**Affected**	
$[Ni]_{sed}$ mg/kg dw			■	
				■
	■	■		

Figure 3-4. Alexander Reservoir Sediment Quality Nickel



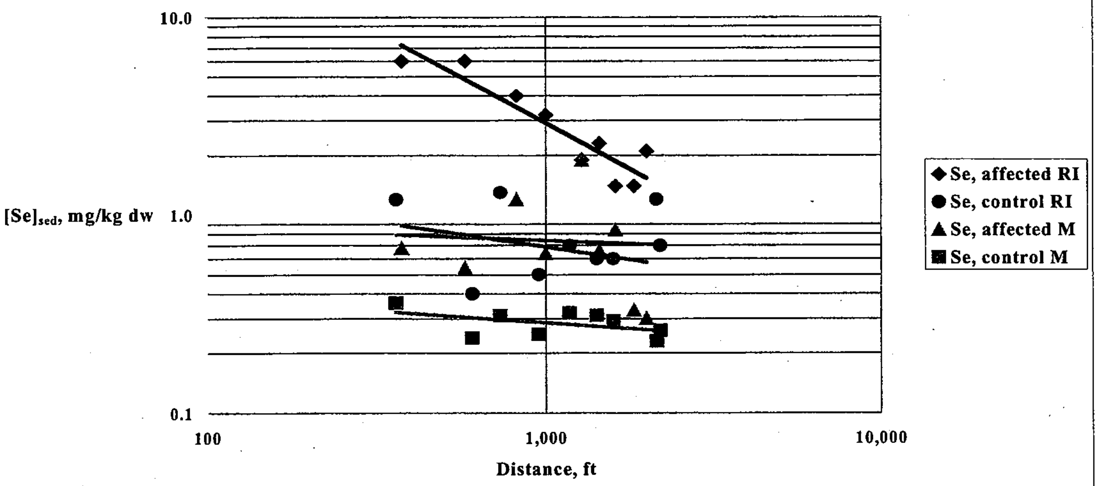
3.1.1.5 Selenium

The medians of the selenium data are presented in Table 3-5, *Alexander Reservoir Selenium Comparisons.* The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically, the RI control is elevated compared to the M control. These results also show that affected area concentrations are elevated, but have decreased over time. The graphical plot in Figure 3-5 confirms the statistical analysis.

TABLE 3-5
ALEXANDER RESERVOIR SELENIUM COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[Se]_{sed}$ mg/kg dw			■	
	■			■
		■		

Figure 3-5. Alexander Reservoir Sediment Quality Selenium



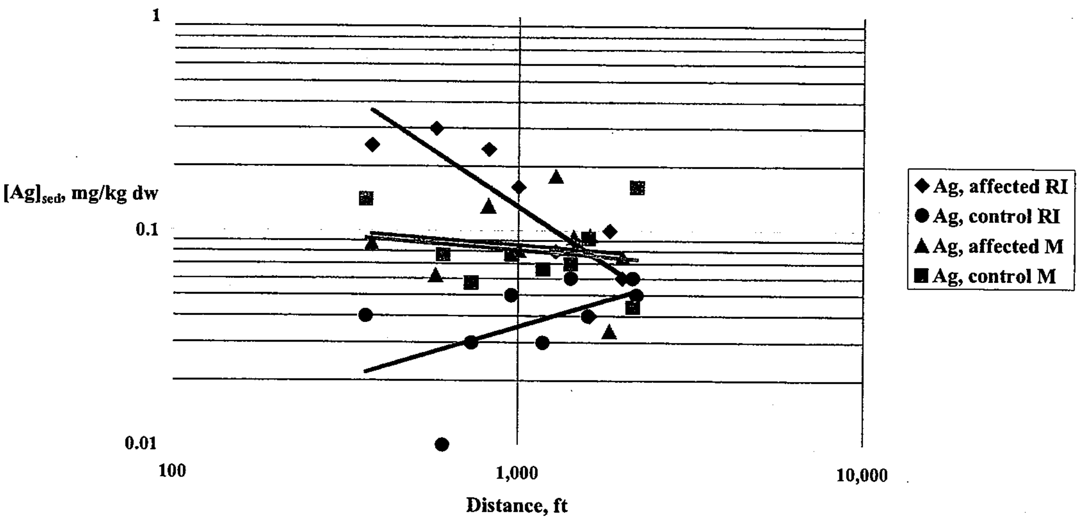
3.1.1.6 Silver

The medians of the silver data are presented in Table 3-6, *Alexander Reservoir Silver Comparisons.* The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically, the M control is elevated compared to the RI control results. These results also show that affected area concentrations are not elevated compared to the M control. The graphical plot in Figure 3-6 confirms the statistical analysis.

TABLE 3-6
ALEXANDER RESERVOIR SILVER COMPARISONS

$[Ag]_{sed}$ mg/kg dw	RI	M	RI	M
	Control		Affected	
		■	■	■
	■			

Figure 3-6. Alexander Reservoir Sediment Quality Silver



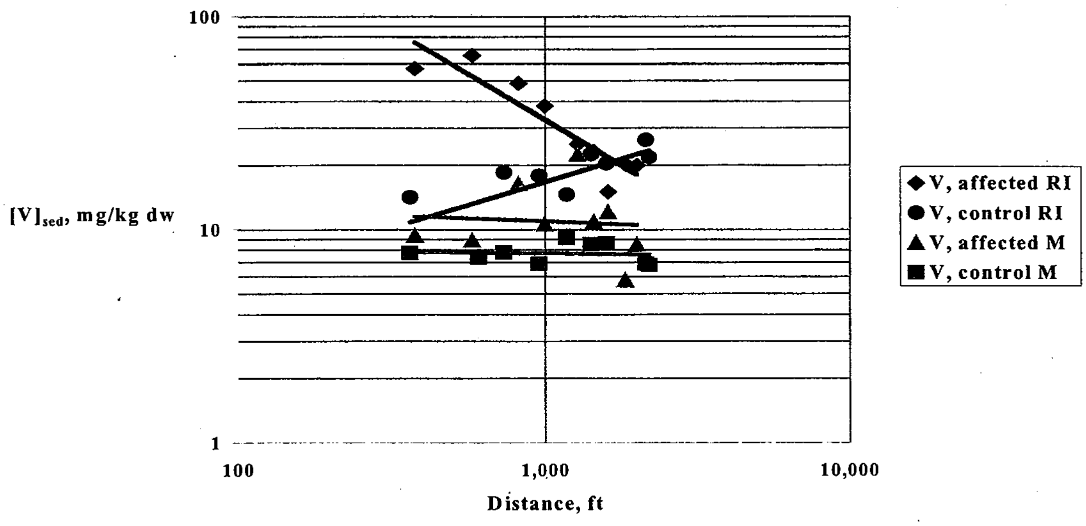
3.1.1.7 Vanadium

The medians of the vanadium data are presented in Table 3-7, *Alexander Reservoir Vanadium Comparisons.* The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically, the RI control is elevated compared to the M control. These results also show that affected area concentrations are elevated, but have decreased over time. The graphical plot in Figure 3-7 confirms the statistical analysis.

TABLE 3-7
ALEXANDER RESERVOIR VANADIUM COMPARISONS

	RI	**M**	**RI**	**M**
	Control		**Affected**	
$[V]_{sed}$ mg/kg dw			■	
	■			■
		■		

Figure 3-7. Alexander Reservoir Sediment Quality Vanadium



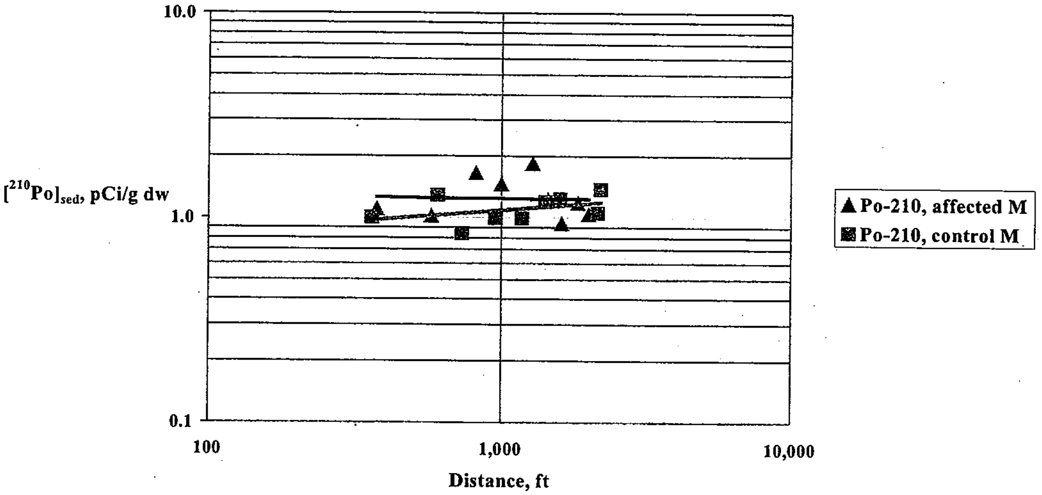
3.1.1.8 Polonium-210

The medians of the polonium-210 data are presented in Table 3-8, *Alexander Reservoir Polonium-210 Comparisons.* The results of the Kruskal-Wallis test and the Fisher's LSD show that statistically, the M control is not significantly different from the M affected area. The graphical plot in Figure 3-8 confirms the statistical analysis.

TABLE 3-8
ALEXANDER RESERVOIR POLONIUM-210 COMPARISONS

[^{210}Po]$_{sed}$ pCi/g dw	RI	M	RI	M
	Control		Affected	
		[redacted]		[redacted]

Figure 3-8. Alexander Reservoir Sediment Quality ^{210}Po



3.1.2 Soda Creek Sediments

Sediment sample medians collected in Soda Creek are presented below. The data presented are from the RI conducted by Golder Associates, and the five-year monitoring conducted by MWH. In the tables below, median concentrations that are indistinguishable from one another are shown with their medians highlighted on the same row. Any differences are denoted by displaying medians on different rows. 'RI' results are from remedial investigation sampling events, and 'M' results are data collected during the five-year monitoring program.

For each analyte two graphical displays of the data plotted against distance from the Monsanto outfall; upstream (for control data) or downstream (for affected data). These plots are provided for visual interpretation. There is only a single control sample from the RI.

3.1.2.1 Arsenic

The medians of the arsenic data are presented in Table 3-9, *Soda Creek Arsenic Comparisons*. These results show that RI and M controls and affected area concentrations are not statistically different. The graphical plots in Figure 3-9 and Figure 3-10 confirm the statistical analysis.

TABLE 3-9
SODA CREEK ARSENIC COMPARISONS

$[As]_{sed}$ mg/kg dw	RI	M	RI	M
	Control		Affected	
	[redacted]	[redacted]	[redacted]	[redacted]

Figure 3-9. Soda Creek Upstream Sediment Quality Arsenic

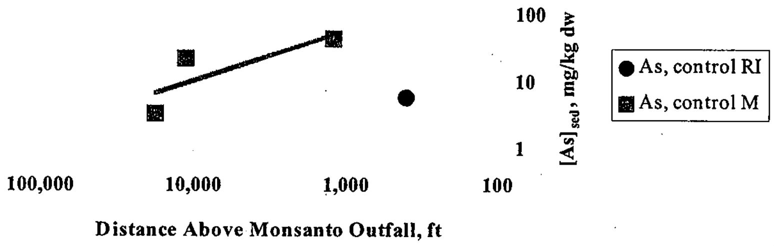
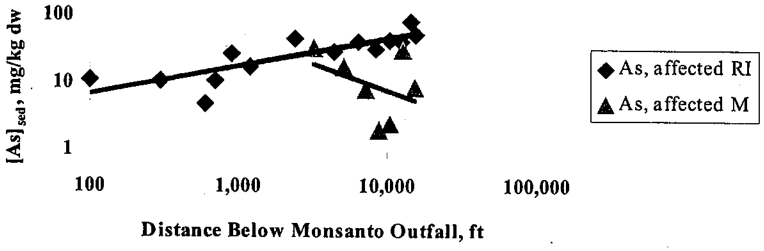


Figure 3-10. Soda Creek Downstream Sediment Quality Arsenic



3.1.2.2 Cadmium

The medians of the cadmium data are presented in Table 3-10, *Soda Creek Cadmium Comparisons*. These results show that RI controls were slightly elevated compared to M controls. Affected area concentrations are elevated, but have decreased over time. The graphical plots in Figure 3-11 and Figure 3-12 confirm the statistical analysis.

TABLE 3-10
SODA CREEK CADMIUM COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[Cd]_{sed}$ mg/kg dw			■	
	■			■
		■		

Figure 3-11. Soda Creek Upstream Sediment Quality Cadmium

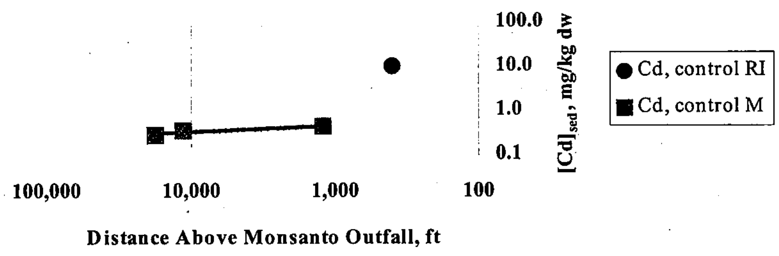
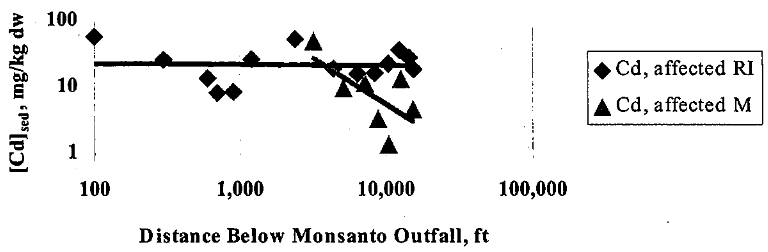


Figure 3-12. Soda Creek Downstream Sediment Quality Cadmium



3.1.2.3 Copper

The medians of the copper data are presented in Table 3-11, *Soda Creek Copper Comparisons*. These data show that the RI control is not significantly different compared to the M control. Affected area concentrations are elevated, but have decreased to control levels over time. The graphical plots in Figure 3-13 and Figure 3-14 confirm the statistical analysis.

TABLE 3-11
SODA CREEK COPPER COMPARISONS

	RI	M	RI	M
$[Cu]_{sed}$ mg/kg dw	Control		Affected	
			[redacted]	
	[redacted]	[redacted]		[redacted]

Figure 3-13. Soda Creek Upstream Sediment Quality Copper

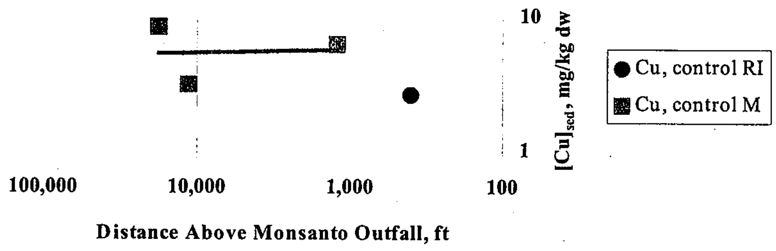
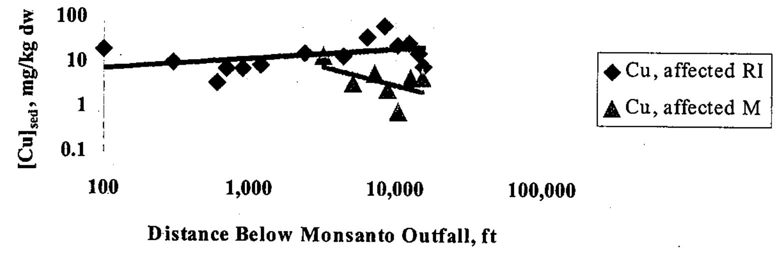


Figure 3-14. Soda Creek Downstream Sediment Quality Copper



3.1.2.4 Nickel

The medians of the nickel data are presented in Table 3-12, *Soda Creek Nickel Comparisons.* These results show that RI and M controls and affected area concentrations are not statistically different. The graphical plots in Figure 3-15 and Figure 3-16 confirm the statistical analysis.

TABLE 3-12
SODA CREEK NICKEL COMPARISONS

	RI	M	RI	M
	Control		Affected	
[Ni]$_{sed}$ mg/kg dw	[redacted]	[redacted]	[redacted]	[redacted]

Figure 3-15. Soda Creek Upstream Sediment Quality Nickel

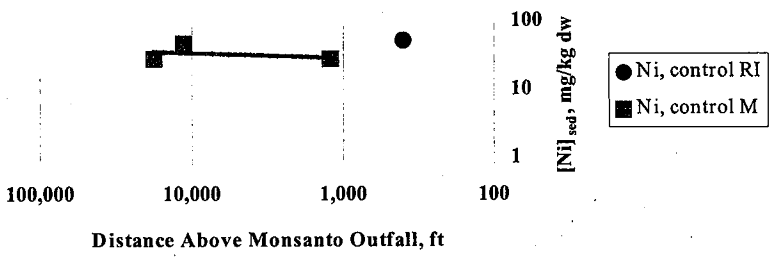
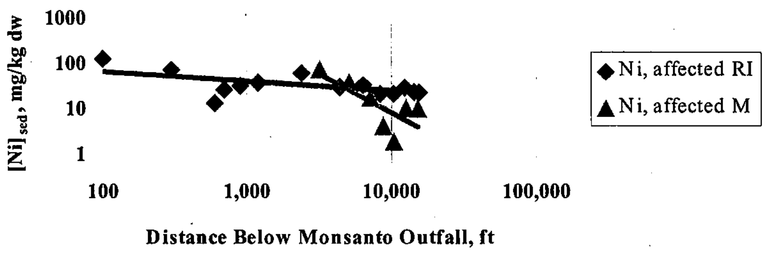


Figure 3-16. Soda Creek Downstream Sediment Quality Nickel



3.1.2.5 Selenium

The medians of the selenium data are presented in Table 3-13, *Soda Creek Selenium Comparisons*. These data show that the RI control is not significantly different compared to the M control. Affected area concentrations are elevated and unchanging in time. The graphical plots in Figure 3-17 and Figure 3-18 confirm the statistical analysis.

TABLE 3-13
SODA CREEK SELENIUM COMPARISONS

	RI	**M**	**RI**	**M**
$[Se]_{sed}$ mg/kg dw	**Control**		**Affected**	

Figure 3-17. Soda Creek Upstream Sediment Quality Selenium

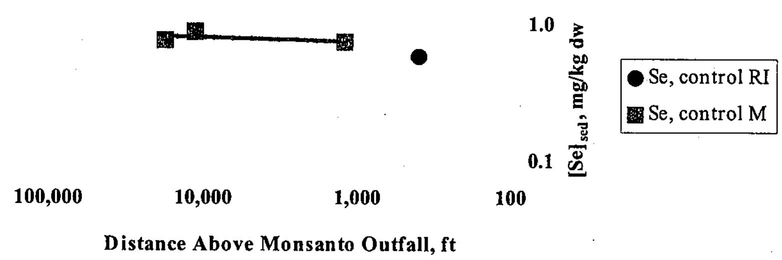
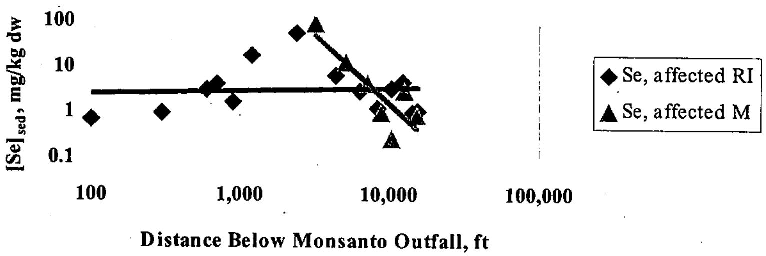


Figure 3-18. Soda Creek Downstream Sediment Quality Selenium



3.1.2.6 Silver

The medians of the silver data are presented in Table 3-14, *Soda Creek Silver Comparisons.* These data show that the RI control is not significantly different compared to the M control. Affected area concentrations are elevated, but have decreased over time to control levels. The graphical plots in Figure 3-19 and Figure 3-20 confirm the statistical analysis.

TABLE 3-14
SODA CREEK SILVER COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[Ag]_{sed}$ mg/kg dw			[redacted]	
	[redacted]			[redacted]

Figure 3-19. Soda Creek Upstream Sediment Quality Silver

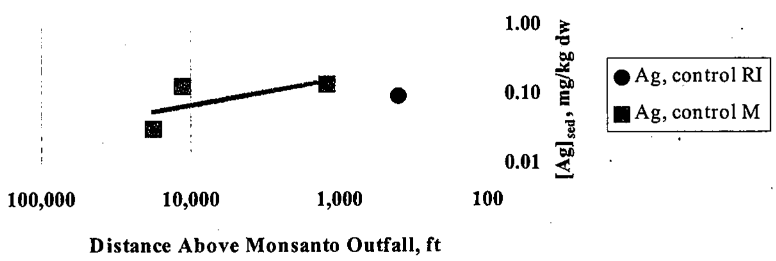
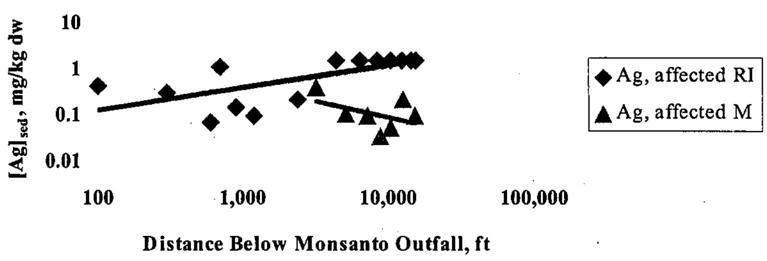


Figure 3-20. Soda Creek Downstream Sediment Quality Silver



3.1.2.7 Vanadium

The medians of the vanadium data are presented in Table 3-15, *Soda Creek Vanadium Comparisons*. These data show that the RI control is not significantly different compared to the M control. Affected area concentrations are elevated, but have decreased over time to control levels. The graphical plots in Figure 3-21 and Figure 3-22 confirm the statistical analysis.

TABLE 3-15
SODA CREEK VANADIUM COMPARISONS

	RI	M	RI	M
	Control		Affected	
$[V]_{sed}$ mg/kg dw			■	
	■	■		■

Figure 3-21. Soda Creek Upstream Sediment Quality Vanadium

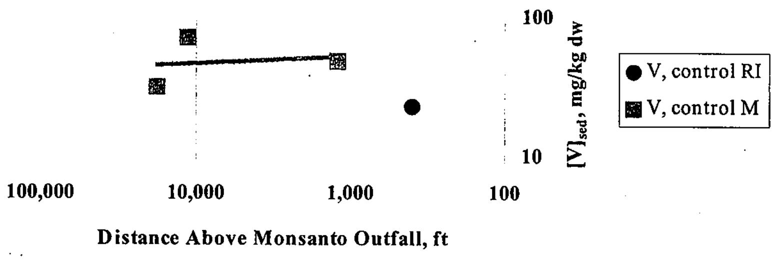
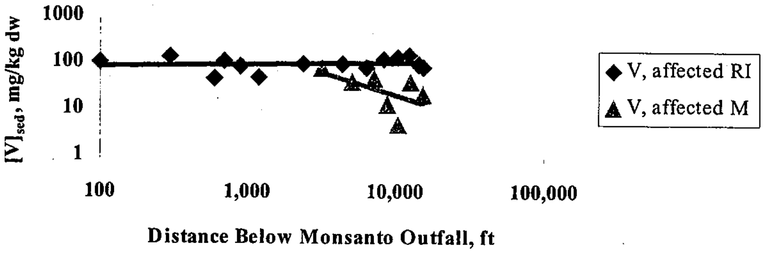


Figure 3-22. Soda Creek Downstream Sediment Quality Vanadium



3.1.2.8 Polonium-210

The medians of the ^{210}Po data are presented in Table 3-16, *Soda Creek Polonium-210 Comparisons*. These results show that the RI and M controls and affected area concentrations are not statistically different. The graphical plots in Figure 3-23 and Figure 3-24 confirm the statistical analysis.

TABLE 3-16
SODA CREEK POLONIUM-210 COMPARISONS

$[^{210}Po]_{sed}$ pCi/g dw	RI	M	RI	M
	Control		Affected	
	[redacted]	[redacted]	[redacted]	[redacted]

Figure 3-23. Soda Creek Upstream Sediment Quality Polonium-210

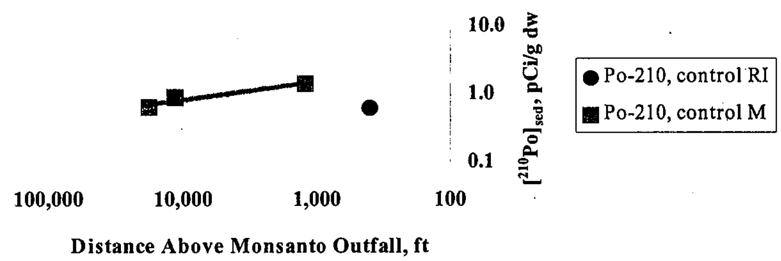
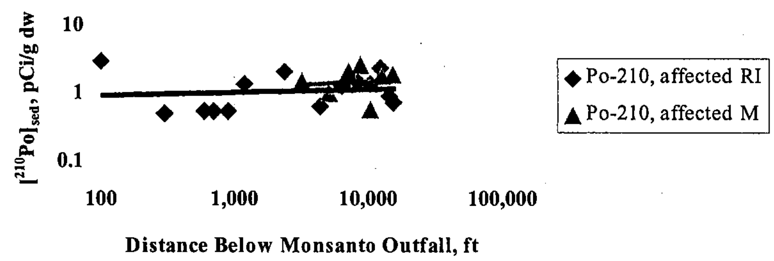


Figure 3-24. Soda Creek Downstream Sediment Quality Polonium-210



3.1.3 Alexander Reservoir Sediment Summary

Table 3-17, *Sediment Quality Summary in Alexander Reservoir* presents a summary of the Kruskal-Wallis and Fisher's LSD test. The right side column presents the interpretation of these data.

TABLE 3-17
SEDIMENT QUALITY SUMMARY IN ALEXANDER RESERVOIR

	RI	M	RI	M	
	Control		Affected		
$[As]_{sed}$ mg/kg dw			■		**Affected area elevated, but decreasing**
				■	
	■	■			
$[Cd]_{sed}$ mg/kg dw			■		**Affected area elevated, but decreasing**
				■	
	■	■			
$[Cu]_{sed}$ mg/kg dw	■		■	■	**Affected area not elevated**
	■	■		■	
$[Ni]_{sed}$ mg/kg dw			■		**Affected area elevated, but decreasing**
				■	
	■	■			
$[Se]_{sed}$ mg/kg dw			■		**Affected area elevated, but decreasing**
	■			■	
		■			
$[Ag]_{sed}$ mg/kg dw		■	■	■	**Affected area not elevated**
	■				
$[V]_{sed}$ mg/kg dw			■		**Affected area elevated, but decreasing**
	■			■	
		■			
$[^{210}Po]_{sed}$ pCi/g dw		■		■	**Affected area not elevated**

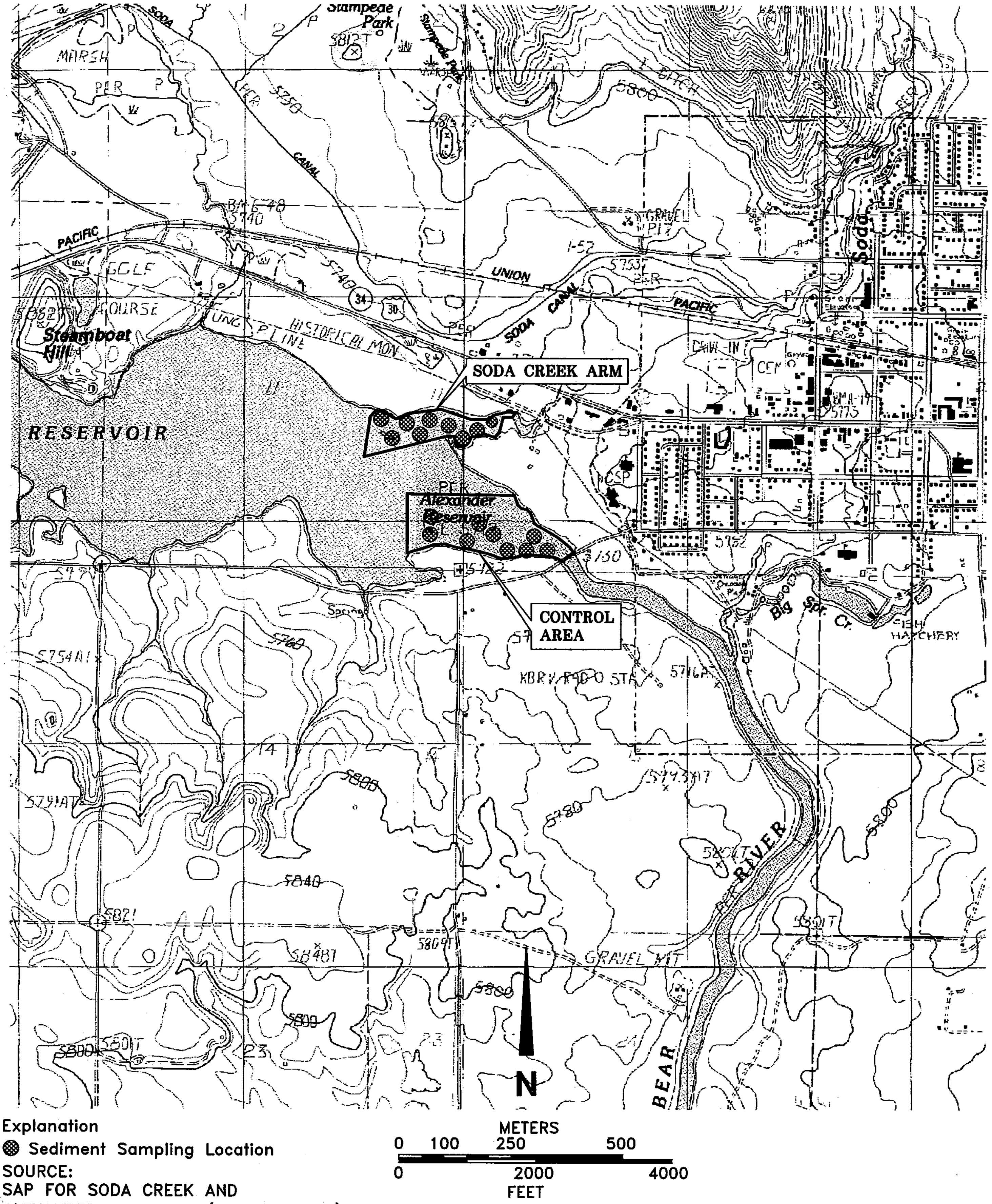
3.1.4 Soda Creek Sediment Summary

Table 3-18, *Sediment Quality Summary in Soda Creek* presents a summary of the Kruskal-Wallis and Fisher's LSD test. The right side column presents the interpretation of these data.

TABLE 3-18
SEDIMENT QUALITY SUMMARY IN SODA CREEK

	RI	M	RI	M	
	Control		Affected		
$[As]_{sed}$ mg/kg dw	■	■	■	■	**Affected area not elevated**
$[Cd]_{sed}$ mg/kg dw	■		■		**Affected area elevated, but decreasing**
	■			■	
	■	■			
$[Cu]_{sed}$ mg/kg dw			■		**Affected area not elevated**
	■	■		■	
$[Ni]_{sed}$ mg/kg dw	■	■	■	■	**Affected area not elevated**
$[Se]_{sed}$ mg/kg dw			■	■	**Affected area elevated**
	■	■			
$[Ag]_{sed}$ mg/kg dw			■		**Affected area not elevated**
	■	■		■	
$[V]_{sed}$ mg/kg dw			■		**Affected area not elevated**
	■	■		■	
$[^{210}Po]_{sed}$ pCi/g dw	■	■	■	■	**Affected area not elevated**

Figure 3-25, *Alexander Reservoir Sample Locations* presents the locations of the sediment samples collected in the Soda Creek and control arms of the reservoir. Figure 3-26, *Five-Year Review Sediment Sampling Locations: Middle and Upper Soda Creek Control Areas* and Figure 3-27, *Five-Year Review Sediment Sampling Locations: Lower Soda Creek Control and Downstream Areas* present the locations for the control and downstream sediment sampling locations.



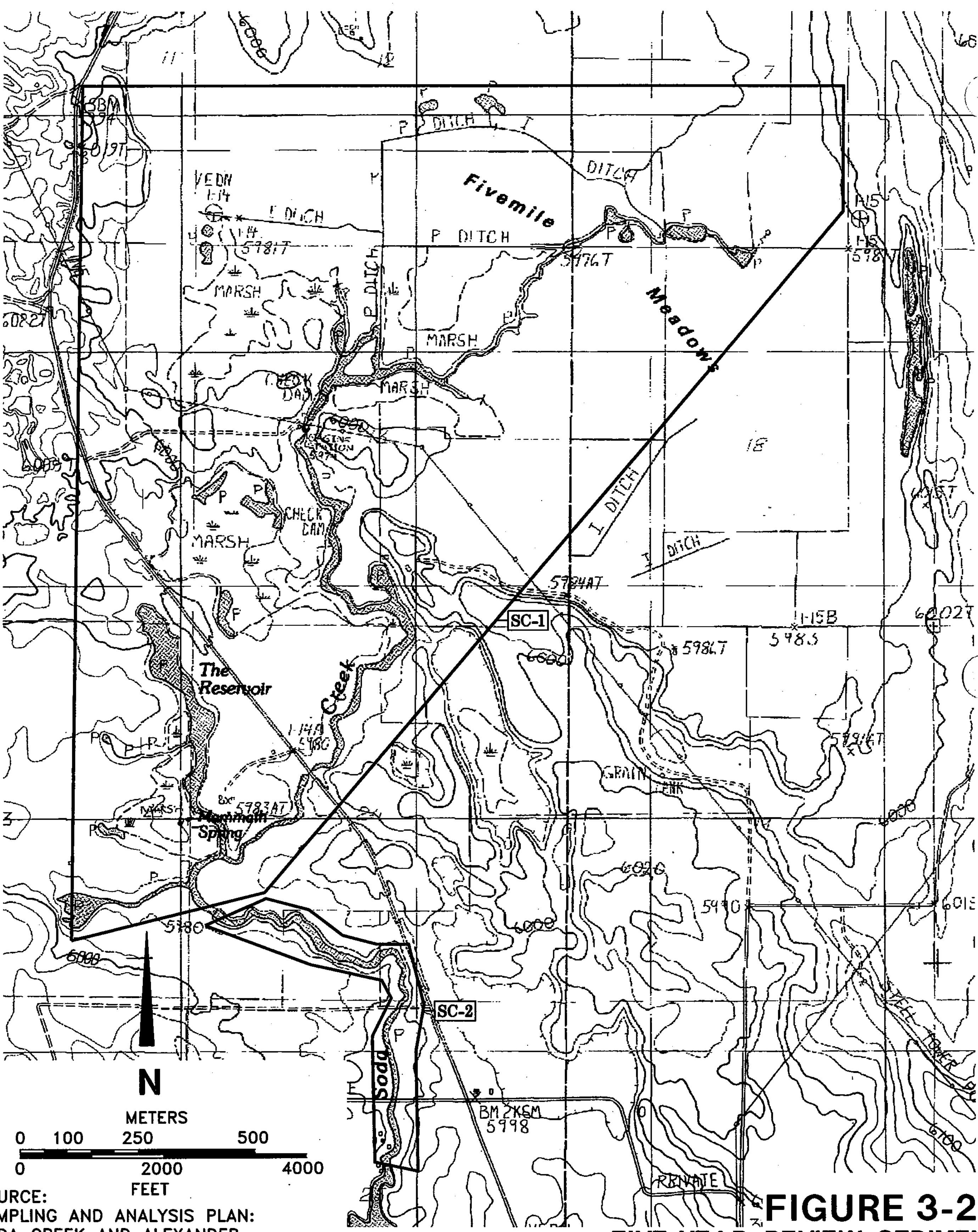
Explanation

● Sediment Sampling Location

SOURCE:
SAP FOR SODA CREEK AND
ALEXANDER RESERVOIR (GOLDER, 1994)
USGS Topographic Maps: Soda
Springs Idaho 1:24,000 (1982),
Alexander Idaho 1:24,000 (1982)

FIGURE 3-25
ALEXANDER RESERVOIR SAMPLE LOCATIONS
MONSANTO/CERCLA FIVE YEAR REVIEW

MWH



SOURCE:
SAMPLING AND ANALYSIS PLAN:
SODA CREEK AND ALEXANDER
RESERVOIR (GOLDER, 1994)

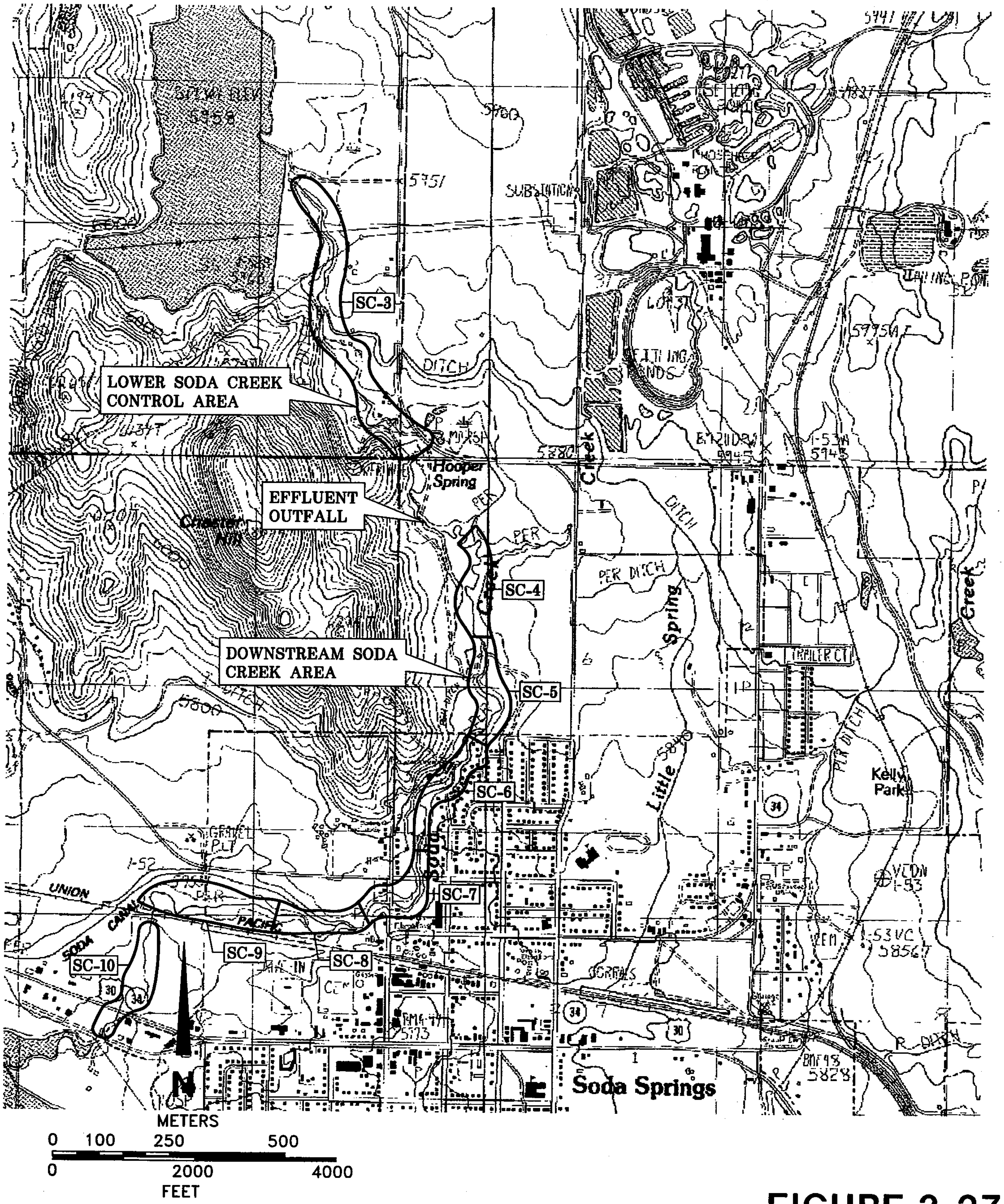
USGS Topographic Maps: Soda
Springs Idaho 1:24,000 (1982),
Alexander Idaho 1:24,000 (1982)

FIGURE 3-26

FIVE-YEAR REVIEW SEDIME
SAMPLING LOCATIONS: MIDDLE A
UPPER SODA CREEK CONTROL AREAS

MONSANTO/CERCLA FIVE YEAR REVIEW

MWH



SOURCE:
SAMPLING AND ANALYSIS PLAN: SODA CREEK AND ALEXANDER RESERVOIR (GOLDER, 1994)
USGS Topographic Maps: Soda Springs Idaho 1:24,000 (1982)

FIGURE 3-27
FIVE-YEAR REVIEW SEDIMENT SAMPLING LOCATIONS: LOWER SODA CREEK CONTROL AND DOWNSTREAM AREAS

MONSANTO/CERCLA FIVE YEAR REVIEW

4.0 STATISTICAL CALCULATIONS

The statistical calculations for the above analyses are presented on the following pages. The calculations were completed in Microsoft Excel.

5.0 REFERENCES

Georgia Institute of Technology, March 2003. *Scientific Approaches for Transportation Research* (http://traffic.ce.gatech.edu/nchrp2045/v2chapter6.html). Prepared for National Coorporative Highway Research Program.

Golder Associates, November 1997. *Monsanto. Selected Text from Phase I and Phase II remedial Investigations and Reports. Relating to Characterization of Soda Creek.* Prepared for Monsanto.

Montgomery Watson Harza (MWH), October 2002. *Final Work Plan for CERCLA Five-year Review. Monsanto Elemental Phosphorous Plant, Soda Springs, Idaho.* Prepared for Monsanto.

USEPA, April 1997. *Record of Decision: Monsanto Chemical Company, Superfund Site, Caribou County, Idaho.* USEPA Region X, Office of Environmental Cleanup.

MONSANTO ™

Monsanto Elemental Phosphorus Plant
CERCLA Five-Year Review
FINAL
APPENDIX B
Monsanto Plant Soil Sampling Results

May 2003

Prepared by

MWH
MONTGOMERY WATSON HARZA

2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005

TABLE OF CONTENTS

TABLES

FIGURES

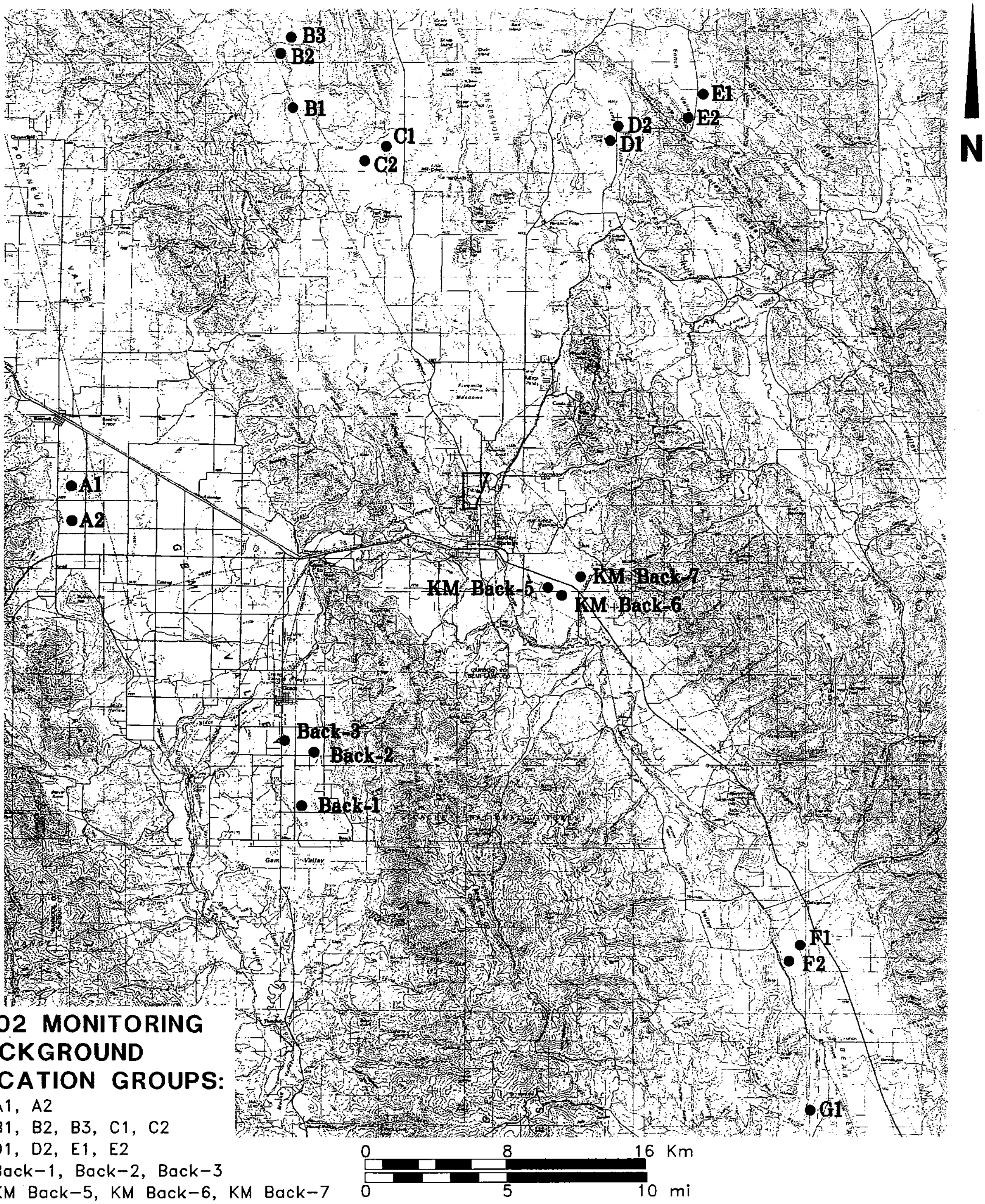
1.0 INTRODUCTION

Soil samples were collected as part of the Phase I & II (1991-1995) Remedial Investigation (RI) and five-year (2002) monitoring program (monitoring) around the Monsanto Soda Springs Phosphorous Plant (plant). These samples were collected in an effort to determine what, if any, impacts the Monsanto Phosphoria plant has on radium-226 (^{226}Ra). Samples collected during the five-year monitoring program were subject, per the Record-of Decision (ROD), to analysis for ^{226}Ra. The reduction in analytes from the RI was approved by USEPA (1997).

2.0 METHODOLOGY

Data collected from the RI and monitoring events were, per USEPA (2002), grouped into control and affected categories for evaluation. Data collected around the Monsanto Plant during the RI spatially matched the monitoring data collected by MWH in 2002. In accordance with the ROD, ^{226}Ra was the only constituent analyzed for soils during the monitoring. During the RI and monitoring, samples were collected from the 0-1 in. depth at selected locations. Fifteen affected stations and six control stations were sampled during the Phase I RI. Twenty-four affected stations and fourteen control stations were sampled during the Phase II RI. MWH sampled all 39 affected soil stations and six control soil stations. The USEPA approved the compositing of clustered control samples. In order to make comparisons with these two data sets, the results from the 20 background stations from the RI were similarly pooled and averaged. Soil collection at control and affected locations followed the field sampling plan (MWH, 2002) and is shown in Figure 2-1, *Five-Year Report Background Soil Sampling Locations*.

Statistical analysis was conducted nonparametrically with a Kruskal-Wallis one-way analysis of variance test accompanied by a Fisher's least significant difference (LSD) test to determine specific differences while controlling experiment-wise error (Georgia Institute of Technology, vol. II, chap. 6). An explanation of the Kruskal-Wallis method can be found in Appendix A of this report. Results from the data interpretation are presented in the Section 3.0. The statistical calculations performed on ^{226}Ra are presented in Section 4.0.



2002 MONITORING BACKGROUND LOCATION GROUPS:

① A1, A2
② B1, B2, B3, C1, C2
③ D1, D2, E1, E2
④ Back-1, Back-2, Back-3
⑤ KM Back-5, KM Back-6, KM Back-7
⑥ F1, F2, G1

SOURCE:

-USGS Topographic Map Soda Springs
Idaho-Wyoming 1:100,000 (1982)
-USGS Topographic Map Preston
Idaho-Wyoming-Utah 1:100,000 (1983)

FIGURE 2-1

FIVE-YEAR REPORT
BACKGROUND SOIL SAMPLING LOCATIONS

MONSANTO/CERCLA FIVE YEAR REVIEW - APPENDIX B

MWH

3.0 SOIL STATISTICAL RESULTS

Soil sample medians collected around the plant are presented below. The data presented are from the RI conducted by Golder Associates, and the monitoring conducted by MWH.

3.1 MONSANTO PLANT SOIL RESULTS

In the table below, sample concentrations that are indistinguishable from one another are shown with their sample medians highlighted on the same row. Any differences are denoted by displaying medians on different rows. 'RI' results are from remedial investigation sampling events, and 'M' results are data collected during the five-year monitoring program.

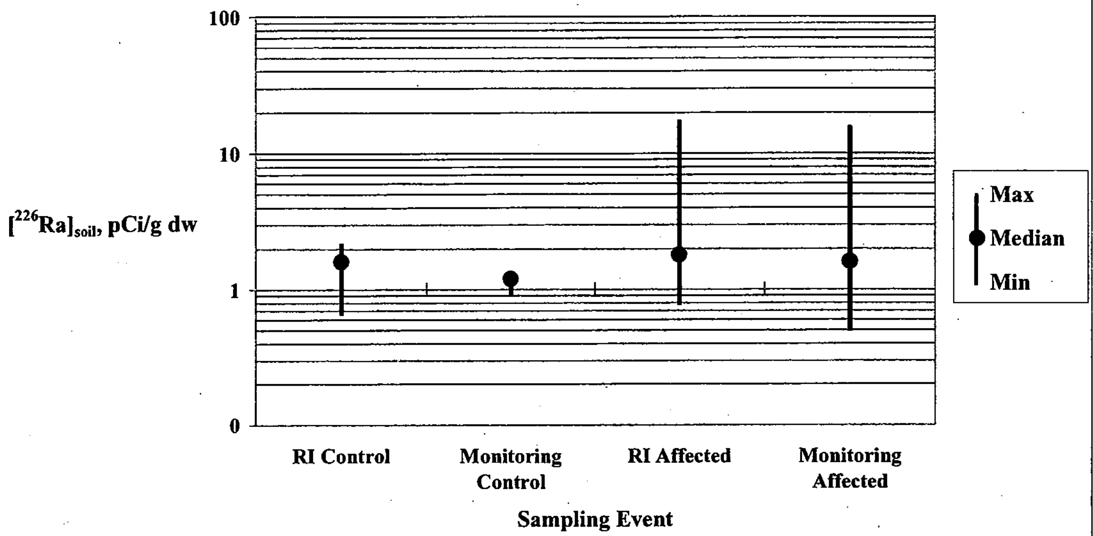
For ^{226}Ra, a graphical display of the data is plotted in Figure 3-1, *Monsanto Plant Soil Quality ^{226}Ra*. The figure shows the maximum, median, and minimum concentrations plotted as RI control, monitoring control, RI affected, or monitoring affected. These plots are provided for visual interpretation.

The medians of the ^{226}Ra data are presented in Table 3-1, *Monsanto Plant Soil Radium-226 Comparisons*. The results of the Kruskal-Wallis and the Fisher's LSD show that statistically there is no difference among the two control sampling events or the two affected events. The M and RI affected results are elevated above the controls. The graphical plot in Figure 3-1 is consistent with the statistical analysis of the ranked concentrations.

TABLE 3-1
MONSANTO PLANT SOIL RADIUM-226 COMPARISONS

	RI	M	RI	M	
$[^{226}Ra]_{soil}$ pCi/g dw	**Control**		**Affected**		
			■	■	
	■	■			**Affected area elevated**

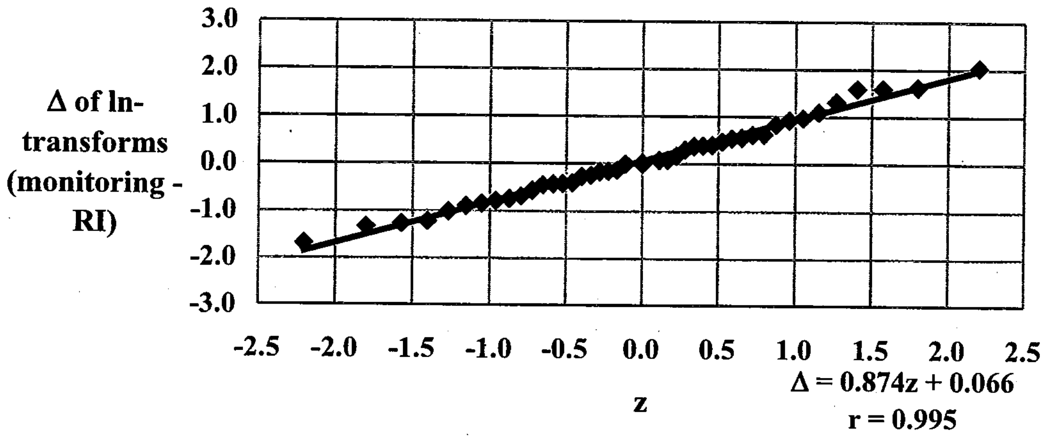
Figure 3-1. Monsanto Plant Soil Quality ^{226}Ra



While the statistical method preferred by USEPA for comparing background to site soil quality, ANOVA, shows no discernible difference in concentrations during monitoring relative to RI results, this method has limitations. A major limitation is that the method does not classify each station as either elevated or not. Yet, determining whether ^{226}Ra is elevated above the ROD's specified cleanup level is important. The reason why ^{226}Ra was identified as a soil contaminant during the RI is because a comparison was made between a control high-end quantile—specifically, the upper 95% confidence bound on the 95th percentile of the control distribution—and the concentration at each site sampling station.

Because environmental data are usually well modeled by means of a lognormal distribution, the difference (Δ) in the two-parameter ln-transforms of the RI and monitoring concentrations are presented in Figure 3-2 below:

Figure 3-2. Lognormal Fit Plot for $[^{226}Ra]_{soil}$



It is quite obvious that there are no outliers in this data set. In other words, there is no evidence of statistical significance of the differences noted above that appear to be significant from a compliance perspective—these differences are well explained as random noise. Thus, it is recommended that no action be taken on stations with differences that seem to be significant from a compliance perspective unless additional, higher resolution sampling is performed in a manner that will provide for replication at each station to allow objective statistical determination of any departures from the target cleanup goal.

What is most germane for a 5-year monitoring review is the difference in concentrations during the RI and during the monitoring event. Some stations have differences that appear to be significant from a compliance perspective in that they were either:

- above the target cleanup goal during the RI and are now below it (S-4, S2-6, S-12, and S-13); or,
- below the target cleanup goal during the RI and are now above it (S-1, MS2-9, MS2-10, and MS2-24).

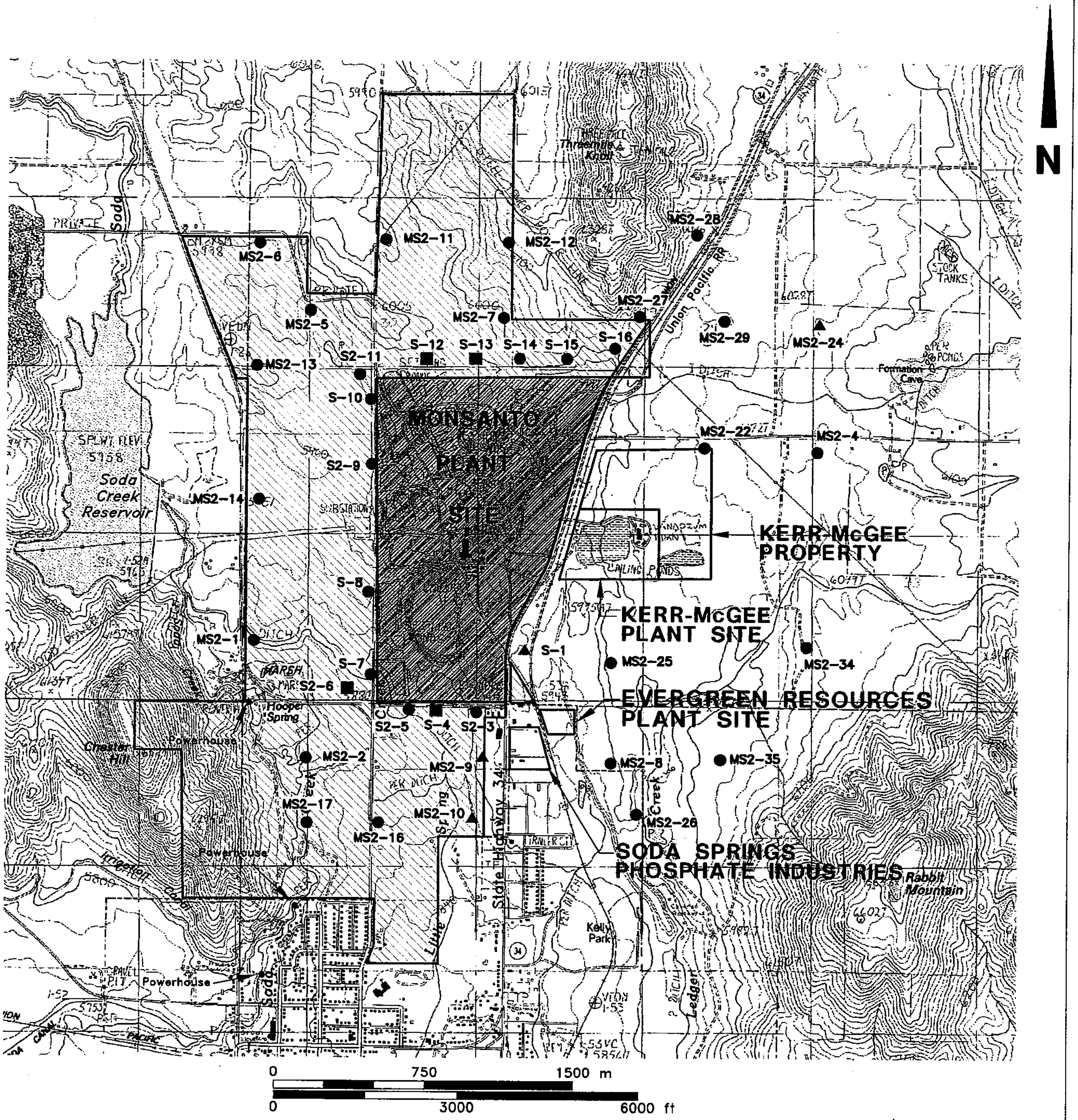
Table 3-2, *Monsanto Plant and Vicinity Soils, Monitoring and RI* $[^{226}Ra,_{soil}]$ presents the data set for the control and affected soil sample locations. Figure 3-3, *Monsanto Plant Vicinity Soils Difference in Radium-226 Concentrations Between RI and Monitoring* shows the locations of the soils collected around the plant. This figure also shows the four samples that are now above the target cleanup goal, and the four samples that are now below the target cleanup goal of 3.7 pCi/g.

TABLE 3-2
MONSANTO PLANT AND VICINITY SOILS, MONITORING AND RI [$^{226}Ra_{,soil}$]

Control Locations	Monitoring	RI[1]	Units
A1A2-0-C10	1.2	1.4	pCi/g
BACK123-0-C15	1.2	1.1	pCi/g
F1F2G1-0-C15	1.2	1.8	pCi/g
KMBACK-567-0-C15	0.95	1.3	pCi/g
B123C12-4-C25	0.65	1.8	pCi/g
D12E12-0-C20	1.0	2.1	pCi/g

Affected Locations	Monitoring	RI	Units
S-1-0-C5	6.3	3.4	pCi/g
S2-3-0-C5	9.2	12	pCi/g
S-4-0-C5	2.7	9.2	pCi/g
S2-5-0-C5	2.8	1.5	pCi/g
S2-6-0-C5	0.98	5.3	pCi/g
S-7-0-C5	1.4	1.6	pCi/g
S-8-4-C5	1.7	3.0	pCi/g
S2-9-0-C5	1.7	3.4	pCi/g
S-10-0-C5	15	10	pCi/g
S2-11-0-C5	6.9	17	pCi/g
S-12-0-C5	1.5	5.7	pCi/g
S-13-0-C5	2.7	9.6	pCi/g
S-14-0-C5	5.6	13	pCi/g
S-15-0-C5	4.9	4.8	pCi/g
S-16-0-C5	1.5	2.3	pCi/g
MS2-1-0-C5	0.51	0.60	pCi/g
MS2-2-0-C5	0.60	0.60	pCi/g
MS2-4-0-C5	1.1	1.4	pCi/g
MS2-5-0-C5	1.6	1.0	pCi/g
MS2-6-0-C5	1.4	0.80	pCi/g
MS2-7-0-C5	1.5	3.3	pCi/g
MS2-8-0-C5	2.8	0.75	pCi/g
MS2-9-0-C5	4.7	0.95	pCi/g
MS2-10-0-C5	4.6	0.90	pCi/g
MS2-11-4-C5	1.6	2.5	pCi/g
MS2-12-0-C5	2.4	0.80	pCi/g
MS2-13-0-C5	1.5	0.65	pCi/g
MS2-14-0-C5	1.1	0.75	pCi/g
MS2-16-4-C5	1.2	0.70	pCi/g
MS2-17-0-C5	1.2	1.2	pCi/g
MS2-22-4-C5	0.99	1.5	pCi/g
MS2-24-0-C5	6.4	1.3	pCi/g
MS2-25-0-C5	1.6	1.6	pCi/g
MS2-26-0-C5	1.3	1.1	pCi/g
MS2-27-0-C5	3.1	0.40	pCi/g
MS2-28-0-C5	0.96	0.65	pCi/g
MS2-29-0-C5	1.9	0.75	pCi/g
MS2-34-0-C5	2.1	0.79	pCi/g
MS2-35-0-C5	1.3	1.2	pCi/g

Notes:
RI control locations were pooled and averaged to be comparable to the combined Monitoring location samples.



LEGEND:

● —— NO SIGNIFICANT CHANGE
■ —— NOW BELOW TARGET CLEANUP GOAL 3.7 pCi/g
▲ —— NOW ABOVE TARGET CLEANUP GOAL 3.7 pCi/g
▨ —— MONSANTO PLANT SITE
▧ —— PROPERTY OWNED OR DEED RESTRICTION PURCHASED BY MONSANTO

SOURCE:
PHASE II RI REPORT (GOLDER, 1995)

USGS Topographic Map Soda Springs
Idaho-Wyoming 1:100,000 (1982)

FIGURE 3-3

MONSANTO PLANT VICINITY SOILS DIFFERENCE IN RADIUM-226 CONCENTRATIONS BETWEEN RI AND MONITORING

4.0 STATISTICAL CALCULATIONS

The statistical calculations for the above analyses are presented on the following pages. The calculations were completed in Microsoft Excel.

Monsanto Plant Soils ^{226}Ra pCi/g **Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples**

Station	RI Control	Rank	Rank^2	Station	RI Affected	Rank	Rank^2	Station	Monitoring Control	Rank	Rank^2	Station	Monitoring Affected	Rank	Rank^2
1C6	2.1	58.5	3,422.25	1A39	3.4	69.5	4,830.25	2C6	1.1	13	169.00	2A39	6.3	79	6,241.00
1C5	1.8	52.5	2,756.25	1A38	12	86	7,396.00	2C5	1.3	27	729.00	2A38	9.2	82.5	6,806.25
1C4	0.70	3	9.00	1A37	1.5	37.5	1,406.25	2C4	0.95	6	36.00	2A37	2.8	65.5	4,290.25
1C3	1.8	52.5	2,756.25	1A36	5.3	76	5,776.00	2C3	1.2	20	400.00	2A36	0.98	8	64.00
1C2	1.1	13	169.00	1A35	9.2	82.5	6,806.25	2C2	1.2	20	400.00	2A35	2.7	63.5	4,032.25
1C1	1.4	31.5	992.25	1A34	1.6	45	2,025.00	2C1	1.2	20	400.00	2A34	1.4	31.5	992.25
				1A33	1.2	20	400.00					2A33	0.51	1	1.00
				1A32	2.5	62	3,844.00					2A32	1.6	45	2,025.00
				1A31	1.3	27	729.00					2A31	1.5	37.5	1,406.25
				1A30	1.5	37.5	1,406.25					2A30	1.1	13	169.00
				1A29	1.4	31.5	992.25					2A29	1.2	20	400.00
				1A28	1.2	20	400.00					2A28	1.2	20	400.00
				1A27	1.2	20	400.00					2A27	0.60	2	4.00
				1A26	2.0	57	3.249.00					2A26	1.6	45	2,025.00
				1A25	1.6	45	2,025.00					2A25	1.4	31.5	992.25
				1A24	10	85	7,225.00					2A24	15	88	7,744.00
				1A23	17	89.5	8,010.25					2A23	6.9	81	6,561.00
				1A22	3.4	69.5	4,830.25					2A22	1.7	49.5	2,450.25
				1A21	3.9	71	5,041.00					2A21	1.7	49.5	2,450.25
				1A20	1.8	52.5	2,756.25					2A20	4.6	72	5,184.00
				1A19	1.6	45	2,025.00					2A19	2.4	61	3,721.00
				1A18	1.8	52.5	2,756.25					2A18	0.99	9	81.00
				1A17	1.6	45	2,025.00					2A17	1.6	45	2,025.00
				1A16	1.1	13	169.00					2A16	1.3	27	729.00
				1A15	0.80	5	25.00					2A15	3.1	68	4,624.00
				1A14	1.3	27	729.00					2A14	0.96	7	49.00
				1A13	1.5	37.5	1,406.25					2A13	1.9	55.5	3,080.25
				1A12	0.79	4	16.00					2A12	2.1	58.5	3,422.25
				1A11	1.2	20	400.00					2A11	1.3	27	729.00
				1A10	1.0	10	100.00					2A10	6.4	80	6,400.00
				1A9	2.9	67	4.489.00					2A9	1.1	13	169.00
				1A8	1.5	37.5	1,406.25					2A8	2.8	65.5	4,290.25
				1A7	1.9	55.5	3,080.25					2A7	4.7	73	5,329.00
				1A6	17	89.5	8,010.25					2A6	1.5	37.5	1,406.25
				1A5	5.7	78	6,084.00					2A5	1.5	37.5	1,406.25
				1A4	9.6	84	7,056.00					2A4	2.7	63.5	4,032.25
				1A3	13	87	7,569.00					2A3	5.6	77	5,929.00
				1A2	4.8	74	5.476.00					2A2	4.9	75	5,625.00
				1A1	2.3	60	3,600.00					2A1	1.5	37.5	1,406.25
	1.6	211.0			1.80	1975.5			1.20	106.0			1.6	1802.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	6
n_2	39
n_3	6
n_4	39
N	90
S^2	681
T	0.03
analytes	1
p	0.999
p_{exp}	0.999
$T_{0.05,3}$	7.81
$T_{0.05,3}$	7.81

Reject H_0 if T > 7.81 (for a per-comparison Type I error rate of 5%)

Reject H_0 if T > 7.81 (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of the per-comparison error rate); retain H_0 (from the perspective of the experiment-wise error rate)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	86
$t_{0.975,v}$	1.988
$t_{0.95,v}$	1.663

	sidedness	LSD	$LSD_{0.05}$	
1C vs. 1A	1	37.154	19.350	!
1C vs. 2C	2	4.167	30.457	
1C vs. 2A	1	32.718	19.350	!
2C vs. 1A	1	32.987	19.350	!
2A vs. 1A	2	4.436	11.946	
2C vs. 2A	1	28.551	19.350	!

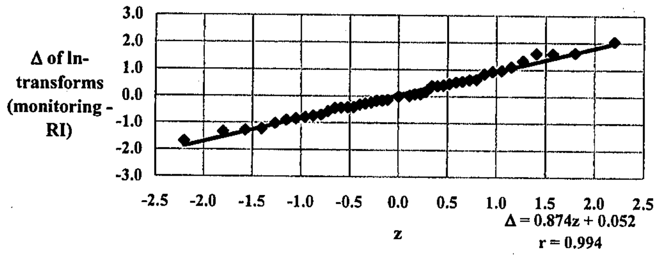
^{226}Ra in soils around Monsanto Plant Site

Station	Value	Ties	Rank
2A33	0.51		1
2A27	0.60		2
1C4	0.70		3
1A12	0.79		4
1A15	0.80		5
2C4	0.95		6
2A14	0.96		7
2A36	0.98		8
2A18	0.99		9
1A10	1.0		10
1C2	1.1		13
1A16	1.1	!	13
2C6	1.1	!	13
2A30	1.1	!	13
2A9	1.1	!	13
1A33	1.2		20
1A28	1.2	!	20
1A27	1.2	!	20
1A11	1.2	!	20
2C3	1.2	!	20
2C2	1.2	!	20
2C1	1.2	!	20
2A29	1.2	!	20
2A28	1.2	!	20
1A31	1.3		27
1A14	1.3	!	27
2C5	1.3	!	27
2A16	1.3	!	27
2A11	1.3	!	27
1C1	1.4		31.5
1A29	1.4	!	31.5
2A34	1.4	!	31.5
2A25	1.4	!	31.5
1A37	1.5		37.5
1A30	1.5	!	37.5
1A13	1.5	!	37.5
1A8	1.5	!	37.5
2A31	1.5	!	37.5
2A6	1.5	!	37.5
2A5	1.5	!	37.5
2A1	1.5	!	37.5
1A34	1.6		45
1A25	1.6	!	45
1A19	1.6	!	45
1A17	1.6	!	45
2A32	1.6	!	45
2A26	1.6	!	45
2A17	1.6	!	45
2A22	1.7		49.5
2A21	1.7	!	49.5
1C5	1.8		52.5
1C3	1.8	!	52.5
1A20	1.8	!	52.5
1A18	1.8	!	52.5
1A7	1.9		55.5
2A13	1.9	!	55.5
1A26	2.0		57
1C6	2.1		58.5
2A12	2.1	!	58.5
1A1	2.3		60
2A19	2.4		61
1A32	2.5		62
2A35	2.7		63.5
2A4	2.7	!	63.5
2A37	2.8		65.5
2A8	2.8	!	65.5
1A9	2.9		67
2A15	3.1		68
1A39	3.4		69.5
1A22	3.4	!	69.5
1A21	3.9		71
2A20	4.6		72
2A7	4.7		73
1A2	4.8		74
2A2	4.9		75
1A36	5.3		76
2A3	5.6		77
1A5	5.7		78
2A39	6.3		79
2A10	6.4		80
2A23	6.9		81
1A35	9.2		82.5
2A38	9.2	!	82.5
1A4	9.6		84
1A24	10		85
1A38	12		86
1A3	13		87
2A24	15		88
1A23	17		89.5
1A6	17	!	89.5

^{226}Ra Soil Analysis	2002	RI	Δ
Station	ln[^{226}Ra]		
A1A2-0-C10	0.18	0.34	-0.15
BACK123-0-C15	0.18	0.10	0.09
F1F2G1-0-C15	0.18	0.59	-0.41
KMBACK-567-0-C15	-0.05	0.26	-0.31
B123C12-4-C25	-0.43	0.59	-1.02
D12E12-0-C20	0.00	0.74	-0.74
	ln	ln	Δ
S-1-0-C5	1.84	1.22	0.62
S2-3-0-C5	2.22	2.48	-0.27
S-4-0-C5	0.99	2.22	-1.23
S2-5-0-C5	1.03	0.41	0.62
S2-6-0-C5	-0.02	1.67	-1.69
S-7-0-C5	0.34	0.47	-0.13
S-8-4-C5	0.53	1.10	-0.57
S2-9-0-C5	0.53	1.22	-0.69
S-10-0-C5	2.71	2.30	0.41
S2-11-0-C5	1.93	2.83	-0.90
S-12-0-C5	0.41	1.74	-1.34
S-13-0-C5	0.99	2.26	-1.27
S-14-0-C5	1.72	2.56	-0.84
S-15-0-C5	1.59	1.57	0.02
S-16-0-C5	0.41	0.83	-0.43
MS2-1-0-C5	-0.67	-0.51	-0.16
MS2-2-0-C5	-0.51	-0.51	0.00
MS2-4-0-C5	0.10	0.34	-0.24
MS2-5-0-C5	0.47	0.00	0.47
MS2-6-0-C5	0.34	-0.22	0.56
MS2-7-0-C5	0.41	1.19	-0.79
MS2-8-0-C5	1.03	-0.29	1.32
MS2-9-0-C5	1.55	-0.05	1.60
MS2-10-0-C5	1.53	-0.11	1.63
MS2-11-4-C5	0.47	0.92	-0.45
MS2-12-0-C5	0.88	-0.22	1.10
MS2-13-0-C5	0.41	-0.43	0.84
MS2-14-0-C5	0.10	-0.29	0.38
MS2-16-4-C5	0.18	-0.36	0.54
MS2-17-0-C5	0.18	0.18	0.00
MS2-22-4-C5	-0.01	0.41	-0.42
MS2-24-0-C5	1.86	0.26	1.59
MS2-25-0-C5	0.47	0.47	0.00
MS2-26-0-C5	0.26	0.10	0.17
MS2-27-0-C5	1.13	-0.92	2.05
MS2-28-0-C5	-0.04	-0.43	0.39
MS2-29-0-C5	0.64	-0.29	0.93
MS2-34-0-C5	0.74	-0.24	0.98
MS2-35-0-C5	0.26	0.18	0.08

differences of ln-transforms: i	Δ	z	r^2	r
1	-1.69	-2.20	0.988	0.994
2	-1.34	-1.80		
3	-1.27	-1.57		
4	-1.23	-1.40		
5	-1.02	-1.27		
6	-0.90	-1.15		
7	-0.84	-1.05		
8	-0.79	-0.96		
9	-0.74	-0.88		
10	-0.69	-0.80		
11	-0.57	-0.72		
12	-0.45	-0.65		
13	-0.43	-0.59		
14	-0.42	-0.52		
15	-0.41	-0.46		
16	-0.31	-0.40		
17	-0.27	-0.34		
18	-0.24	-0.28		
19	-0.16	-0.22		
20	-0.15	-0.17		
21	-0.13	-0.11		
23	0.0	0.00		
23	0.0	0.00		
23	0.0	0.00		
25	0.02	0.11		
26	0.08	0.17		
27	0.09	0.22		
28	0.17	0.28		
29	0.38	0.34		
30	0.39	0.40		
31	0.41	0.46		
32	0.47	0.52		
33	0.54	0.59		
34	0.56	0.65		
35	0.62	0.72		
36	0.62	0.80		
37	0.84	0.88		
38	0.93	0.96		
39	0.98	1.05		
40	1.10	1.15		
41	1.32	1.27		
42	1.59	1.40		
43	1.60	1.57		
44	1.63	1.80		
45	2.05	2.20		

Figure 3-2. Lognormal Fit Plot for [^{226}Ra]$_{soil}$



Alexander Reservoir Arsenic mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	$Rank^2$	Station	RI Affected	Rank	$Rank^2$	Station	Monitoring Control	Rank	$Rank^2$	Station	Monitoring Affectec	Rank	$Rank^2$
1C9	1.9	6.5	42.25	1A9	18	35	1,225.00	2C9	2.0	9.5	90.25	2A9	4.6	26	676.00
1C8	1.7	2.5	6.25	1A8	24	36	1,296.00	2C8	1.9	6.5	42.25	2A8	3.6	23.5	552.25
1C7	2.4	15	225.00	1A7	11	34	1,156.00	2C7	1.7	2.5	6.25	2A7	5.0	27.5	756.25
1C6	1.9	6.5	42.25	1A6	7.2	32	1,024.00	2C6	1.6	1	1.00	2A6	3.7	25	625.00
1C5	2.4	15	225.00	1A5	5.6	30	900.00	2C5	1.9	6.5	42.25	2A5	9.7	33	1,089.00
1C4	2.7	18	324.00	1A4	5.9	31	961.00	2C4	2.3	12	144.00	2A4	3.4	22	484.00
1C3	2.3	12	144.00	1A3	5.0	27.5	756.25	2C3	2.4	15	225.00	2A3	2.6	17	289.00
1C2	2.9	19.5	380.25	1A2	3.6	23.5	552.25	2C2	1.8	4	16.00	2A2	2.0	9.5	90.25
1C1	2.9	19.5	380.25	1A1	5.1	29	841.00	2C1	2.3	12	144.00	2A1	3.1	21	441.00
	2.4	114.5			5.9	278.0			1.9	69.0			3.6	204.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.67
T	26.19
analytes	8
p	0.000009
p_{exp}	0.000070
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{\text{all}\\ \text{ranks}}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

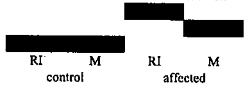
Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	18.167	4.408
1C vs. 2C	2	5.056	5.300
1C vs. 2A	1	10.000	4.408
2C vs. 1A	1	23.222	4.408
2A vs. 1A	2	8.167	5.300
2C vs. 2A	1	15.056	4.408

Station	Value	Ties	Rank
2C6	1.6		1
1C8	1.7		2.5
2C7	1.7	1	2.5
2C2	1.8		4
1C9	1.9		6.5
1C6	1.9	1	6.5
2C8	1.9	1	6.5
2C5	1.9	1	6.5
2A2	2.0		9.5
2C9	2.0	1	9.5
1C3	2.3		12
2C4	2.3	1	12
2C1	2.3	1	12
1C7	2.4		15
1C5	2.4	1	15
2C3	2.4	1	15
2A3	2.6		17
1C4	2.7		18
1C2	2.9		19.5
1C1	2.9	1	19.5
2A1	3.1		21
2A4	3.4		22
1A2	3.6		23.5
2A8	3.6	1	23.5
2A6	3.7		25
2A9	4.6		26
1A3	5.0		27.5
2A7	5.0	1	27.5
1A1	5.1		29
1A5	5.6		30
1A4	5.9		31
1A6	7.2		32
2A5	9.7		33
1A7	11		34
1A9	18		35
1A8	24		36

As in Sediment in Alexander Reservoir



Alexander Reservoir Cadmium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	Rank^2
1C9	0.30	4.5	20.25	1A9	30	36	1,296.00	2C9	0.46	11.5	132.25	2A9	3.5	25	625.00
1C8	0.10	1	1.00	1A8	25	35	1,225.00	2C8	0.48	13	169.00	2A8	2.7	22	484.00
1C7	0.30	4.5	20.25	1A7	21	34	1,156.00	2C7	0.50	15.5	240.25	2A7	6.3	29	841.00
1C6	0.15	2.5	6.25	1A6	12	32.5	1,056.25	2C6	0.44	9.5	90.25	2A6	2.8	23	529.00
1C5	0.15	2.5	6.25	1A5	8.9	31	961.00	2C5	0.44	9.5	90.25	2A5	12	32.5	1,056.25
1C4	0.50	15.5	240.25	1A4	6.2	28	784.00	2C4	0.46	11.5	132.25	2A4	3.0	24	576.00
1C3	0.50	15.5	240.25	1A3	6	27	729.00	2C3	0.37	7	49.00	2A3	2.4	21	441.00
1C2	0.50	15.5	240.25	1A2	5	26	676.00	2C2	0.31	6	36.00	2A2	1.4	20	400.00
1C1	0.40	8	64.00	1A1	8	30	900.00	2C1	0.52	18	324.00	2A1	0.62	19	361.00
	0.30	69.5			8.9	279.5			0.46	101.5			2.8	215.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.79
T	28.89
analytes	8
p	0.0000024
p_{exp}	0.000019
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if T > 7.81 (for a per-comparison Type I error rate of 5%)

Reject H_0 if T > 12.31 (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{\text{all}\\ \text{ranks}}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

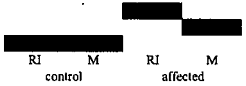
Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	23.333	3.673
1C vs. 2C	2	3.556	4.417
1C vs. 2A	1	16.222	3.673
2C vs. 1A	1	19.778	3.673
2A vs. 1A	2	7.111	4.417
2C vs. 2A	1	12.667	3.673

Station	Value	Ties	Rank
1C8	0.10		1
1C6	0.15		2.5
1C5	0.15	1	2.5
1C9	0.30		4.5
1C7	0.30	1	4.5
2C2	0.31		6
2C3	0.37		7
1C1	0.40		8
2C6	0.44		9.5
2C5	0.44	1	9.5
2C9	0.46		11.5
2C4	0.46	1	11.5
2C8	0.48		13
1C4	0.50		15.5
1C3	0.50	1	15.5
1C2	0.50	1	15.5
2C7	0.50	1	15.5
2C1	0.52		18
2A1	0.62		19
2A2	1.4		20
2A3	2.4		21
2A8	2.7		22
2A6	2.8		23
2A4	3.0		24
2A9	3.5		25
1A2	5		26
1A3	6		27
1A4	6.2		28
2A7	6.3		29
1A1	8		30
1A5	8.9		31
2A5	12		32.5
1A6	12	1	32.5
1A7	21		34
1A8	25		35
1A9	30		36

Cd in Sediment in Alexander Reservoir



Alexander Reservoir Nickel mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	Rank^2
1C9	6.0	4.5	20.25	1A9	35	35.5	1,260.25	2C9	7.3	12	144.00	2A9	11	22	484.00
1C8	3.0	1	1.00	1A8	35	35.5	1,260.25	2C8	6.8	7	49.00	2A8	11	22	484.00
1C7	8.0	15	225.00	1A7	30	34	1,156.00	2C7	7.2	10.5	110.25	2A7	13	27.5	756.25
1C6	7.0	9	81.00	1A6	20	31.5	992.25	2C6	6.6	6	36.00	2A6	11	22	484.00
1C5	6.0	4.5	20.25	1A5	20	31.5	992.25	2C5	7.2	10.5	110.25	2A5	24	33	1,089.00
1C4	9.0	17	289.00	1A4	15	30	900.00	2C4	8.0	15	225.00	2A4	11	22	484.00
1C3	8.0	15	225.00	1A3	12	25.5	650.25	2C3	7.6	13	169.00	2A3	12	25.5	650.25
1C2	10	19	361.00	1A2	13	27.5	756.25	2C2	5.9	3	9.00	2A2	5.8	2	4.00
1C1	11	22	484.00	1A1	14	29	841.00	2C1	6.9	8	64.00	2A1	9.6	18	324.00
	8.0	107.0			20	280.0			7.2	85.0			11	194.0	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.57
T	23.94
analytes	8
p	0.0000257
p_{exp}	0.000206
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T=\frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i}-\frac{N(N+1)^2}{4}\right)$$

$$S^2=\frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}}R(X_{ij})^2-\frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i}-\frac{R_j}{n_j}\right|>t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

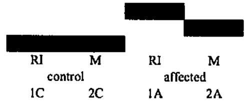
Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	19.222	4.937
1C vs. 2C	2	2.444	5.937
1C vs. 2A	1	9.667	4.937
2C vs. 1A	1	21.667	4.937
2A vs. 1A	2	9.556	5.937
2C vs. 2A	1	12.111	4.937

Station	Value	Ties	Rank
1C8	3.0		1
2A2	5.8		2
2C2	5.9		3
1C9	6.0		4.5
1C5	6.0	'	4.5
2C6	6.6		6
2C8	6.8		7
2C1	6.9		8
1C6	7.0		9
2C7	7.2		10.5
2C5	7.2	!	10.5
2C9	7.3		12
2C3	7.6		13
1C7	8.0		15
1C3	8.0	!	15
2C4	8.0	'	15
1C4	9.0		17
2A1	9.6		18
1C2	10		19
1C1	11		22
2A9	11	!	22
2A8	11	!	22
2A6	11	!	22
2A4	11	!	22
1A3	12		25.5
2A3	12	'	25.5
1A2	13		27.5
2A7	13	'	27.5
1A1	14		29
1A4	15		30
1A6	20		31.5
1A5	20	'	31.5
2A5	24		33
1A7	30		34
1A9	35		35.5
1A8	35	'	35.5

Ni in Sediment in Alexander Reservoir



Alexander Reservoir Copper mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	$Rank^2$
1C9	5.1	12.5	156.25	1A9	10	33	1,089.00	2C9	5.6	14.5	210.25	2A9	5.8	16.5	272.25
1C8	2.2	1	1.00	1A8	13	36	1,296.00	2C8	4.7	7.5	56.25	2A8	4.7	7.5	56.25
1C7	6.7	26	676.00	1A7	12	35	1,225.00	2C7	4.6	5.5	30.25	2A7	8.1	31	961.00
1C6	5.6	14.5	210.25	1A6	11	34	1,156.00	2C6	5.1	12.5	156.25	2A6	6.4	24.5	600.25
1C5	4.8	9	81.00	1A5	6.4	24.5	600.25	2C5	5.9	19	361.00	2A5	8.0	30	900.00
1C4	7.7	28	784.00	1A4	6.3	23	529.00	2C4	6.0	21	441.00	2A4	6.1	22	484.00
1C3	7.1	27	729.00	1A3	4.0	3	9.00	2C3	5.8	16.5	272.25	2A3	4.6	5.5	30.25
1C2	7.8	29	841.00	1A2	5.9	19	361.00	2C2	5.0	10.5	110.25	2A2	3.4	2	4.00
1C1	9.3	32	1,024.00	1A1	5.0	10.5	110.25	2C1	4.3	4	16.00	2A1	5.9	19	361.00
	6.7	179.0			6.4	218.0			5.1	111.0			5.9	158.0	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.84
T	5.98
analytes	8
p	0.1128
p_{exp}	0.6162
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if T > 7.81 (for a per-comparison Type I error rate of 5%)

Reject H_0 if T > 12.31 (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

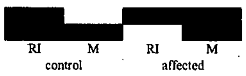
$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{\text{all}\\ \text{ranks}}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	32		
$t_{0.975,32}$	2.037		
$t_{0.95,32}$	1.694		
	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	4.333	8.006
1C vs. 2C	2	7.556	9.628
1C vs. 2A	1	-2.333	8.006
2C vs. 1A	1	11.889	8.006
2A vs. 1A	2	6.667	9.628
2C vs. 2A	1	5.222	8.006

Cu in Sediment in Alexander Reservoir



Station	Value	Ties	Rank
1C8	2.2		1
2A2	3.4		2
1A3	4.0		3
2C1	4.3		4
2C7	4.6		5.5
2A3	4.6	!	5.5
2C8	4.7		7.5
2A8	4.7	'	7.5
1C5	4.8		9
1A1	5.0		10.5
2C2	5.0	'	10.5
1C9	5.1		12.5
2C6	5.1	!	12.5
1C6	5.6		14.5
2C9	5.6	'	14.5
2C3	5.8		16.5
2A9	5.8	!	16.5
1A2	5.9		19
2C5	5.9	'	19
2A1	5.9	!	19
2C4	6.0		21
2A4	6.1		22
1A4	6.3		23
1A5	6.4		24.5
2A6	6.4	'	24.5
1C7	6.7		26
1C3	7.1		27
1C4	7.7		28
1C2	7.8		29
2A5	8.0		30
2A7	8.1		31
1C1	9.3		32
1A9	10		33
1A6	11		34
1A7	12		35
1A8	13		36

Alexander Reservoir Selenium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	Rank²
1C9	1.2	24	576.00	1A9	6.0	35.5	1,260.25	2C9	0.36	11	121.00	2A9	0.68	19	361.00
1C8	0.40	12	144.00	1A8	6.0	35.5	1,260.25	2C8	0.24	2	4.00	2A8	0.54	14	196.00
1C7	1.3	26	676.00	1A7	4.0	34	1,156.00	2C7	0.31	7.5	56.25	2A7	1.2	24	576.00
1C6	0.50	13	169.00	1A6	3.2	33	1,089.00	2C6	0.25	3	9.00	2A6	0.64	17	289.00
1C5	0.70	20.5	420.25	1A5	1.9	29.5	870.25	2C5	0.32	9	81.00	2A5	1.9	29.5	870.25
1C4	0.60	15.5	240.25	1A4	2.3	32	1,024.00	2C4	0.31	7.5	56.25	2A4	0.66	18	324.00
1C3	0.60	15.5	240.25	1A3	1.4	27.5	756.25	2C3	0.29	5	25.00	2A3	0.84	22	484.00
1C2	0.70	20.5	420.25	1A2	1.4	27.5	756.25	2C2	0.26	4	16.00	2A2	0.33	10	100.00
1C1	1.2	24	576.00	1A1	2.1	31	961.00	2C1	0.23	1	1.00	2A1	0.30	6	36.00
	0.70	171.0			2.3	285.5			0.29	50.0			0.66	159.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.86
T	27.87
analytes	8
p	0.0000039
p_{exp}	0.000031
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an.experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T=\frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i}-\frac{N(N+1)^2}{4}\right)$$

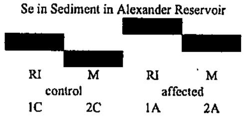
$$S^2=\frac{1}{N-1}\left(\sum_{\substack{\text{all}\\\text{ranks}}}R(X_{ij})^2-\frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i}-\frac{R_j}{n_j}\right|>t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	12.722	3.970
1C vs. 2C	2	13.444	4.774
1C vs. 2A	1	-1.278	3.970
2C vs. 1A	1	26.167	3.970
2A vs. 1A	2	14.000	4.774
2C vs. 2A	1	12.167	3.970



Station	Value	Ties	Rank
2C1	0.23		1
2C8	0.24		2
2C6	0.25		3
2C2	0.26		4
2C3	0.29		5
2A1	0.30		6
2C4	0.31		7.5
2C7	0.31	!	7.5
2C5	0.32		9
2A2	0.33		10
2C9	0.36		11
1C8	0.40		12
1C6	0.50		13
2A8	0.54		14
1C3	0.60		15.5
1C4	0.60	!	15.5
2A6	0.64		17
2A4	0.66		18
2A9	0.68		19
1C2	0.70		20.5
1C5	0.70	!	20.5
2A3	0.84		22
1C9	1.2		24
1C1	1.2	!	24
2A7	1.2	!	24
1C7	1.3		26
1A2	1.4		27.5
1A3	1.4	!	27.5
1A5	1.9		29.5
2A5	1.9	!	29.5
1A1	2.1		31
1A4	2.3		32
1A6	3.2		33
1A7	4.0		34
1A8	6.0		35.5
1A9	6.0	!	35.5

Alexander Reservoir Silver mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	$Rank^2$
1C9	0.040	6	36.00	1A9	0.25	35	1,225.00	2C9	0.14	30	900.00	2A9	0.087	23	529.00
1C8	0.010	1	1.00	1A8	0.30	36	1,296.00	2C8	0.077	19.5	380.25	2A8	0.062	15	225.00
1C7	0.030	2.5	6.25	1A7	0.24	34	1,156.00	2C7	0.057	11	121.00	2A7	0.13	29	841.00
1C6	0.050	9.5	90.25	1A6	0.16	31.5	992.25	2C6	0.077	19.5	380.25	2A6	0.081	22	484.00
1C5	0.030	2.5	6.25	1A5	0.080	21	441.00	2C5	0.066	16	256.00	2A5	0.18	33	1,089.00
1C4	0.060	13	169.00	1A4	0.090	24	576.00	2C4	0.070	17	289.00	2A4	0.093	26	676.00
1C3	0.040	6	36.00	1A3	0.040	6	36.00	2C3	0.092	25	625.00	2A3	0.095	27	729.00
1C2	0.050	9.5	90.25	1A2	0.10	28	784.00	2C2	0.16	31.5	992.25	2A2	0.034	4	16.00
1C1	0.060	13	169.00	1A1	0.060	13	169.00	2C1	0.044	8	64.00	2A1	0.075	18	324.00
	0.040	63.0			0.1	228.5			0.077	177.5			0.087	197.0	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.83
T	15.65
analytes	8
p	0.0013393
p_{exp}	0.010664
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

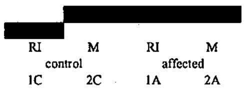
Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	18.389	6.537
1C vs. 2C	2	12.722	7.861
1C vs. 2A	1	14.889	6.537
2C vs. 1A	1	5.667	6.537
2A vs. 1A	2	3.500	7.861
2C vs. 2A	1	2.167	6.537

Station	Value	Ties	Rank
1C8	0.010		1
1C7	0.030		2.5
1C5	0.030	'	2.5
2A2	0.034		4
1C9	0.040		6
1C3	0.040	'	6
1A3	0.040	'	6
2C1	0.044		8
1C6	0.050		9.5
1C2	0.050	'	9.5
2C7	0.057		11
1C4	0.060		13
1C1	0.060	'	13
1A1	0.060	'	13
2A8	0.062		15
2C5	0.066		16
2C4	0.070		17
2A1	0.075		18
2C8	0.077		19.5
2C6	0.077	'	19.5
1A5	0.080		21
2A6	0.081		22
2A9	0.087		23
1A4	0.090		24
2C3	0.092		25
2A4	0.093		26
2A3	0.095		27
1A2	0.10		28
2A7	0.13		29
2C9	0.14		30
1A6	0.16		31.5
2C2	0.16	'	31.5
2A5	0.18		33
1A7	0.24		34
1A9	0.25		35
1A8	0.30		36

Ag in Sediment in Alexander Reservoir



Alexander Reservoir Vanadium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank2	Station	RI Affected	Rank	Rank2	Station	Monitoring Control	Rank	Rank2	Station	Monitoring Affectec	Rank	Rank²
1C9	14	18	324.00	1A9	57	35	1,225.00	2C9	7.8	7	49.00	2A9	9.4	14	196.00
1C8	7.5	6	36.00	1A8	66	36	1,296.00	2C8	7.4	5	25.00	2A8	8.9	12	144.00
1C7	19	23	529.00	1A7	49	34	1,156.00	2C7	7.8	8	64.00	2A7	16	21	441.00
1C6	18	22	484.00	1A6	38	33	1,089.00	2C6	6.9	3.5	12.25	2A6	11	15	225.00
1C5	15	19.5	380.25	1A5	25	31	961.00	2C5	9.1	13	169.00	2A5	23	29	841.00
1C4	23	29	841.00	1A4	23	29	841.00	2C4	8.5	9.5	90.25	2A4	11	16	256.00
1C3	20	25	625.00	1A3	15	19.5	380.25	2C3	8.6	11	121.00	2A3	12	17	289.00
1C2	22	27	729.00	1A2	20	25	625.00	2C2	6.8	2	4.00	2A2	5.8	1	1.00
1C1	26	32	1,024.00	1A1	20	25	625.00	2C1	6.9	3.5	12.25	2A1	8.5	9.5	90.25
	19	201.5			25	267.5			7.8	62.5			11	134.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_i	9
N	36
S^2	110.84
T	23.32
analytes	8
p	0.0000346
p_{exp}	0.000277
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T=\frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i}-\frac{N(N+1)^2}{4}\right)$$

$$S^2=\frac{1}{N-1}\left(\sum_{\substack{\text{all}\\ \text{ranks}}}R(X_{ij})^2-\frac{N(N+1)^2}{4}\right)$$

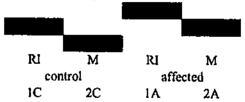
$$\left|\frac{R_i}{n_i}-\frac{R_j}{n_j}\right|>t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	32
$t_{0.975,32}$	2.037
$t_{0.95,32}$	1.694

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	7.333	5.079
1C vs. 2C	2	15.444	6.107
1C vs. 2A	1	-7.444	5.079
2C vs. 1A	1	22.778	5.079
2A vs. 1A	2	14.778	6.107
2C vs. 2A	1	8.000	5.079

V in Sediment in Aloxander Reservoir



Station	Value	Ties	Rank
2A2	5.8		1
2C2	6.8		2
2C6	6.9		3.5
2C1	6.9	!	3.5
2C8	7.4		5
1C8	7.5		6
2C9	7.8		7
2C7	7.8		8
2C4	8.5		9.5
2A1	8.5	!	9.5
2C3	8.6		11
2A8	8.9		12
2C5	9.1		13
2A9	9.4		14
2A6	11		15
2A4	11		16
2A3	12		17
1C9	14		18
1C5	15		19.5
1A3	15	!	19.5
2A7	16		21
1C6	18		22
1C7	19		23
1C3	20		25
1A2	20	!	25
1A1	20	!	25
1C2	22		27
2A5	23		29
1C4	23	!	29
1A4	23	!	29
1A5	25		31
1C1	26		32
1A6	38		33
1A7	49		34
1A9	57		35
1A8	66		36

Alexander Reservoir ^{210}Po pCi/g dw

Mann-Whitney Test - Hypothesis about Population Means for Two Independent Samples

Station	Affected	Rank	Rank^2	Station	Affected	Rank	Rank^2
1A9	1.1	8.5	72.25	1C9	1.0	6	36
1A8	1.0	6	36	1C8	1.3	14	196
1A7	1.7	17	289	1C7	0.84	1	1
1A6	1.5	16	256	1C6	0.99	3.5	12.25
1A5	1.8	18	324	1C5	0.99	3.5	12.25
1A4	1.2	11.5	132.25	1C4	1.2	11.5	132.25
1A3	0.94	2	4	1C3	1.2	11.5	132.25
1A2	1.2	11.5	132.25	1C2	1.4	15	225
1A1	1.0	6	36	1C1	1.1	8.5	72.25
	9	96.5	1281.75		9	74.5	819.25
	1.2				1.1		

$$T_1 = \frac{T - mean}{std\ deviation} = \frac{T - n\dfrac{N-1}{2}}{\sqrt{\dfrac{nm}{N(N-1)}\sum_{i=1}^{N} R_i^{\ 2} - \dfrac{nm(N-1)^2}{4(N-1)}}}$$

for *T - mean*	-2.000		
		1st part	**2nd part**
for *std deviation*	21.56	0.2647	1756.75
T_1 =	-0.09275		
z_p		1.645	
ϖ =	104.1	85.50	18.63
G	4		
N1	9		
N2	9		
mean	85.50		
part a stdev	6.750		
part b stdev	19.00		
part c stdev	306.0		
g_1	6		
g_2	24		
g_3	6		
g_4	60		
part d stdev	96.00		
variance	126.1		
sqrt variance	11.23		
sqrt variance + z_p	104.0		

No difference among groups if sum of ranks (96.5) is less than 104.0

1C7	0.84		1
1A3	0.94		2
1C6	0.99		3.5
1C5	0.99	!	3.5
1A8	1.0		6
1A1	1.0	!	6
1C9	1.0	!	6
1A9	1.1		8.5
1C1	1.1	!	8.5
1A4	1.2		11.5
1A2	1.2	!	11.5
1C4	1.2	!	11.5
1C3	1.2	!	11.5
1C8	1.3		14
1C2	1.4		15
1A6	1.5		16
1A7	1.7		17
1A5	1.8		18

Soda Creek Cadmium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	$Rank^2$	Station	RI Affected	Rank	$Rank^2$	Station	Monitoring Control	Rank	$Rank^2$	Station	Monitoring Affectec	Rank	$Rank^2$
1C1	11	10	100.00	1A14	61	25	625.00	2C3	0.30	1	1.00	2A7	51	23	529.00
				1A13	27	19	361.00	2C2	0.38	2	4.00	2A6	10	9	81.00
				1A12	14	12.5	156.25	2C1	0.47	3	9.00	2A5	12	11	121.00
				1A11	8.6	7	49.00					2A4	3.4	5	25.00
				1A10	8.9	8	64.00					2A3	1.4	4	16.00
				1A9	28	20	400.00					2A2	14	12.5	156.25
				1A8	56	24	576.00					2A1	4.8	6	36.00
				1A7	20	16.5	272.25								
				1A6	17	14.5	210.25								
				1A5	17	14.5	210.25								
				1A4	24	18	324.00								
				1A3	38	22	484.00								
				1A2	29	21	441.00								
				1A1	20	16.5	272.25								
	11	10.0			22	238.5			0.38	6.0			10	70.5	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	54.10
T	12.20
analytes	8
p	0.0067
p_{exp}	0.053
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

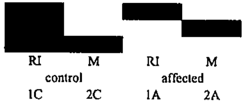
Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	7.036	9.821
1C vs. 2C	2	8.000	13.241
1C vs. 2A	1	0.071	10.143
2C vs. 1A	1	15.036	6.036
2A vs. 1A	2	6.964	5.308
2C vs. 2A	1	8.071	6.547

Station	Value	Ties	Rank
2C3	0.30		1
2C2	0.38		2
2C1	0.47		3
2A3	1.4		4
2A4	3.4		5
2A1	4.8		6
1A11	8.6		7
1A10	8.9		8
2A6	10		9
1C1	11		10
2A5	12		11
2A2	14		12.5
1A12	14		12.5
1A5	17		14.5
1A6	17		14.5
1A1	20		16.5
1A7	20		16.5
1A4	24		18
1A13	27		19
1A9	28		20
1A2	29		21
1A3	38		22
2A7	51		23
1A8	56		24
1A14	61		25

Cd in Sediment in Soda Creek



Soda Creek Arsenic mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	$Rank^2$	Station	RI Affected	Rank	$Rank^2$	Station	Monitoring Control	Rank	$Rank^2$	Station	Monitoring Affectec	Rank	$Rank^2$
1C1	6.2	5	25.00	1A14	12	9	81.00	2C3	3.6	3	9.00	2A7	35	18	324.00
				1A13	12	9	81.00	2C2	24	13	169.00	2A6	18	11	121.00
				1A12	5.3	4	16.00	2C1	47	22	484.00	2A5	8.4	6	36.00
				1A11	12	9	81.00					2A4	2.1	1	1.00
				1A10	29	14	196.00					2A3	2.6	2	4.00
				1A9	19	12	144.00					2A2	33	16	256.00
				1A8	49	23	529.00					2A1	9.2	7	49.00
				1A7	31	15	225.00								
				1A6	44	19	361.00								
				1A5	34	17	289.00								
				1A4	46	21	441.00								
				1A3	45	20	400.00								
				1A2	88	25	625.00								
				1A1	56	24	576.00								
	6.2	5.0			33	221.0			24	38.0			9.2	61.0	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	54.08
T	5.58
analytes	8
p	0.13
p_{exp}	0.68
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if T > 7.81 (for a per-comparison Type I error rate of 5%)

Reject H_0 if T > 12.31 (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{Rj}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{nj}\right)}$$

Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	10.786	12.269
1C vs. 2C	2	7.667	16.541
1C vs. 2A	1	3.714	12.672
2C vs. 1A	1	3.119	7.541
2A vs. 1A	2	7.071	6.631
2C vs. 2A	1	-3.952	8.179

As in Sediment in Soda Creek

[redacted]

RI	M	RI	M
control		affected	
1C	2C	1A	2A

Station	Value	Ties	Rank
2A4	2.1		1
2A3	2.6		2
2C3	3.6		3
1A12	5.3		4
1C1	6.2		5
2A5	8.4		6
2A1	9.2		7
1A14	12		9
1A13	12		9
1A11	12		9
2A6	18		11
1A9	19		12
2C2	24		13
1A10	29		14
1A7	31		15
2A2	33		16
1A5	34		17
2A7	35		18
1A6	44		19
1A3	45		20
1A4	46		21
2C1	47		22
1A8	49		23
1A1	56		24
1A2	88		25

Soda Creek Copper mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank^2	Station	RI Affected	Rank	Rank^2	Station	Monitoring Control	Rank	Rank^2	Station	Monitoring Affectec	Rank	Rank^2
1C1	2.7	2	4.00	1A14	22	21	441.00	2C3	8.6	13	169.00	2A7	16	17.5	306.25
				1A13	12	16	256.00	2C2	3.2	4	16.00	2A6	3.9	5	25.00
				1A12	4.0	6	36.00	2C1	6.4	9.5	90.25	2A5	6.4	9.5	90.25
				1A11	8.4	11.5	132.25					2A4	2.8	3	9.00
				1A10	8.4	11.5	132.25					2A3	0.91	1	1.00
				1A9	10	15	225.00					2A2	5.1	7	49.00
				1A8	19	19.5	380.25					2A1	5.2	8	64.00
				1A7	16	17.5	306.25								
				1A6	43	24	576.00								
				1A5	76	25	625.00								
				1A4	28	22	484.00								
				1A3	31	23	529.00								
				1A2	19	19.5	380.25								
				1A1	9.4	14	196.00								
	2.7	2.0			17.5	245.5			6.4	26.5			5	51	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	54.08
T	12.75
analytes	8
p	0.0052
p_{exp}	0.041
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

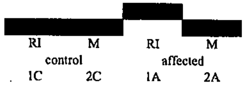
$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$	
1C vs. 1A	1	15.536	9.586	!
1C vs. 2C	2	6.833	12.924	
1C vs. 2A	1	5.286	9.901	
2C vs. 1A	1	8.702	5.892	!
2A vs. 1A	2	10.250	5.181	!
2C vs. 2A	1	-1.548	6.391	

Cu in Sediment in Soda Creek



Station	Value	Ties	Rank
2A3	0.9		1
1C1	2.7		2
2A4	2.8		3
2C2	3.2		4
2A6	3.9		5
1A12	4.0		6
2A2	5.1		7
2A1	5.2		8
2C1	6.4		9.5
2A5	6.4	!	9.5
1A11	8.4		11.5
1A10	8.4	!	11.5
2C3	8.6		13
1A1	9.4		14
1A9	10		15
1A13	12		16
1A7	16		17.5
2A7	16.0	!	17.5
1A8	19		19.5
1A2	19	!	19.5
1A14	22		21
1A4	28		22
1A3	31		23
1A6	43		24
1A5	76		25

Soda Creek Nickel mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank^2	Station	RI Affected	Rank	Rank^2	Station	Monitoring Control	Rank	Rank^2	Station	Monitoring Affectec	Rank	Rank^2
1C1	55	21	441.00	1A14	150	25	625.00	2C3	30	11.5	132.25	2A7	88	24	576.00
				1A13	86	23	529.00	2C2	50	20	400.00	2A6	44	18	324.00
				1A12	16	5	25.00	2C1	30	11.5	132.25	2A5	20	6	36.00
				1A11	31	13	169.00					2A4	4.8	2	4.00
				1A10	38	16	256.00					2A3	2.2	1	1.00
				1A9	45	19	361.00					2A2	12	4	16.00
				1A8	72	22	484.00					2A1	12	3	9.00
				1A7	35	14.5	210.25								
				1A6	39	17	289.00								
				1A5	25	7	49.00								
				1A4	25	8	64.00								
				1A3	35	14.5	210.25								
				1A2	28	10	100.00								
				1A1	27	9	81.00								
	55.3	21.0			35	203.0			30.0	43.0			12	58	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	54.13
T	4.74
analytes	8
p	0.19
p_{exp}	0.82
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

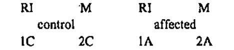
$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	-6.500	12.550
1C vs. 2C	2	6.667	16.920
1C vs. 2A	1	-12.714	12.962
2C vs. 1A	1	0.167	7.714
2A vs. 1A	2	6.214	6.783
2C vs. 2A	1	-6.048	8.367

Ni in Sediment in Soda Creek



Station	Value	Ties	Rank
2A3	2.2		1
2A4	4.8		2
2A1	12		3
2A2	12		4
1A12	16		5
2A5	20		6
1A5	25		7
1A4	25		8
1A1	27		9
1A2	28		10
2C3	30		11.5
2C1	30	1	11.5
1A11	31		13
1A3	35		14.5
1A7	35	1	14.5
1A10	38		16
1A6	39		17
2A6	44		18
1A9	45		19
2C2	50		20
1C1	55		21
1A8	72		22
1A13	86		23
2A7	88		24
1A14	150		25

Soda Creek Selenium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank^2	Station	RI Affected	Rank	Rank^2	Station	Monitoring Control	Rank	Rank^2	Station	Monitoring Affectec	Rank	Rank^2
1C1	0.60	2.5	6.25	1A14	0.8	6	36.00	2C3	0.79	5	25.00	2A7	100	26	676.00
1C2	0.60	2.5	6.25	1A13	1.1	10	100.00	2C2	0.92	7	49.00	2A6	14	23	529.00
				1A12	3.6	17	289.00	2C1	0.77	4	16.00	2A5	4.7	19	361.00
				1A11	4.8	20	400.00					2A4	1.1	10	100.00
				1A10	1.9	14	196.00					2A3	0.29	1	1.00
				1A9	20	24	576.00					2A2	3.3	15.5	240.25
				1A8	63	25	625.00					2A1	1.0	8	64.00
				1A7	7.3	22	484.00								
				1A6	3.3	15.5	240.25								
				1A5	1.4	13	169.00								
				1A4	3.8	18	324.00								
				1A3	5.2	21	441.00								
				1A2	1.1	10	100.00								
				1A1	1.2	12	144.00								
	0.6	5.0			3.45	227.5			0.8	16.0			3	103	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	2
n_2	14
n_3	3
n_4	7
N	26
S^2	58.38
T	9.54
analytes	8
p	0.023
p_{exp}	0.17
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

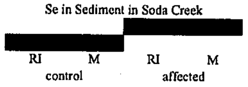
$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{\text{all}\\ \text{ranks}}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	22
$t_{0.975,v}$	2.074
$t_{0.95,v}$	1.717

	sidedness	LSD	$LSD_{0.05}$	
1C vs. 1A	1	13.750	8.313	'
1C vs. 2C	2	2.833	12.125	
1C vs. 2A	1	12.143	8.818	!
2C vs. 1A	1	10.917	6.997	'
2A vs. 1A	2	1.607	6.148	
2C vs. 2A	1	9.310	7.589	'



Station	Value	Ties	Rank
2A3	0.29		1
1C1	0.60		2.5
1C2	0.60	'	2.5
2C1	0.77		4
2C3	0.79		5
1A14	0.8		6
2C2	0.92		7
2A1	1.0		8
1A13	1.1		10
1A2	1.1	!	10
2A4	1.1	!	10
1A1	1.2		12
1A5	1.4		13
1A10	1.9		14
1A6	3.3		15.5
2A2	3.3	!	15.5
1A12	3.6		17
1A4	3.8		18
2A5	4.7		19
1A11	4.8		20
1A3	5.2		21
1A7	7.3		22
2A6	14		23
1A9	20		24
1A8	63		25
2A7	100		26

Soda Creek Silver mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	$Rank^2$	Station	RI Affected	Rank	$Rank^2$	Station	Monitoring Control	Rank	$Rank^2$	Station	Monitoring Affectec	Rank	$Rank^2$
1C1	0.10	5	25.00	1A14	0.5	17	289.00	2C3	0.034	1	1.00	2A7	0.46	16	256.00
				1A13	0.35	15	225.00	2C2	0.14	10	100.00	2A6	0.12	9	81.00
				1A12	0.08	4	16.00	2C1	0.15	11	121.00	2A5	0.11	7	49.00
				1A11	1.3	18	324.00					2A4	0.039	2	4.00
				1A10	0.17	12	144.00					2A3	0.060	3	9.00
				1A9	0.11	7	49.00					2A2	0.25	13.5	182.25
				1A8	0.25	13.5	182.25					2A1	0.11	7	49.00
				1A7	1.8	22	484.00								
				1A6	1.8	22	484.00								
				1A5	1.8	22	484.00								
				1A4	1.8	22	484.00								
				1A3	1.8	22	484.00								
				1A2	1.8	22	484.00								
				1A1	1.8	22	484.00								
	0.10	5.0			1.6	240.5			0.14	22.0			0	58	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	52.90
T	10.68
analytes	8
p	0.014
p_{exp}	0.10
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: ·Reject H_0 and accept H_1 (from the perspective of the per-comparison error rate); retain H_0 (from the perspective of the experiment-wise error rate)

$$T=\frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i}-\frac{N(N+1)^2}{4}\right)$$

$$S^2=\frac{1}{N-1}\left(\sum_{\substack{\text{all}\\\text{ranks}}}R(X_{ij})^2-\frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i}-\frac{R_j}{n_j}\right|>t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

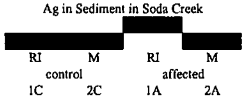
Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	12.179	10.316
1C vs. 2C	2	2.333	13.908
1C vs. 2A	1	3.214	10.654
2C vs. 1A	1	9.845	6.340
2A vs. 1A	2	8.964	5.575
2C vs. 2A	1	0.881	6.877

Station	Value	Ties	Rank
2C3	0.034		1
2A4	0.039		2
2A3	0.060		3
1A12	0.08		4
1C1	0.10		5
1A9	0.11		7
2A5	0.11		7
2A1	0.11		7
2A6	0.12		9
2C2	0.14		10
2C1	0.15		11
1A10	0.17		12
1A8	0.25		13.5
2A2	0.25		13.5
1A13	0.35		15
2A7	0.46		16
1A14	0.5		17
1A11	1.3		18
1A7	1.8		22
1A6	1.8		22
1A5	1.8		22
1A4	1.8		22
1A3	1.8		22
1A2	1.8		22
1A1	1.8		22

Ag in Sediment in Soda Creek



Soda Creek Vanadium mg/kg dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	$Rank^2$	Station	RI Affected	Rank	$Rank^2$	Station	Monitoring Control	Rank	$Rank^2$	Station	Monitoring Affectec	Rank	$Rank^2$
1C1	23	4	16.00	1A14	110	20	400.00	2C3	33	5	25.00	2A7	84	13	169.00
				1A13	150	23.5	552.25	2C2	74	12	144.00	2A6	42	7	49.00
				1A12	50	9	81.00	2C1	50	9	81.00	2A5	50	9	81.00
				1A11	120	21	441.00					2A4	14	2	4.00
				1A10	92	16	256.00					2A3	5.1	1	1.00
				1A9	53	11	121.00					2A2	41	6	36.00
				1A8	100	18	324.00					2A1	22	3	9.00
				1A7	100	18	324.00								
				1A6	86	14	196.00								
				1A5	130	22	484.00								
				1A4	150	23.5	552.25								
				1A3	160	25	625.00								
				1A2	100	18	324.00								
				1A1	87	15	225.00								
	23.3	4.0			100	254.0			50	26.0			41	41	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	53.98
T	16.02
analytes	8
p	0.0011
p_{exp}	0.0090
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error.rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Reject H_0 and accept H_1 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

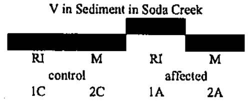
$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ ranks}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$	
1C vs. 1A	1	14.143	8.067	!
1C vs. 2C	2	4.667	10.875	
1C vs. 2A	1	1.857	8.331	
2C vs. 1A	1	9.476	4.958	!
2A vs. 1A	2	12.286	4.360	!
2C vs. 2A	1	-2.810	5.378	



Station	Value	Ties	Rank
2A3	5.1		1
2A4	14		2
2A1	22		3
1C1	23		4
2C3	33		5
2A2	41		6
2A6	42		7
2A5	50		9
2C1	50	!	9
1A12	50	!	9
1A9	53		11
2C2	74		12
2A7	84		13
1A6	86		14
1A1	87		15
1A10	92		16
1A2	100		18
1A8	100	!	18
1A7	100	!	18
1A14	110		20
1A11	120		21
1A5	130		22
1A4	150		23.5
1A13	150	!	23.5
1A3	160		25

Soda Creek ^{210}Po pCi/g dw

Kruskal-Wallis One-Way Analysis of Variance by Ranks Test for Several Independent Samples

Station	RI Control	Rank	Rank^2	Station	RI Affected	Rank	Rank^2	Station	Monitoring Control	Rank	Rank^2	Station	Monitoring Affectec	Rank	Rank^2
1C1	0.67	6	36.00	1A14	3.3	25	625.00	2C3	0.69	7	49.00	2A7	1.6	17.5	306.25
				1A13	0.55	1	1.00	2C2	0.96	10	100.00	2A6	1.1	12	144.00
				1A12	0.60	3	9.00	2C1	1.5	15	225.00	2A5	2.3	21.5	462.25
				1A11	0.60	3	9.00					2A4	2.8	24	576.00
				1A10	0.60	3	9.00					2A3	0.62	5	25.00
				1A9	1.5	15	225.00					2A2	2.0	19	361.00
				1A8	2.3	21.5	462.25					2A1	2.1	20	400.00
				1A7	0.70	8	64.00								
				1A6	1.4	13	169.00								
				1A5	1.6	17.5	306.25								
				1A4	1.5	15	225.00								
				1A3	2.6	23	529.00								
				1A2	1.0	11	121.00								
				1A1	0.80	9	81.00								
	0.67	6.0			1.2	168.0			1.0	32.0			2.0	119	

Kruskal-Wallis One-Way ANOVA

H_0: All four medians are equal.

H_1: At least two medians are different.

Each sample was selected systematically and can be assumed to be random.

k	4
n_1	1
n_2	14
n_3	3
n_4	7
N	25
S^2	53.96
T	3.55
analytes	8
p	0.31
p_{exp}	0.95
$T_{0.05,3}$	7.81
$T_{0.006391,3}$	12.31

Reject H_0 if $T > 7.81$ (for a per-comparison Type I error rate of 5%)

Reject H_0 if $T > 12.31$ (for an experiment-wise Type I error rate of 5%)

Conclusion: Retain H_0 (from the perspective of both error rates)

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{\text{all}\\\text{ranks}}} R(X_{ij})^2 - \frac{N(N+1)^2}{4}\right)$$

$$\left|\frac{R_i}{n_i} - \frac{R_j}{n_j}\right| > t_{1-(\alpha/2)}\sqrt{\left(S^2\frac{N-1-T}{N-k}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

Fisher's LSD

v	21
$t_{0.975,v}$	2.080
$t_{0.95,v}$	1.721

	sidedness	LSD	$LSD_{0.05}$
1C vs. 1A	1	6.000	12.912
1C vs. 2C	2	4.667	17.409
1C vs. 2A	1	11.000	13.336
2C vs. 1A	1	1.333	7.936
2A vs. 1A	2	5.000	6.979
2C vs. 2A	1	6.333	8.608

Po^{210} in Sediment in Soda Creek

RI	M	RI	M
control		affected	
1C	2C	1A	2A

Station	Value	Ties	Rank
1A13	0.55		1
1A12	0.60		3
1A11	0.60	'	3
1A10	0.60	'	3
2A3	0.62		5
1C1	0.67		6
2C3	0.69		7
1A7	0.70		8
1A1	0.80		9
2C2	0.96		10
1A2	1.0		11
2A6	1.1		12
1A6	1.4		13
1A9	1.5		15
1A4	1.5	'	15
2C1	1.5	'	15
1A5	1.6		17.5
2A7	1.6	'	17.5
2A2	2.0		19
2A1	2.1		20
2A5	2.3		21.5
1A8	2.3	'	21.5
1A3	2.6		23
2A4	2.8		24
1A14	3.3		25

5.0 REFERENCES

Georgia Institute of Technology. *Scientific Approaches for Transportation Research* (http://traffic.ce.gatech.edu/nchrp2045/v2chapter6.html). Prepared for National Cooperative Highway Research Program. Website accessed 2 April, 2003.

Golder Associates, November 1997. *Monsanto. Selected Text from Phase I and Phase II remedial Investigations and Reports. Relating to Characterization of Soda Creek.* Prepared for Monsanto.

Montgomery Watson Harza (MWH), October 2002. *Final Work Plan for CERCLA Five-year Review. Monsanto Elemental Phosphorous Plant, Soda Springs, Idaho.* Prepared for Monsanto.

USEPA, September 2002. *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites.* Office of Solid Waste and Emergency Response. EPA 540-R-01-003. Publication 9285.7-41.

USEPA, April 1997. *Record of Decision: Monsanto Chemical Company, Superfund Site, Caribou County, Idaho.* USEPA Region X, Office of Environmental Cleanup.

MONSANTO

Monsanto Elemental Phosphorus Plant
CERCLA Five-Year Review
FINAL
APPENDIX C
Sediment Data Validation and Quality Control Summary Report

May 2003

Prepared by

MWH
MONTGOMERY WATSON HARZA

2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005

CERCLA Five Year Review Monsanto

Sediment Data Validation and Quality Control Summary Report

The following is a summary of the data validation and quality control (QC) review conducted for the CERCLA five year review conducted in October of 2002. This effort was completed on the behalf of Monsanto Elemental Phosphorous Plant. Severn Trent Laboratories (STL) was the primary analytical laboratory performing the analyses. General Engineering Laboratories (GEL) was the quality assurance (QA) laboratory tasked with analyzing QA sediment samples. Both laboratories were selected prior to sampling, and both were proficient in the analysis of metals and other parameters as requested by the United States Environmental Protection Agency (USEPA). Data analyzed by STL and GEL were subjected to validation procedures outlined by the *Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses* (USEPA, December 1994). Validation guidelines for radiochemistry data have not been developed therefore the *Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses* was also used to validate the polonium-210 (^{210}Po) data even though this is beyond the purpose of these guidelines.

Twenty-eight sediment samples were collected and submitted to STL where they were homogenized and dried. In addition twelve blank aqueous samples were sent to STL to be used as QC samples on the equipment and field methods. Three of the twenty-eight samples were selected and labeled as a "QA/QC sample." These samples were homogenized and split into four parts. One part of each sample was submitted to GEL for analysis. The other three parts were run by STL. All sample submittals were made under chain-of-custody protocols. The STL analyzed the sediment for the following:

- SW 846 6020 ICP-MS(As, Ag, Cd, Cu, Ni, Se, V)
- RICH-RC-5012 Alpha Spectrometry (^{210}Po)

The GEL laboratory analyzed the sediment for the following:

- ILM 4.0 CLP Metals (Ag, As, Cd, Cu, Ni, Se, V)
- DOE EML HASL 300 (^{210}Po)

Data quality objectives (DQOs) are qualitative and quantitative statements that specify the quality of these data required to meet the goals of site investigation and/or to support decisions made in environmental management activities. DQOs for the October 2002 CERCLA five year review were expressed in terms of precision, accuracy, representativeness, completeness, and comparability (PARCC). The results of QC samples were evaluated against the DQOs and the quality of the data was assessed according to the PARCC parameters. QC sample results that fall outside these criteria serve to signal unacceptable or biased data that could result in corrective actions being implemented, or qualification of the data. The following is a summary review of these data, including data qualification that resulted from the data validation.

Precision and Accuracy

Precision and accuracy were evaluated based on the QC results generated from calibrations, spiked samples, laboratory duplicates, interference check samples, laboratory control samples and serial dilutions.

All STL calibrations and GEL calibrations were acceptable. Non-radiochemistry calibrations were run as initial calibration verifications and continuing calibration verifications. No calibration data is present in the raw data for ^{210}Po. However, calibrations were performed on a monthly basis by both laboratories with acceptable results.

STL did not performed spike recovery on ^{210}Po. Inorganic results were acceptable according to the criteria. All GEL spike recoveries were acceptable according to the criteria.

STL did not run laboratory duplicates on the inorganic samples. STL ^{210}Po duplicate results contained unacceptable duplicate performance data therefore the sample data were qualified as estimated (J), according to the criteria. GEL performed laboratory duplicate analyses for all analytes and all duplicates were acceptable.

Interference check samples were not analyzed for ^{210}Po by either laboratory. All other Interference check sample results were satisfactory for both laboratories.

Laboratory control samples (LCS) were analyzed by both laboratories for all analytes. All results from STL were acceptable, except Ag where the data were qualified as estimated (J), according to the criteria. GEL results for the LCS were acceptable according to the criteria.

Neither laboratory performed serial dilutions.

Representativeness

Representativeness is evaluated by reviewing blank results. Blanks are analyzed before and during the analytical process. GEL analyzed blanks using initial calibration blanks and continuing calibration blanks (ICB/CCB). STL also used ICB and CCB results and included preparation blanks for the inorganic analytes. STL results showed three detected blanks for Ag at 0.24 µg/kg, Cd at 0.44 µg/kg, and Se at 0.32 µg/kg. GEL results indicated two detected blanks for Cd at 0.3 µg/kg and Ni at 0.9 µg/kg. The sample results associated with the detected blanks that were greater than the method detection limit and less than five times the detected blank were qualified as undetected. All other blank results were below detection limit and no field sample results were qualified.

Completeness

All samples were collected and analyzed as specified in the *Work Plan for CERCLA Five-Year Review* (MWH, 2002). STL field data was complete. GEL field data and laboratory QC data was complete. Both laboratories provided raw data packets that contained information on the specific analytes for which sediment samples were analyzed. Field QA/QC samples were collected and analyzed by STL and GEL as required. Analytical data were discoverable in raw data packets from STL and GEL. GEL performed QA/QC analyses on all samples analyzed by STL. There are no holding times established for sediment matrices. However, all samples were analyzed within six months of collection. Spike quantities were printed on various QC sheets.

Comparability

Comparability was achieved by STL and GEL analyzing the samples according to the required methods. Each laboratory used acceptable methodology, which is recognized by the EPA in analyzing samples. Detection limits were reported by each laboratory for each specific analyte and included in either the raw data packet or electronic files.

Summary of Data Quality

The evaluation of the PARCC criteria provided information on the quality of the data. The data were considered usable as a result of the validation.

References

US Environmental Protection Agency, 1994. “Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses.” Publication 9240.1-26, EPA/540/R/94/083, PB95-963525. Office of Solid Waste and Emergency Response, USEPA, Washington, D.C.

Montgomery Watson Harza, 2002. “Field Sampling Plan for CERCLA Five-Year Review Soil and Sediment Investigation.” September 2002 – Draft. Bellevue, Washington.

Montgomery Watson Harza, 2002. “Work Plan for CERCLA Five-Year Review.” September 2002 -Draft. Bellevue, Washington.

INORGANIC DATA ASSESSMENT SUMMARY

PROJECT: CERCLA Five Year Review	SITE: Southeast Idaho
LABORATORY: Primary Laboratory: STL QA Laboratory: GEL	SDG:
SAMPLES/MATRIX/ANALYSES:	
• October 2002	
• Matrix: Sediment	
• Method: SW 846 6020 ICP-MS, RICH-RC-5012 Alpha Spectrometry, ILM 4.0 CLP Metals, DOE EML HASL 300	
• Analyses: As, Ag, Cd, Cu, Ni, Se, V, ^{210}Po	

DATA ASSESSMENT SUMMARY

REVIEW ITEM	ICP	AA	HG	CYANIDE	OTHER
1. Data completeness	O				
2. Holding Times	O				
3. Calibration	O				
4. Blanks	O				
5. ICS	O				
6. LCS	O				
7. Duplicate RPD	O				
8. Spike Recovery	O				
9. MSA	NA				
10. Other QC	NA				
11. Field Duplicates	O				
12. Result Verification	O				
13. Overall Assessment	O				

O=Data had no problems/or qualified due to minor problems.
M=Data qualified due to major problems.
NA=Data review item not applicable.
X=Problems but do not affect data.
Z=Data unacceptable.

Comments/Qualified Results:

- This data validation summary summarizes all individual analyte data assessments for October 2002 CERCLA sediment data. See individual sections below for a summary of the results from the individual analyte data assessments. All data were acceptable with some qualifications.

Verified and Validated by: ______________________ Date: __________
Reviewed and Approved by: ______________________ Date: __________

INORGANIC DATA ASSESSMENT SUMMARY

Acceptable
Yes No

1. Data package completeness (check if present) _X_ ___

_X_Case narrative
_X_Chain of custody
_X_Sample Results
_X_ICV/CCV Results
_X_Blank Results
_X_ICP Interference Check Results
_X_Spike Recovery Results
_X_Duplicate Results
_X_LCS Results
___Standard Addition Results
___ICP Serial Dilution

_X_Instrument Det. Limits
    ___ICP Correction Factors
    ___ICP Linear Ranges
    _X_Preparation Logs
_X_Analysis Run Logs
_X_ICP Raw Data
    ___GFAA Raw Data
    ___Hg Raw Data
    ___Cyanide Raw Data
    ___Other________________

Comments/Qualified Results:

- Spike recovery analyses were not performed by STL for ^{210}Po.
- ICP interference checks completed for inorganic analytes only.
- Duplicate results were not analyzed for inorganic analytes by STL.

2. Holding times (check all that apply) _X_ ___

_X_ICP/GFAA metals completed in <6 mos from collection
___Mercury analyzed in <28 days from collection
___Cyanide completed in 14 days from collection

Qualify as estimated (J, UJ) all results analyzed past the holding times listed but within 2 X the limit. Qualify detects as estimated (J) and non-detects unusable (UR) for results analyzed greater than 2 X above the limit. If soil data are qualified based on water holding time criteria, note.

Comments/Qualified Results:

- Above holding times are for water matrices. There are no holding times established for sediment matrices. However, all samples were analyzed within six months of collection.

INORGANIC DATA ASSESSMENT SUMMARY

Acceptable
Yes No

---

3. Calibrations (check all that apply) __X_ ___

___GFAA/Hg correlation coefficient <0.995, results estimated (J, UJ)
_X_ICV/CCV %R, ICP 89-111%, Hg 80-120%, Cn 85-115%, results acceptable
___ICV/CCV %R, ICP 75-89%, Hg 65-79%, Cn 70-84%m results <IDL estimated (UJ)
___ICV/CCV %R, ICP <75%, Hg <65%, Cn <70%, results unusable (R)
___ICV/CCV %R, ICP >125%, Hg >135%, Cn >130%, results >IDL unusable (R), <IDL acceptable
___ICV/CCV %R, ICP 75-89% or 111-125%, Hg 65-79% or 121-135%, Cn 70-84% or 116-130%, results >IDL estimated (J)

Comments/Qualified Results:

- STL - All calibrations were acceptable.
- GEL – All calibrations were acceptable.
- ^{210}Po calibrations were performed on a monthly basis by both laboratories with acceptable results.

4. Blanks (check all that apply) _X_ ___

_x_Detects reported ICB/CCB, list:

Ag at 0.24 µg/kg	Cd at 0.3 µg/kg
Cd at 0.44 µg/kg	Ni at 0.9 µg/kg
Se at 0.32 µg/kg	

___Detects in preparation blanks, list:

___Detects in field blanks, list:

Qualify as undetected (U) all sample concentrations ≤5 X any blank concentrations.

Comments/Qualified Results:

- STL – three analytes had detected blanks (listed above). Data less than 5x the detected blank were qualified as undetected (U).
- GEL – two analytes had detected blanks (listed above). Data less than 5x the detected blank were qualified as undetected (U).
- All other blanks were below the detection limit and data was not qualified.

INORGANIC DATA ASSESSMENT SUMMARY

Acceptable
Yes No

5. Interference Checks (check all that apply) __X_ ___

_X_ICS A/B Recoveries Acceptable
___Al, Ca, Fe, Mg sample concentrations >ICS concentrations
___ICS %R> 120%, results > IDL estimated (J)
___ICS %R 50-79%, results>IDL estimated (J), possible false negative
___ICS %R 50-79%, results <IDL estimated (UJ)
___ICS %R <50%, results >IDL and <IDL rejected (R/UR)
___ICS %R>120, results <IDL acceptable

Comments/Qualified Results:

- STL - ICP interference check samples for inorganic analytes were acceptable.
- GEL - ICP interference check samples for inorganic analytes were acceptable.

6. Laboratory Control Samples (check all that apply) __X_ ___

_X_LCS %R 80-120 (Ag, Sb no limits); if 95% confidence range is given, such range prevails.
_X_LCS %R 50-79% or >120%, results>IDL estimated (J); or outside of 95% confidence range.
_X_LCS %R 50-79% and results <IDL estimated (UJ); or outside the lower end of 95% confidence range.
___ LCS %R <50% and all results rejected (R/UR)
___LCS %R >120%, results <IDL acceptable; or outside the upper end of 95% confidence range.

Comments/Qualified Results:

- STL – LCS for silver was qualified as estimated (J) for sample concentrations >1.2 µg/L. (Refer to section 4. Blanks). Sample results <IDL and <1.2 µg/L are already qualified. All other analytes were acceptable and were not qualified.
- GEL – LCS were acceptable and the data were not qualified.

7. Duplicate (check all that apply) __X_ ___

_X_Duplicate RPD $\leq$20% for waters ($\leq$35% for soils) for results >5X CRDL
_X_Duplicate Range is within $\pm$CRDL ($\pm$2xCRDL for soils) for results $\leq$ 5X CRDL
_X_Qualify positive results estimated (J) if the above criteria were not met.

Comments/Qualified Results:

- STL- duplicate analyses were not performed on inorganic analytes. ^{210}Po duplicate results were not acceptable and the data were qualified as estimated (J).
- GEL - laboratory duplicate analyses for all analytes and all duplicates were acceptable.

INORGANIC DATA ASSESSMENT SUMMARY

	Acceptable Yes	No
8. Spike Recovery (check all that apply)	X	

_X_Spike %R with 75-125%
___Spike %R 30-74%, >125%, results >IDL estimated (J)
___Spike %R 30-74% results <IDL estimated (UJ)
___Spike %R <30%, results <IDL rejected (UR)
___Field blank used for spike analysis
___Spike % R >125%, results <IDL acceptable
___Sample concentration exceeds spike concentration by a factor of >4x, acceptable

Comments/Qualified Results:

- STL – inorganic results were acceptable.
- GEL – results for all analytes were acceptable.

9. GFAA Performance (check all that apply) NA

___Duplicate injection RSD<20%
___Duplicate injection RSD>20%, results >CRDL estimated (J)
___Analytical spike %R 85-115%
___Analytical spike %R 40-85%, results >IDL estimated (J)
___Analytical spike %R 10-40%, results <IDL estimated (UJ)
___Analytical spike %R <10%, results <IDL rejected (R)
___Analytical spike %R <40%, results >IDL estimated (J)
___MSA required but not run, results estimated (J)
___MSA run at incorrect level, results estimated (J)
___MSA correlation coefficient <0.995, results estimated (J)

Comments/Qualified Results:

- STL – not analyzed.
- GEL – not analyzed.

10. Serial Dilution (check all that apply) NA

___Serial Dilution %D within 10% for sample results >50x the IDL
___Serial Dilution %D greater than 10%, results >50x the IDL estimated (J)

Comments/Qualified Results:

- STL – not analyzed.
- GEL – not analyzed.

Acceptable
Yes No

---

11. Field Duplicates (check all that apply) __X_ ___

_x_Field duplicate RPD ≤20% waters (≤35% for soils)
_x_Field duplicate range is within ±CRDL (±2x CRDL for soils) for results <5xCRDL

Note: There are no qualification requirements for field QC samples exceeding limits.

Comments/Qualified Results:

- STL- all field duplicates were acceptable.
- GEL- no field duplicates collected.

12. Result Verification (check all that apply) __X_ ___

_X_All results supported in raw data

Comments/Qualified Results:

- STL- all results below the respective detection limits were reported as BDL (below detection limit). Data not checked 100%, but no transcription errors/anomalies were noted on items checked.
- GEL- all results below the respective detection limits were reported as BDL (below detection limit). Data not checked 100%, but no transcription errors/anomalies were noted on items checked.

13. Overall Assessment __X_ ___

- STL and GEL data were acceptable. Data were qualified (flagged) as estimated (UJ, J) and undetected (U) for various reasons. Discussion is included in the above sections, as well as in the data assessment summary for each analyte from STL and GEL.
- Sample results <MDL were qualified as U for the following analytes:

  STL
  Ag, As, Cd, Ni, Se, V

  GEL
  As

MONSANTO

Monsanto Elemental Phosphorus Plant
CERCLA Five-Year Review
FINAL
APPENDIX D
Soil Data Validation and Quality Control Summary Report

May 2003

Prepared by

MWH
MONTGOMERY WATSON HARZA

2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005

CERCLA Five Year Review Monsanto

Soil Data Validation and Quality Control Summary Report

The following is a summary of the data validation and quality control (QC) review conducted for the CERCLA five year review conducted in October of 2002. This effort was completed on the behalf of Monsanto Elemental Phosphorous Plant. Severn Trent Laboratories (STL) performed the primary analytical laboratory analyses. General Engineering Laboratories (GEL) was the quality assurance (QA) laboratory tasked with analyzing QA soil samples. Both laboratories were selected prior to sampling, and both were proficient in the analysis of metals and other parameters as requested by the United States Environmental Protection Agency (USEPA). Data analyzed by STL and GEL were subjected to validation procedures. Data validation guidelines for radiochemistry data have not been developed therefore the *Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses* was used to validate the radium-226 (^{226}Ra) data even though this is beyond the purpose of these guidelines.

Forty-five soil samples were collected and submitted to STL where they were homogenized and dried. In addition ten blank aqueous samples were sent to STL to be used as QC samples on the equipment and field methods. Five of the forty-five samples were selected and labeled as a "QA/QC sample." These samples were homogenized and split into four parts. One part of each sample was submitted to GEL for analysis. The other three parts were run by STL. All sample submittals were made under chain-of-custody protocols. The STL analyzed the soil for the following:

- DOE EML HASL 300 (^{226}Ra for soil)
- Total Alpha RA SW846 9315 MOD, and GFPC SW846 9320 SW 846 6020 ICP-MS (^{226}Ra for water blanks and equipment blanks)

The GEL laboratory analyzed the soil for DOE EML HASL 300 (^{226}Ra).

Data quality objectives (DQOs) are qualitative and quantitative statements that specify the quality of these data required to meet the goals of site investigation and/or to support decisions made in environmental management activities. DQOs for the October 2002 CERCLA five year review were expressed in terms of precision, accuracy, representativeness, completeness, and comparability (PARCC). The results of QC samples were evaluated against the DQOs and the quality of the data was assessed according to the PARCC parameters. QC sample results that fall outside these criteria serve to signal unacceptable or biased data that could result in corrective actions being implemented, or qualification of the data. The following is a summary review of these data, including data qualification that resulted from the data validation.

Precision and Accuracy

Precision and accuracy were evaluated based on the QC results generated from calibrations, spiked samples, laboratory duplicates, interference check samples, laboratory control samples and serial dilutions.

All STL calibrations and GEL calibrations were acceptable. No calibration data is present in the raw data for ^{226}Ra. However, calibrations were performed on a monthly basis by both laboratories with acceptable results.

STL and GEL did not performed spike recovery on ^{226}Ra.

STL duplicate results were acceptable for both soil and blank methods. GEL laboratory duplicate analyses were acceptable for all duplicates.

Interference check samples were not analyzed for ^{226}Ra by either laboratory.

Laboratory control samples (LCS) were analyzed by STL laboratories for both blank and soil methods with acceptable results. GEL did not run LCS for ^{226}Ra.

Neither laboratory performed serial dilutions.

Representativeness

Representativeness is evaluated by reviewing blank results. Blanks are analyzed before and during the analytical process. STL results showed one detected blank for the water and equipment method blank was detected at 0.19 pCi/g. All blanks for the soil method were not detected. The results associated with the detected blank that were greater than the method detection limit and less than five times the detected blank were qualified as undetected. All other blank results were below detection limit and no field sample results were qualified.

Completeness

All samples were collected and analyzed as specified in the *Work Plan for CERCLA Five-Year Review* (MWH, 2002). STL field data were complete. GEL field data and laboratory QC data were complete. Both laboratories provided raw data packets that contained information on the specific analytes for which soil samples were analyzed. Field QA/QC samples were collected and analyzed by STL and GEL as required. Analytical data were discoverable in raw data packets from STL and GEL. GEL performed QA/QC analyses on all analytes analyzed by STL. There are no holding times established for soil matrices. However, all samples were analyzed within six months of collection.

Comparability

Comparability was achieved by STL and GEL analyzing the samples according to the required methods. Each laboratory used acceptable methodology, which is recognized by the USEPA in analyzing samples. Detection limits were reported by each laboratory for each specific analyte and included in either the raw data packet or electronic files.

Summary of Data Quality

The evaluation of the PARCC criteria provided information on the quality of the data. The data were considered usable as a result of the validation.

References

US Environmental Protection Agency, 1994. "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses." Publication 9240.1-26, EPA/540/R/94/083, PB95-963525. Office of Solid Waste and Emergency Response, USEPA, Washington, D.C.

Montgomery Watson Harza, 2002. "Field Sampling Plan for CERCLA Five-Year Review Soil and Sediment Investigation." September 2002 – Draft. Bellevue, Washington.

Montgomery Watson Harza, 2002. "Work Plan for CERCLA Five-Year Review." September 2002 -Draft. Bellevue, Washington.

INORGANIC DATA ASSESSMENT SUMMARY

PROJECT: CERCLA Five Year Review	SITE: Southeast Idaho
LABORATORY: Primary Laboratory: STL QA Laboratory: GEL	SDG:

SAMPLES/MATRIX/ANALYSES:

- October 2002
- Matrix: Soil
- Method: DOE EML HASL 300, Total Alpha RA SW846 9315 MOD, and GFPC SW846 9320 SW 846 6020 ICP-MS
- Analyses: ^{226}Ra

DATA ASSESSMENT SUMMARY

REVIEW ITEM	ICP	AA	HG	CYANIDE	OTHER
1. Data completeness	O				
2. Holding Times	O				
3. Calibration	O				
4. Blanks	O				
5. ICS	NA				
6. LCS	O				
7. Duplicate RPD	O				
8. Spike Recovery	NA				
9. MSA	NA				
10. Other QC	NA				
11. Field Duplicates	O				
12. Result Verification	O				
13. Overall Assessment	O				

O=Data had no problems/or qualified due to minor problems.
M=Data qualified due to major problems.
NA=Data review item not applicable.
X=Problems but do not affect data.
Z=Data unacceptable.

Comments/Qualified Results:

- This data validation summary summarizes ^{226}Ra data assessments for October 2002 CERCLA soil data. All data were acceptable with one qualification.

Verified and Validated by: ______________________ Date: ______________
Reviewed and Approved by: ______________________ Date: ______________

INORGANIC DATA ASSESSMENT SUMMARY

Acceptable
Yes No

1. Data package completeness (check if present) _X_ ___

_X_Case narrative
_X_Chain of custody
_X_Sample Results
_X_ICV/CCV Results
_X_Blank Results
___ICP Interference Check Results
___Spike Recovery Results
_X_Duplicate Results
_X_LCS Results
___Standard Addition Results
___ICP Serial Dilution
_X_Instrument Det. Limits
___ICP Correction Factors
___ICP Linear Ranges
_X_Preparation Logs
_X_Analysis Run Logs
_X_ICP Raw Data
___GFAA Raw Data
___Hg Raw Data
___Cyanide Raw Data
___Other________________

Comments/Qualified Results:

- STL or GEL did not perform spike recovery analyses for ^{226}Ra.
- STL or GEL did not perform ICP interference checks for ^{226}Ra.
- LSC analyses were only run by STL.

2. Holding times (check all that apply) _X_ ___

_X_ICP/GFAA metals completed in <6 mos from collection
___Mercury analyzed in <28 days from collection
___Cyanide completed in 14 days from collection

Qualify as estimated (J, UJ) all results analyzed past the holding times listed but within 2 X the limit. Qualify detects as estimated (J) and non-detects unusable (UR) for results analyzed greater than 2 X above the limit. If soil data are qualified based on water holding time criteria, note.

Comments/Qualified Results:

- Above holding times are for water matrices. There are no holding times established for soil matrices. However, all samples were analyzed within six months of collection.

INORGANIC DATA ASSESSMENT SUMMARY

	Acceptable Yes	 No
3. Calibrations (check all that apply)	X	

___GFAA/Hg correlation coefficient <0.995, results estimated (J, UJ)
_X_ICV/CCV %R, ICP 89-111%, Hg 80-120%, Cn 85-115%, results acceptable
___ICV/CCV %R, ICP 75-89%, Hg 65-79%, Cn 70-84%m results <IDL estimated (UJ)
___ICV/CCV %R, ICP <75%, Hg <65%, Cn <70%, results unusable (R)
___ICV/CCV %R, ICP >125%, Hg >135%, Cn >130%, results >IDL unusable (R), <IDL acceptable
___ICV/CCV %R, ICP 75-89% or 111-125%, Hg 65-79% or 121-135%, Cn 70-84% or 116-130%, results >IDL estimated (J)

Comments/Qualified Results:

- ^{226}Ra calibrations were performed on a monthly basis by both laboratories with acceptable results.

	Yes	No
4. Blanks (check all that apply)	X	

_x_Detects reported ICB/CCB, list:
0.19 pCi/g

___Detects in preparation blanks, list:

___Detects in field blanks, list:

Qualify as undetected (U) all sample concentrations ≤ 5 X any blank concentrations.

Comments/Qualified Results:

- STL – results showed one detected blank for the water and equipment method blank (shown above). The results associated with the detected blank that were greater than the method detection limit and less than five times the detected blank were qualified as undetected. All blanks for the soil method were not detected.
- GEL – blanks were below the detection limit and data was not qualified.

INORGANIC DATA ASSESSMENT SUMMARY

	Acceptable Yes No
5. Interference Checks (check all that apply)	NA

___ICS A/B Recoveries Acceptable
___Al, Ca, Fe, Mg sample concentrations >ICS concentrations
___ICS %R> 120%, results > IDL estimated (J)
___ICS %R 50-79%, results>IDL estimated (J), possible false negative
___ICS %R 50-79%, results <IDL estimated (UJ)
___ICS %R <50%, results >IDL and <IDL rejected (R/UR)
___ICS %R>120, results <IDL acceptable

Comments/Qualified Results:
- STL – not analyzed.
- GEL – not analyzed.

6. Laboratory Control Samples (check all that apply) __X_ ___

_X_LCS %R 80-120 (Ag, Sb no limits); if 95% confidence range is given, such range prevails.
___LCS %R 50-79% or >120%, results>IDL estimated (J); or outside of 95% confidence range.
___LCS %R 50-79% and results <IDL estimated (UJ); or outside the lower end of 95% confidence range.
___ LCS %R <50% and all results rejected (R/UR)
___LCS %R >120%, results <IDL acceptable; or outside the upper end of 95% confidence range.

Comments/Qualified Results:
- STL – LCS were acceptable and the data were not qualified
- GEL – LCS were not analyzed

7. Duplicate (check all that apply) __X_ ___

_X_Duplicate RPD ≤20% for waters (≤35% for soils) for results >5X CRDL
_X_Duplicate Range is within ±CRDL (±2xCRDL for soils) for results ≤ 5X CRDL
___Qualify positive results estimated (J) if the above criteria were not met.

Comments/Qualified Results:
- STL- laboratory duplicate analyses for all duplicates were acceptable.
- GEL - laboratory duplicate analyses for all duplicates were acceptable.

INORGANIC DATA ASSESSMENT SUMMARY

	Acceptable Yes No
8. Spike Recovery (check all that apply)	NA

___Spike %R with 75-125%
___Spike %R 30-74%, >125%, results >IDL estimated (J)
___Spike %R 30-74% results <IDL estimated (UJ)
___Spike %R <30%, results <IDL rejected (UR)
___Field blank used for spike analysis
___Spike % R >125%, results <IDL acceptable
___Sample concentration exceeds spike concentration by a factor of >4x, acceptable

Comments/Qualified Results:

- STL – not analyzed.
- GEL – not analyzed.

9. GFAA Performance (check all that apply)	NA

___Duplicate injection RSD<20%
___Duplicate injection RSD>20%, results >CRDL estimated (J)
___Analytical spike %R 85-115%
___Analytical spike %R 40-85%, results >IDL estimated (J)
___Analytical spike %R 10-40%, results <IDL estimated (UJ)
___Analytical spike %R <10%, results <IDL rejected (R)
___Analytical spike %R <40%, results >IDL estimated (J)
___MSA required but not run, results estimated (J)
___MSA run at incorrect level, results estimated (J)
___MSA correlation coefficient <0.995, results estimated (J)

Comments/Qualified Results:

- STL – not analyzed.
- GEL – not analyzed.

10. Serial Dilution (check all that apply)	NA

___Serial Dilution %D within 10% for sample results >50x the IDL
___Serial Dilution %D greater than 10%, results >50x the IDL estimated (J)

Comments/Qualified Results:

- STL – not analyzed.
- GEL – not analyzed.

INORGANIC DATA ASSESSMENT SUMMARY

Acceptable
Yes No

---

11. Field Duplicates (check all that apply) __X_ ___

___Field duplicate RPD ≤20% waters (≤35% for soils)
_x_Field duplicate range is within ±CRDL (±2x CRDL for soils) for results <5xCRDL

Note: There are no qualification requirements for field QC samples exceeding limits.

Comments/Qualified Results:

- STL- all field duplicates were acceptable.
- GEL- no field duplicates collected.

12. Result Verification (check all that apply) __X_ ___

_X_All results supported in raw data

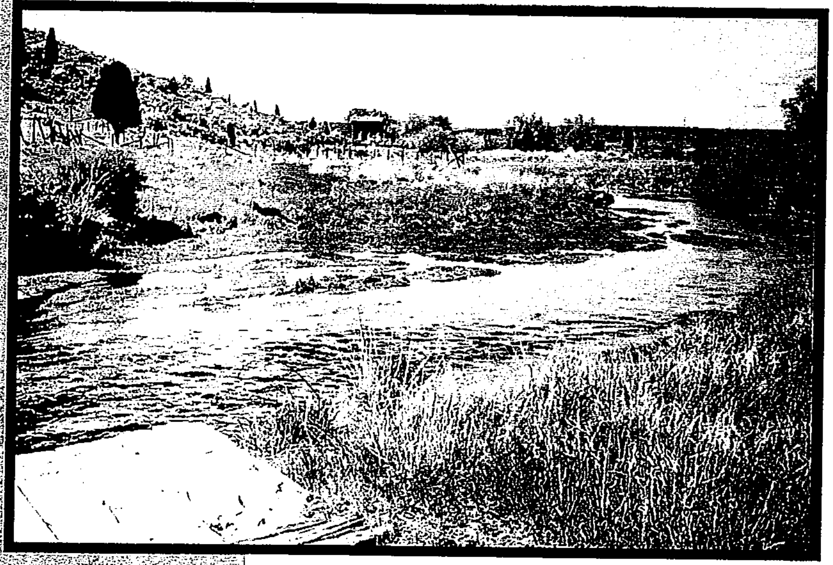
Comments/Qualified Results:

- STL- Data not checked 100%, but no transcription errors/anomalies were noted on items checked.
- GEL- Data not checked 100%, but no transcription errors/anomalies were noted on items checked.

13. Overall Assessment __X_ ___

- STL and GEL data were acceptable. Data were qualified (flagged) as estimated, undetected (U) for a blank detection. Discussion is included in the above sections, as well as in the data assessment summary for each analyte from STL and GEL.
- Sample results <MDL were qualified as U.

Submitted to:
Monsanto Soda Springs Plant
Highway 34
Soda Springs, ID 83276



FIRST FIVE-YEAR REVIEW REPORT FOR GROUNDWATER CONDITIONS AT THE MONSANTO SODA SPRINGS PLANT SODA SPRINGS, ID

MAY 2003

Golder Associates

Golder Associates Inc.

18300 NE Union Hill Road, Suite 200
Redmond, WA USA 98052-3333
Telephone (425) 883-0777
Fax (425) 882-5498
www.golder.com

Golder Associates

FIRST FIVE-YEAR REVIEW REPORT FOR GROUNDWATER CONDITIONS AT THE MONSANTO SODA SPRINGS PLANT SODA SPRINGS, IDAHO

Submitted to:

Monsanto
Soda Springs Plant
Highway 34
Soda Springs, Idaho 83276

Submitted by:

Golder Associates, Inc.
18300 NE Union Hill Road
Redmond, WA 98052

DCrawford
Diane Crawford
Senior Environmental Scientist

Michael Klisch
Michael Klisch
Project Hydrogeologist

David Banton
Principal Hydrogeologist

May 27, 2003

913-1101.001.605
052703dc1

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ATTACHMENTS

Attachment A	Theoretical Background of Statistical Methods
Attachment B	Output of Statistical Analyses—MAKESENS Graphs
Attachment C	RI Solute Transport Model Output
Attachment D	Goldsim Solute Transport Model Output
Attachment E	Geochemical Modeling Memorandum

LIST OF ACRONYMS AND ABBREVIATIONS

amsl	Above Mean Sea Level
AOC	Administrative Order on Consent
bgs	Below Ground Surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	Constituent of Concern
EPA	U.S. Environmental Protection Agency
gpm	Gallons per Minute
LBZ	Lower Basalt Zone
MCL	Maximum Contaminant Level
mg/L	milligrams per liter
NCP	National Contingency Plan
NPL	National Priorities List
RAO	Remedial Action Objective
RG	Remedial Goal
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
UBZ	Upper Basalt Zone
UFS	Underflow Solids (Pond)

1.0 INTRODUCTION

The purpose of the Five-Year Review is to determine whether the remedy at the Monsanto site is protective of human health and the environment. The methods, findings, and conclusions of reviews are documented in Five-Year Review reports. In addition, Five-Year Review reports identify issues found during the review, if any, and identify recommendations to address them.

This Five-Year Review report is being prepared pursuant to CERCLA § 121 and the National Contingency Plan (NCP). CERCLA § 121 states:

> *If the President selects a remedial action that results in any hazardous substances, pollutants, or contaminants remaining at the site, the President shall review such remedial action no less often than each five years after the initiation of such remedial action to assure that human health and the environment are being protected by the remedial action being implemented. In addition, if upon such review it is the judgment of the President that action is appropriate at such site in accordance with section [104] or [106], the President shall take or require such action. The President shall report to Congress a list of facilities for which such review is required, the results of all such reviews, and any actions taken as a result of such reviews.*

This requirement is further interpreted by the Environmental Protection Agency (EPA) in the NCP 40 CFR § 300.430(f)(ii), which states:

> *If a remedial action is selected that results in hazardous substances, pollutants, or contaminants remaining at the site above levels that allow for unlimited use and unrestricted exposure, the lead agency shall review such action no less often than every five years after the initiation of the selected remedial action.*

Golder Associates Inc. (Golder) conducted this Five-Year Review of the groundwater remedy employed at the Monsanto Soda Springs Plant located in Caribou County, Idaho. This review was conducted for groundwater conditions based on data collected up to June 2002. The portion of the Five-Year Review pertaining to the soils remedy implemented at the plant was conducted by MWH.

This review is required because the selected groundwater remedy resulted in constituents remaining on-site above remediation goals. This and future reviews will be used to evaluate whether the remedy remains protective, to confirm that constituent concentration trends in groundwater are declining as predicted, and, eventually, to confirm the achievement of the Remediation Goals (RG's). The triggering action for this statutory review is the initiation of the remedial action on April 30, 1997.

The goals of this Five-Year Review report include:

- Review and assessment of groundwater and outfall monitoring data (collected and evaluated at least annually);
- Comparison of groundwater and outfall quality and the extent of constituent plumes to regulatory levels, remediation goals, and groundwater modeling projections. This comparison will be used to determine if/when remediation goals have been achieved, and if not, that institutional controls are still in place and effectively preventing human exposure; and
- Evaluation of need to re-evaluate the groundwater model and/or groundwater remedial actions if groundwater recovery appears to significantly differ from model projections.

2.0 SITE CHRONOLOGY

TABLE 1

Summary of Site Chronology

Event	Date
Monsanto purchased site and initiated elemental phosphorus production on the property from locally mined phosphorus ore. The site was previously used for agricultural and domestic purposes.	1952
Landowner immediately south of the former plant boundary identified local groundwater impacts, notably excess-fluoride-related health problems in livestock drinking groundwater from nearby springs.	Early 1980's
Monsanto purchased land immediately south (Harris and Ponderosa) and southwest (Kackley) of the former plant boundary	Early to Mid 1980's
Golder was employed to assess the impacts of past and current operations on groundwater and surface water quality. The results of this investigation indicated that groundwater beneath the plant contained elevated concentrations of several metals and anions, including cadmium, selenium, fluoride, and sulfate.	1984
CERCLA site inspection was conducted by Ecology and Environment (an EPA contractor) that included additional groundwater sampling and analysis. The findings were consistent with Monsanto's earlier findings (Golder 1985) and found elevated levels of fluoride, cadmium, selenium, and sulfate in monitoring and production wells.	April 1988
EPA placed the Monsanto Company (Monsanto) elemental phosphorus plant in Soda Springs, Idaho, on the National Priorities List (NPL)	August 30, 1990
Administrative Order on Consent (AOC) issued by EPA and agreed to by Monsanto for the preparation and performance of a remedial investigation and feasibility study (RI/FS) for the Soda Springs Plant	March 19, 1991
A RI/FS was conducted for the Soda Springs plant.	March 1991 to November 1995
Monsanto sampled between 50 and 60 monitoring wells, offsite wells, and springs every six months as part of the RI/FS Work Plan.	1991 to 1998
EPA submitted a Record of Decision (ROD) for the Monsanto site that documents the selected remedy for environmental media affected by operations at the Soda Springs Plant.	April 30, 1997
Wells and springs have been sampled annually as part of remediation monitoring.	1998 to Date

3.0 SITE BACKGROUND

3.1 Site and Vicinity Description

The Monsanto Soda Springs Plant is located in southeastern Idaho approximately one mile north of the City of Soda Springs, Caribou County, Idaho (Figure 1). CERCLA regulations define the term "site" as the areal extent of affected areas and all suitable areas in very close proximity to the affected areas necessary for implementation of the response action. The term "plant" is used in this document to refer to those portions of the site that are owned by Monsanto and used for their elemental phosphorus manufacturing operations. The plant covers an area of approximately 540 acres, with the entire site covering an area of approximately 800 acres.

With elevations ranging from 5,880 feet to 5,990 feet above mean sea level (amsl), the plant lies in a tributary valley to the Bear River that is drained by Soda Creek. The valley is broad and rural, with mixed agriculture, residential, and industrial uses, and is bordered on the east by the Aspen Range and on the west by the Soda Springs Hills and Chesterfield Range. The largest population center in the area is the City of Soda Springs, with a population of approximately 3,000 people. A number of other industrial sites are located in the valley. These include:

- Kerr-McGee Chemical Corporation (former production of vanadium compounds), located east of Highway 34 from the plant;
- Evergreen Resources (fertilizer products), located about 1,000 to 2,000 feet southeast of the plant;
- Soda Springs Phosphate Industries (fertilizer products), located adjacent to Evergreen Resources;
- Nu-West Industries (phosphoric acid production and fertilizer products), located approximately four miles north of the plant; and
- N.A. Degerstrom (gallium and silver extraction), located approximately two miles north of the plant.

The City of Soda Springs obtains its municipal water from two springs located in the eastern portion of the valley: Formation Spring to the northeast of the Monsanto plant and Ledger Springs to the southeast of the Monsanto plant. Both springs are in different hydrogeologic systems from those at the site and, thus, are unaffected by site conditions. Twenty-two domestic water supply wells are registered within three miles of the site (most of them upgradient of the site), as well as seven irrigation wells. Hooper Springs, located downgradient of the site but showing no evidence of elevated levels of constituents of concern, is occasionally used by tourists and residents for drinking. The only domestic wells known to have been affected by groundwater from the site are at a home located 0.2 miles south of the plant (Lewis Well) and a well located about 600 feet south of the fence line (Harris Well). The Lewis home was connected to municipal water by Monsanto after elevated levels of selenium were found in the well. The Harris property was purchased by Monsanto and the well is no longer used for drinking water supply purposes.

The Monsanto Plant is located outside the limits of the City of Soda Springs and employs approximately 400 people. Potable water at the site is provided from the supply well PW-04, which is located at the northern (upgradient) edge of the plant.

3.1.1 History of Groundwater Effects

Monsanto purchased agricultural land in 1952 to construct the elemental phosphorus production plant using locally mined phosphorus ore. The site was previously used for agricultural and domestic purposes. In the early 1980's, a landowner immediately south of the former plant boundary identified local groundwater effects after livestock drinking water from several nearby springs experienced problems related to excess fluoride exposure. In 1984, Golder was employed to assess the effects of past and current operations on groundwater and surface water quality. The results of this investigation indicated that groundwater beneath the plant contained elevated concentrations of several metals and anions, including cadmium, selenium, fluoride, and sulfate. The sources of these constituents were determined to be the old underflow solids ponds, the northwest pond, and the Old Hydroclarifier. The investigation also concluded that groundwater under the southeastern portion of the plant contained elevated concentrations of vanadium, chloride, and sulfate.

Based on groundwater flow directions and geochemical data, the elevated concentrations beneath the southeast corner of the plant were attributed to the Kerr-McGee Chemical Corporation located to the east across Highway 34 from the plant. In April 1988, a CERCLA site inspection was conducted by Ecology and Environment (an EPA contractor) that included additional groundwater sampling and analysis. The findings were consistent with Monsanto's earlier findings (Golder 1985) and found elevated levels of fluoride, cadmium, selenium, and sulfate in monitoring and production wells.

3.1.2 Geology

The geology (and resultant hydrogeology) in the vicinity of the site is complex. Regionally, the plant is located near the southern end of the Blackfoot Lava Field that has infilled a generally north-northwest trending valley bordered by the Chesterfield Range and the Soda Hills on the west and by the Aspen Range on the east. The plant is located within the Bear River graben.

Locally, the site is underlain by a thin veneer of soils that overlie the basalt flows of the Blackfoot Lava Field. Five basalt flows separated by interbeds or weathered basalt zones are present beneath the plant. The basalt flows vary in thickness from less than 10 feet to 80 feet. The sedimentary units and weathered basalt zones range in thickness from 1 to 23 feet. The basalt flows overlie the Salt Lake Formation.

Northwest-trending, en-echelon normal faults (both west- and east-side-down relative displacement) are present in the site area and commonly form narrow grabens that are typically 1,000 to 1,500 feet wide and up to 2.5 to 3 miles long (Figure 2 and 3). These faults extend from the southeast of the plant north to the Blackfoot Reservoir. A prominent fault (Monsanto fault) enters the plant near the northwest corner and appears to die out just west of the southeast corner of the plant. A subsidiary fault parallels this fault approximately 1,500 feet to the southwest. Fault displacement has interrupted lateral groundwater flow and created springs in the vicinity of the plant.

Several normal faults exist east of the plant that appear to act as a hydraulic barrier, such that groundwater west of the Finch Spring fault apparently does not flow into the Ledger Creek Springs area.

3.1.3 Hydrogeology

This section presents a summary of the hydrogeological conditions at the site. Details are presented in the RI report (Golder, 1995). The wells and springs at and in the vicinity of the Monsanto Plant are shown on Figures 2 and 3. Figure 4 shows the locations of various operational facilities. As described in the Phase II RI Report (Golder 1995), the two primary hydrostratigraphic zones underlying the Monsanto Plant are the Upper Basalt Zone (UBZ) and the Lower Basalt Zone (LBZ). The UBZ is the principal aquifer and is found in most places beneath the plant to a depth of about 100 feet below ground surface (bgs). The depth to the water table varies across the plant from about 20 feet bgs in the northeast corner of the plant to about 100 feet bgs in the center of the plant. The LBZ is less permeable than the UBZ (with a hydraulic conductivity of at least three orders of magnitude less) and underlies the UBZ to a depth of at least 250 feet bgs.

Groundwater flow in the UBZ and the LBZ is influenced by faulting, regional hydrogeological conditions, and pumping of the plant production wells (Figures 5 and 6). The groundwater flow direction beneath the plant is generally from north to south paralleling the geological structures. Both the major fault and the subsidiary fault running beneath the plant appear to act as barriers to groundwater flow.

The ambient (control) groundwater quality beneath the plant correlates to one of the three regional systems: the Shallow Groundwater System, the Mead Thrust Aquifer System, and the Chesterfield Range Aquifer System. The Shallow Groundwater System consists of fresh water that comes into contact with surface soil and basaltic units. The Mead Thrust Aquifer System also consists of fresh water, and receives recharge from the mountains to the east of the Monsanto Plant. The Chesterfield Range Aquifer System consists of sodic water and receives recharge from the Chesterfield Range to the west of the plant.

The UBZ and LBZ have been divided into smaller regions, based primarily on hydrogeological controls and groundwater quality. The breakdown of the UBZ and LBZ regions is shown on Figures 2 and 3, respectively, and is described below:

UBZ-1 & LBZ-1

These zones are located in the immediate southwestern corner of the plant and are bounded by the subsidiary fault to the northeast. Control groundwater quality in UBZ-1 consists of sodic water and mixed sodic and fresh water. Control groundwater quality in LBZ-1 is sodic.

The springs in the vicinity of Soda Creek and the Harris well are included in UBZ-1 (Figure 2). However, as shown in the cross-section in Figure 3-11 of the Phase II RI Report (Golder 1995), the Harris well may be completed within both the UBZ-1 and the LBZ-1 zones. Thus, some of the constituents observed in control sodic groundwater in LBZ-1 occur in this well.

UBZ-2 & LBZ-2

These zones are located in the southwestern central portion of the plant and are bounded by the major and subsidiary faults running beneath the plant. The old underflow solids ponds are located above these zones. Control groundwater quality in UBZ-2 is assumed to be fresh (Shallow Groundwater System). Control groundwater quality in LBZ-2 is sodic.

As shown in the cross-section in Figure 3-8 of the Phase II RI Report (Golder 1995), TW-34 and TW-35 are completed in the transition zone between UBZ-2 and LBZ-2. Some sodic groundwater occurs in these wells due to the upward hydraulic gradient from LBZ-2. Thus, these wells contain groundwater with elevated constituents that occur naturally in the deeper sodic groundwater, such as manganese.

UBZ-3 & LBZ-3

These zones are included within the eastern and southeastern portions of the plant and are influenced by Kerr-McGee operations. Control groundwater quality in UBZ-3 is fresh, and is assumed to be that of the Mead Thrust Aquifer System, with minor mixing with the Shallow Groundwater System. Water quality in these zones is also influenced by operations at the Kerr-McGee plant. Constituents such as vanadium, ammonium, and molybdenum have been found in elevated concentrations in this system. These constituents are associated with the Kerr-McGee operations.

UBZ-4 & LBZ-4

The zones primarily underlie the northern and central portions of the plant. Plant facilities located above these zones include the northwest pond and the old hydroclarifier. Control groundwater quality in UBZ-4 is primarily fresh (mostly Shallow Groundwater System), however, the groundwater quality in the immediate northwestern corner of the plant is sodic. Control groundwater quality in LBZ-4 is primarily sodic.

The four production wells (PW-1, PW-2, PW-3, and PW-4) are open to up to four interflow zones, including both the UBZ and the LBZ. Two monitoring wells (TW-18 and TW-44) are completed in LBZ-4.

3.1.4 Sources of Affected Groundwater

Groundwater affected by Monsanto activities is predominantly confined to the UBZ within the plant site area. Groundwater flow in the UBZ is toward the south plant fenceline. The wells located at the South Fenceline and at the Southern Boundary (and within Monsanto boundaries) monitor the migration of the plumes originating within plant boundaries.

There are two constituent plumes on the site originating from Monsanto operations. Affected groundwater originates from three principal source areas within the Monsanto Plant (Figure 4):

- Old underflow solids (UFS) ponds (UBZ-2);
- Northwest pond (UBZ-4); and
- Old hydroclarifier (UBZ-4).

The plume from the old UFS ponds occurs in the UBZ-2 groundwater zone and flows within the groundwater system toward the south. The plumes from the Northwest Pond and the Old Hydroclarifier occur in the UBZ-4 zone and flow southward toward the plant production wells used for non-contact cooling water supply. Pumping from the production wells PW-01, PW-02, and PW-03 from UBZ-4 contains the plumes originating from the Northwest Pond and the Old Hydroclarifier areas to prevent offsite migration. There are other minor source areas on the site such as the former sewage lagoon, the unlined non-contact cooling water ponds, and the old coke and quartz ponds. A fourth plume originates on Kerr McGee's plant site, and has spread onto the southeastern portion of the Monsanto Plant site.

3.1.5 Summary of Previous Investigations

In 1978, Monsanto installed five groundwater monitoring wells (TW-2, TW-3, TW-4, TW-5, and TW-6) and initiated a quarterly groundwater sampling program that continued until 1984. Two additional wells (TW-7 and TW-8) were installed downgradient of the first five wells in 1982. Some off-site spring sampling was conducted by Monsanto in 1983.

In 1984, Golder was employed to assess the impacts of past and current operations on groundwater and surface water quality (Golder 1985). Thirty-one monitoring wells were installed to supplement seven existing monitoring wells and quarterly sampling was continued. The results of this investigation indicated that groundwater beneath the plant contained elevated concentrations of several metals and anions, including cadmium, selenium, vanadium, fluoride, sulfate, and other inorganic constituents of less concern. The sources of these elevated concentrations were hypothesized to be the old Underflow Solids Ponds, the Northwest Pond, and the Old Hydroclarifier. A separate plume containing elevated levels of chloride, sulfate, and vanadium was found in the southeast portion of the site that later, based on groundwater flow directions and geochemical data, was attributed to the Kerr-McGee Chemical Corporation located to the east across Highway 34 from the plant.

In April 1988, a CERCLA site inspection was conducted by Ecology and Environment (an EPA contractor) that included additional groundwater sampling and analysis. The findings were consistent with Monsanto's earlier findings (Golder 1985) and found elevated levels of fluoride, cadmium, selenium, and sulfate in monitoring and production wells.

Monsanto collected groundwater samples from approximately 40 wells and springs on a regular basis prior to 1991. From 1991 to 1998, Monsanto sampled between 50 and 60 monitoring wells, offsite wells, and springs every six months as part of the RI/FS Work Plan. From 1998 to date, wells and springs have been sampled annually.

As part of the Phase II RI for the Monsanto Plant, Golder developed a solute transport model to predict the fate and transport of constituents in groundwater in the vicinity of the plant (Golder 1993; Golder 1995). First, a groundwater flow model was developed for the Blackfoot Lava Field, which includes both the upper basalt zone and the lower basalt zone aquifers. Second, a solute transport model was developed for the UBZ-2 zone to predict the travel time for constituents to three selected endpoints to the south of the plant (the southern plant boundary, the estimated discharge point of the plume into Soda Creek, and the estimated discharge point of the plume into Bear River). The model predicted that all constituents within the UBZ-2 plume migrating to the southern plant boundary should achieve background levels within 5 to 30 years, depending on the constituent and its rate of retardation in groundwater.

4.0 REMEDIAL ACTIONS

4.1 Remedial Measures Prior to Record of Decision

Prior to implementation of the remedial action designated in the ROD, significant environmental improvements were conducted at the plant, some made independently by Monsanto and others were done to comply with state and/or federal requirements. Those related to groundwater include:

- August 1985: Removal of the Old Hydroclarifier, which was suspected as potentially affecting groundwater, and replacement with a new unit that includes a synthetic liner, a leachate collection system, and a monitoring well network.
- 1986: Four underground fuel storage tanks were replaced with aboveground tanks with concrete sumps. The underground tanks were removed to comply with new regulations and there was no indication that the tanks had leaked.
- 1987: Four wells (TW-3, TW-4, TW-5, and TW-6) that were discovered to be creating hydraulic connection between the upper and lower aquifers due to poor construction (and, thus, possible constituent migration) were abandoned in accordance with regulatory guidelines.
- 1983 to 1988: The old Underflow Solids Ponds, suspected as sources of groundwater contamination, were taken out of service. In 1988, the upper layer of contaminated soil was removed and the depression was backfilled with material excavated from the northwest pond and clean material. The ponds were then filled with molten slag and sealed with a bentonite cap to isolate the remaining underflow solids from infiltration and prevent further migration of constituents. Solids that remained in the pond are below the cap, but above the water table.
- 1988: The Northwest Pond, suspected as a source of groundwater contamination, was closed and excavated. Discolored soils were removed and deposited in the old underflow solids ponds. The base of the pond was sealed with bentonite. The area is currently permitted by the Idaho Department of Environmental Quality to receive plant sanitary solid waste and is being operated as a lined general waste landfill.
- 1985 to 1989: Several wells were installed around the hydroclarifier and used as recovery wells to intercept contaminated groundwater. The groundwater was pumped into the new hydroclarifier. Three wells were pumped intermittently at a rate of approximately 12 gallons per minute (gpm) per well until 1989. In the spring of 1989, the plant stopped pumping these wells because of potential listing of the plant for the NPL and has not resumed.
- 1993: Plant sewage evaporation ponds were taken out of service and the plant connected to the municipal wastewater collection system. The ponds were closed in 1995.

4.2 Remedy Selection

On April 30, 1997, the EPA submitted the Record of Decision for the site that documents the selected remedy for environmental media affected by operations at the Soda Springs Plant (EPA 1997). The ROD identified the constituents of potential concern for soil, sediments, and groundwater based on exceedances of EPA risk screening criteria. The selected remedy for groundwater is monitored natural attenuation with institutional controls (such as legally enforceable prohibitions on drinking water wells in the affected area) to prevent human exposure to groundwater until groundwater quality recovers to background conditions. Except for the annual monitoring of groundwater, relevant springs, and the plant discharge outfall, no further action was deemed necessary because there are no current drinking water users of the affected groundwater and because the combination of past remedial actions and natural attenuation is projected to restore groundwater to levels that allow for unrestricted use and exposure within 30 years.

The ROD established groundwater remediation goals for the constituents of concern: cadmium, fluoride, nitrate, selenium, and manganese. The remediation goals are the MCLs under the Safe Drinking Water Act for cadmium, fluoride, nitrate, and selenium, and a risk-based concentration for manganese, as shown below in Table 2.

TABLE 2

Groundwater Remediation Goals for the Monsanto Site

Parameter	Remediation Goal (mg/L)	Regulatory Source
Cadmium	0.005	Maximum Contaminant Level
Fluoride	4	Maximum Contaminant Level
Nitrate as NO_3/ Nitrate as N	44 / 10	Maximum Contaminant Level
Selenium	0.05	Maximum Contaminant Level
Manganese	0.18	Risk-Based Concentration

The ROD established the points of compliance for remediation goal monitoring. Well TW-19 (in UBZ) is listed in the ROD as a point of compliance, however, that well does not produce sufficient water. Well TW-20 (also in UBZ) is located in the same well pair as TW-19, and therefore replaces that well as a point of compliance. The ROD also lists TW-29 as a point of compliance. This well is located at the north end of the plant where groundwater is unaffected by plant operations. It was assumed that the listing of TW-29 in the ROD was a typographical error, and that TW-39 was the intended point of compliance. Well TW-39 is located at the south plant fence line and is completed in the UBZ. Based on these modifications, the point of compliance wells are listed below:

- Production Wells - Wells PW-01, PW-02, and PW-03;
- South Fence Line - Wells TW-20, TW-34, TW-35, and TW-39;
- Southern Plant Boundary - Wells TW-53, TW-54, TW-55, and Harris well; and
- Soda Creek.

Well TW-34 is affected by naturally occurring manganese concentrations because it is completed in the transition zone between the UBZ (fresh water) and LBZ (sodic water containing naturally elevated manganese concentrations). TW-34 is therefore not appropriate for monitoring the UBZ. The South Fence Line wells are located inside the southern plant fence line near Hooper Springs

Road. The Southern Plant Boundary wells are located within the Monsanto property boundary near its southern margin (about 1,200 ft south of the fence line).

In May 2001, two sample stations on Soda Creek were established at locations upstream and downstream of the effluent discharge (non-contact cooling water) pipe, as shown in Figure 2. Surface water samples were collected from the two new Soda Creek locations during the 2001 and 2002 sampling rounds.

4.3 Operation and Maintenance

Long-term operations and maintenance for groundwater at the site consist of annual long-term groundwater sampling. This sampling has been on-going at the site since the ROD was signed and is continuing with annual reports sent to the EPA. This activity is adequately funded and a budget for the future is in-place by Monsanto.

5.0 FIVE-YEAR REVIEW PROCESS

5.1 Document Review

This Five-Year Review consisted of a review of the following relevant documents:

- Phase I Remedial Investigation/Feasibility Study, Preliminary Site Characterization Summary Report for the Soda Springs Elemental Phosphorus Plant (Golder 1993);
- Phase II Remedial Investigation Report for the Soda Springs Elemental Phosphorus Plant (Golder 1995);
- Record of Decision, Monsanto Chemical Company Superfund Site, Caribou County, Idaho (EPA 1997); and
- 1998 through 2002 Annual Groundwater Sampling Summary Reports (Golder 1998; Golder 1999; Golder 2000; Golder 2001; Golder 2002).

5.2 Data Review

As stated in the ROD, the following elements are required for this Data Review portion of Five-Year Review:

- Review and assess groundwater and outfall monitoring data (collected and evaluated at least annually); and
- Compare groundwater and outfall quality and extent of constituent plumes to regulatory levels, remediation goals, and groundwater modeling projections. Determine if/when remediation goals have been achieved, and if not, that institutional controls are still in place and effectively preventing human exposure.

The first element of data review for the five-year review (Evaluation of Groundwater and Outfall Monitoring Data) is presented in Section 5.3. The second element of the five-year review is presented in two sections: Evaluation of Extent of Constituent Plumes (Section 5.4) and Evaluation of Groundwater Modeling Projections (Section 5.5).

5.3 Evaluation of Groundwater and Outfall Monitoring Data

5.3.1 Status of Attaining Remediation Goals

Based on the June 2002 sampling results, most points of compliance are below remediation goals for the constituents of concern. The 2002 concentrations are compared to remediation goals in Table 3. For fluoride and nitrate, all compliance points are below remediation goals. However, cadmium exceeds remediation goals at four compliance wells (PW-01, TW-20, TW-39, and TW-54); manganese at one compliance point (TW-34), and selenium at six compliance points (PW-01, TW-20, TW-39, TW-53, TW-54, and Harris Well). However, all exceedances are located at points within Monsanto boundaries and constituents have not migrated offsite, thus institutional controls are still effective.

5.3.2 Evaluation of Constituent Concentration Trends

To quantitatively assess if the constituents of concern are declining as projected in the RI, statistical analyses were performed on the groundwater quality data from the time 1991 (start of RI process) through the most recent sampling round conducted in June 2002. For many compliance points, water quality data are available for earlier than 1991. Earlier data are not used because they are not as temporally consistent and samples were not collected according to the strict QA/QC guidelines that were adhered to for samples collected from 1991 to 2002.

As with the annual summary reports on groundwater conditions at the Soda Springs Plant, constituents included in the statistical analyses include the constituents of concern listed in the ROD (cadmium, fluoride, nitrate as N, selenium, and manganese), as well as several other indicator constituents (chloride, molybdenum, and sulfate). Analyses were conducted at the points of compliance identified in the ROD, in addition to analyses for several different areas not specified in the ROD. These additional points are mainly in areas of the original contamination sources. The points of compliance and additional points include:

Points of Compliance:

- Production Wells – PW-01, PW-02, and PW-03 (as well as PW-04, though not defined as a point of compliance);
- South Fence Line Wells – TW-20, TW-34, TW-35, and TW-39;
- Southern Plant Boundary Wells – TW-53, TW-54, TW-55, and Harris well; and
- Soda Creek.

Additional Points:

- Northwest Pond Area Wells – TW-16, TW-17, and TW-18;
- Old Underflow Solids Ponds Area Wells – TW-22, TW-24, TW-37, and TW-45;
- Hydroclarifier Area Wells – TW-40 and TW-44; and
- Springs South of Plant – Homestead, Calf, and Mormon Springs.

5.3.2.1 Methods of Trend Analysis

The statistical methods employed for this analysis are summarized below. Theoretical details of each method and the Excel template application are provided in Attachment A.

5.3.2.1.1 Mann-Kendall Test

To assess whether constituent concentrations were increasing or decreasing after source removal, the Mann-Kendall non-parametric estimator of trends (Mann 1945; Kendall 1975; Gilbert 1987) was used. This procedure is useful for evaluating environmental data because missing values are allowed, a small data set ($n \geq 5$) is sufficient, the data do not need to conform to a particular distribution, the test is not affected by gross outliers or data errors, and data reported as less than the detection limit are allowed (Gilbert 1987). The Mann-Kendall Test is a non-parametric test of sequential signs (positive or negative) that indicates monotonic increases or decreases in successive data that persist over several sampling intervals. Depending on the size of the data set, the output of the Mann-Kendall test is the S statistic ($5 < n < 10$) or the Z statistic ($n \geq 10$, unless there are many tied data values). Positive and negative S or Z statistics indicate increasing (positive) or decreasing (negative) concentration trends. In order for a trend to be positively identified, the degree of confidence (significance level) that a trend exists should be very high. Golder suggests a significance level of α

≤ 0.05. In other words, there is only a 5% or less probability that a statistically significant trend does not exist. Details of the equations used for calculating the S and Z statistics are included in Attachment A and Gilbert (1987).

With the Mann-Kendall test, the null hypothesis, H_0, of no trend in the data (i.e. the observed concentrations are randomly ordered in time) is tested against the alternative hypothesis, H_A, of an increasing or decreasing monotonic trend. If S or Z is positive with a significance level (α) less than 0.05, the H_0 is rejected in favor of H_A for an increasing concentration trend; likewise if S or Z is negative with a significance level (α) less than 0.05, the H_0 is rejected in favor of H_A for a decreasing concentration trend. In other words, if α was calculated as greater than 0.05, no significant trend was defined. If α was calculated as equal to or less than 0.05, a significant increasing or decreasing trend was defined, depending on the sign of the Z/S statistic.

5.3.2.1.2 Sen's Method

If a linear trend is present in the time series of concentration data, the true slope of data (change in concentration per unit time) can be estimated using the non-parametric Sen's Method for Estimation of Slope (Sen 1968; Gilbert 1987). Unlike calculation of true slope by computing the least-squares estimate of the slope by linear regression models, Sen's method is not greatly affected by gross data errors or outliers, and the calculation allows missing data values. Sen's method is closely related to the Mann-Kendall method and, similar to the S and Z-statistics, positive and negative slopes indicate increasing and decreasing concentration trends, respectively. The magnitude of the slope indicates the rate at which the constituent concentrations are changing; the sign of the slope indicates if it is increasing (+) or decreasing (-). Details of the equations used to compute Sen's estimate of slope can be found in Gilbert (1987).

5.3.2.1.3 MAKESENS Excel Template

An Excel template MAKESENS (Mann-Kendall test for trend and Sen's slope estimates) was used for detecting and estimating constituent concentration trends in data from the Monsanto site by computing the Mann-Kendall and Sen's methods (Salmi et al. 2002). MAKESENS analyzes for the presence of increasing or decreasing trends by first testing with the Mann-Kendall test and secondly the slope of a linear trend is estimated with Sen's method. When $n<10$, MAKESENS automatically computes the S statistic, but Sen's method is not computed because the normal approximation is not valid. When $n \geq 10$, MAKESENS automatically computes the Z statistic followed by the linear slope with Sen's method.

5.3.2.1.4 Results of Statistical Analyses

Graphical portrayal of the input and output files to MAKESENS for each constituent and sampling point are provided in Attachment B. Summary tables of the statistical results are provided in Tables 4a through 4h. Often during the earlier years of the statistical analysis (1992, 1993, and 1994), water quality samples were collected biannually in late Spring and late Fall. Because the statistical methods employed require a single annual average, if two results were available for the year, the average of the values was calculated and used for the annual value. In the majority of sampling years, however, all samples were collected in late spring.

A number of wells exhibit increasing then decreasing concentrations, suggesting the passage of a slug of the constituent past the well. The statistical methods employed for these analyses assume linear, monotonic distributions (significant trend) or random distributions (no trend). If a dual trend is present, no trend will be detected or it will be skewed to the stronger of the two and not give a representative analysis. For these cases, the entire monitoring period is analyzed, followed by an analysis of the latter portion of the slug passage.

Production Wells

In the production wells, cadmium, chloride, and molybdenum concentrations are decreasing or stable. Fluoride is stable in PW-01, but increasing in PW-02, PW-03, and PW-04. Manganese, nitrate, selenium, and sulfate are stable in all wells. Details of the statistical analyses results are presented below.

Cadmium

In production wells PW-01, PW-02, and PW-03, cadmium exhibits a significant decreasing concentration trend since 1991 (Z = -2.15, -3.02, and -2.89, respectively, with $\alpha = 0.05$, 0.01, and 0.01, respectively). The slopes of the respective decreasing concentrations are: -0.004, -0.001, and -0.0004 mg/L per year calculated from Sen's Q. Cadmium in PW-04 has been, for the most part, non-detected, thus no significant increasing or decreasing trend was computed.

Fluoride

Fluoride concentrations in production well PW-01 show a stable trend since 1991. However, PW-02, PW-03, and PW-04 exhibit significant increasing concentration trends since 1991 (Z = 2.95, 2.15, 3.10, respectively, with $\alpha = 0.01$, 0.05, 0.01) with slowly increasing concentration slopes of 0.03, 0.03, and 0.02 mg/L per year, respectively.

Manganese

In all four production wells (PW-01, PW-02, PW-03, and PW-04), manganese concentrations are mostly non-detect and, thus, show no significant concentration trend ($\alpha > 0.1$ for all wells).

Nitrate as N

Nitrate as N concentrations in all four production wells (PW-01, PW-02, PW-03, and PW-04) do not show significant concentration trends ($\alpha \geq 0.1$ for all wells) and have been statistically stable since 1991.

Selenium

In all four production wells (PW-01, PW-02, PW-03, and PW-04), there is no significant selenium concentration trend since 1991 ($\alpha > 0.1$ for all wells).

Chloride

Chloride concentrations in PW-01 exhibit a significant decreasing concentration trend since 1991 (Z= -2.50 with $\alpha = 0.05$) with a slope of approximately -5.7 mg/L per year. No significant concentration trends are exhibited by PW-02, PW-03, or PW-04 ($\alpha > 0.1$ for all three wells), with all three showing statistically stable concentrations since 1991.

Molybdenum

Since 1991, molybdenum concentrations in pumping wells PW-01 and PW-03 exhibit significant decreasing concentration trends (PW-01: S = -22.0 with $\alpha = 0.01$; PW-03: Z = -2.89 with $\alpha = 0.01$). Because n for PW-01 is less than 10, Sen's estimate of slope could not be calculated. However, the estimated slope for PW-03 is approximately -0.005 mg/L per year. PW-02 shows no significant concentration trend since 1991. PW-04 also shows no significant concentration trend, but molybdenum concentrations have all be non-detected since 1991.

Sulfate

Since 1991, sulfate concentrations in all four pumping wells (PW-01, PW-02, PW-03, and PW-04) show no significant concentration trend ($\alpha > 0.1$) and appear to be statistically stable.

South Fence Line Wells

In the South Fence Line wells, cadmium, nitrate, chloride, molybdenum and sulfate are stable or decreasing in all wells. Fluoride is increasing in TW-35, but stable or decreasing in TW-20, TW-34, and TW-39. Manganese and selenium are stable in all wells.

Cadmium

TW-20 is the only well in the South Fence Line area that exhibits a significant decreasing concentration trend (Z = -3.30 with $\alpha = 0.001$) with a concentration slope of -0.001 mg/L per year. TW-34 and TW-35 are mostly non-detected and, thus, show no significant trend. TW-39, though mostly all detected concentrations, also shows no significant trend and has remained statistically stable since 1991.

Fluoride

Fluoride concentrations in TW-20 and TW-39 exhibit significant decreasing concentration trends since 1991 (Z = -3.50 and -3.10, respectively, with $\alpha = 0.001$ and 0.01, respectively) with a decreasing concentration slope of approximately -0.53 mg/L per year for TW-20 and approximately -0.18 mg/L per year for TW-39. TW-34 shows no significant concentration trend. However TW-35 shows a slight, but significant, increasing concentration trend (Z = 2.00 with $\alpha = 0.05$) with an concentration slope of approximately 0.02 mg/L per year since 1991.

Manganese

All wells in the South Fence Line area (TW-20, TW-34, TW-35, and TW-39) show no significant concentration trend ($\alpha > 0.1$ for all wells) since 1991.

Nitrate as N

In TW-20, nitrate as N concentrations exhibit a significant decreasing concentration trend (Z = -2.26 with $\alpha = 0.05$) with a slope of -0.327 mg/L per year since 1991. TW-34, TW-35, and TW-39 show no significant concentration trend. However, the lack of a significant trend in TW-39 appears to be caused by a slug of nitrate moving through the well from 1991 to 2002. From 1997 to 2002, nitrate as N concentrations exhibit a significant decreasing concentration trend (S = -12 with a $\alpha = 0.05$). Because n is less than 10 for this period of analysis, Sen's Q could not be calculated.

Selenium

All wells in the South Fence Line area (TW-20, TW-34, TW-35, and TW-39) show no significant selenium concentration trend ($\alpha \geq 0.1$ for all wells) since 1991. In TW-20, the statistics were recalculated without the anomalously high value from 2002, but the trend was still insignificant ($\alpha = 0.1$).

Chloride

Chloride concentrations in TW-20, TW-35, and TW-39 exhibit significant decreasing concentration trends ($Z = -2.47$, -2.20, and -3.36, respectively, with $\alpha = 0.05$, 0.05, and 0.001), with slopes of -7.4, -1.2, and -6.8 mg/L per year, respectively. Chloride concentrations in TW-34 show no significant concentration trend ($\alpha > 0.1$).

Molybdenum

In the South Fence Line wells, TW-20 exhibits a significant decreasing concentration trend ($Z = -3.58$ with $\alpha = 0.001$) with a slope of -0.01 mg/L per year. TW-34, TW-35, and TW-39 show no significant concentration trend ($\alpha > 0.1$); molybdenum in TW-34 and TW-35 has remained non-detected since 1991, while TW-39 has detected concentrations that exhibit no increasing or decreasing trend.

Sulfate

For TW-20, the 2002 sulfate concentration is possibly anomalous. As a result, two statistical analyses were run—the first with 2002, the second without the 2002 data point. With the anomalously high 2002 concentration, TW-20 shows no significant concentration trend ($\alpha > 0.1$). However, with the 2002 point removed, TW-20 shows a significant decreasing concentration trend since 1991 ($Z = -2.73$ with $\alpha = 0.01$) with a concentration slope of -32.8 mg/L per year. TW-34, TW-35, and TW-39 do not show significant concentration trends since 1991.

Southern Boundary Wells

In the Southern Boundary wells (TW-53, TW-54, TW-55, and TW-56, all in the UBZ), cadmium, nitrate, selenium, chloride, and sulfate are stable or decreasing in all four wells. Fluoride is increasing in TW-53, TW-55, and TW-56, but decreasing in TW-54. Manganese is stable in all wells. Molybdenum is increasing in TW-53, but decreasing in TW-54 and stable in TW-55 and TW-56.

Cadmium

Cadmium concentrations in TW-53, TW-55, and TW-56 were non-detected in all years since 1991 and no trend was computed. In TW-54, though there were some detected concentrations, no trend was computed.

Fluoride

Concentration trends at Southern Boundary Wells TW-53, TW-55, and TW-56 are computed as significant increasing trends since 1991 (Z = 2.96, 3.67, 3.05, respectively, with α = 0.01, 0.001, and 0.01). Rates of concentration increase approximated by Sen's Q are 0.3, 0.03, and 0.03 mg/L per year, respectively. TW-54 exhibits a decreasing concentration trend (Z = -2.02 with α = 0.05) with a decreasing slope of -0.3 mg/L per year.

Manganese

Manganese concentrations in the Southern Boundary area wells (TW-53, TW-54, TW-55, and TW-56) show no significant concentration trend (α > 0.1 for all wells) since 1991.

Nitrate as N

Southern Boundary Area wells TW-53, TW-55, and TW-56 show no significant concentration trend since 1991 (α > 0.1 for all three wells). TW-54, however, exhibits a significant decreasing concentration trend (Z = -2.11 with α = 0.05) with a slope of -0.2 mg/L per year since 1991.

Selenium

For the analysis period 1992 to 2002, selenium concentrations in TW-53 show no significant concentration trend. However, there appears to be passage of a selenium plume through this well, with concentrations increasing from 1992 to 1994, followed by decreasing concentrations from 1994 to 2002. Therefore, concentration trend was analyzed from 1994 to 2002 to assess the trend following passage of the plume. For this period, selenium concentrations exhibit a significant decreasing trend (S = -32 with α = 0.001). Because n is less than 10, Sen's Q could not be calculated. In TW-54, the 2002 selenium concentration is anomalously high, thus possibly falsely skewing the trend analysis. With this data point included in the analysis, there is no significant concentration trend (α = 0.1). However, with the anomalous point removed, a significant decreasing trend is exhibited (Z = -2.68 with α = 0.01) with a slope of -0.04 mg/L per year. Selenium concentrations in TW-55 show a significant decreasing concentration trend (Z = -3.89 with α = 0.001) with a slope of -0.02 mg/L per year. TW-56 shows no significant selenium concentration trend (α > 0.1), with most of the concentrations being non-detected.

Chloride

Chloride concentrations in TW-53 and TW-56 show no significant concentration trend from 1992 to 2002 (α ≥ 0.1). However, TW-53 shows concentrations suggesting passage of a plume of chloride with increasing concentrations from 1992 to 1994, followed by decreasing concentrations from 1994 to 2002. To better analyze the latter trend, a trend analysis was conducted for the period of 1994 to 2002. This analysis shows a significant decreasing concentration trend (S = -20 with α = 0.01). Because n is less than 10, Sen's Q could not be calculated. TW-54 and TW-55 exhibit significant decreasing concentration trends (Z = -2.49 and –2.80, respectively, with α = 0.05 and 0.01, respectively) with slopes of -13.0 and -3.9 mg/L per year.

Molybdenum

Well TW-53 exhibits a significant increasing concentration trend since 1992 (Z = 3.27 with α = 0.01) with a concentration slope of 0.007 mg/L per year. TW-54, however, exhibits a significant decreasing concentration trend ($Z = -2.34$ with $\alpha = 0.05$) with a slope of -0.006 mg/L per year. TW-55 shows no significant concentration trend since 1991 because molybdenum has been non-detected in all samples. TW-56 also shows no significant concentration trend, but all concentrations are detected ($\alpha > 0.1$) and have remained statistically stable since 1991.

Sulfate

Sulfate concentrations in Southern Boundary Wells TW-53, TW-54, and TW-56 show no significant concentration trends ($\alpha > 0.1$). Though TW-53 does not show a statistically significant trend, it should be noted that the concentrations have been increasing and decreasing since 1992. TW-55, however, exhibits a significant decreasing concentration trend ($Z = -3.45$ with $\alpha = 0.001$) with a slope of approximately -11.4 mg/L per year.

Harris Well and Mormon A Spring

In Harris Well and Mormon A Spring, cadmium, manganese, and nitrate are stable. Fluoride and molybdenum are stable in Mormon A Spring, but increasing in Harris Well. Selenium and sulfate are increasing in Mormon A Spring and stable in Harris Well. Chloride is decreasing in Mormon A and stable in Harris.

Cadmium

Cadmium in the Harris Well and Mormon A Spring shows no concentration trend. Mormon A Spring shows stable cadmium concentrations, while cadmium in Harris Well is mostly non-detect since 1991.

Fluoride

Fluoride concentrations in Mormon A Spring exhibit no significant trend. Fluoride concentrations in Harris Well show a significant increasing concentration trend ($Z = 2.34$ with $\alpha = 0.05$) with a slope of 0.31 mg/L per year. However, it should be noted that fluoride concentrations appear to be decreasing since 1999, possibly indicating the beginning of a decreasing trend.

Manganese

Manganese concentrations in Mormon A Spring and the Harris well show no significant concentration trend ($\alpha > 0.1$ for all wells) since 1991.

Nitrate as N

Nitrate as N concentrations in both Mormon A Spring and the Harris well show no significant concentration trend ($\alpha \geq 0.1$).

Selenium

Since 1991, selenium concentrations in Mormon A Spring exhibit a significant increasing concentration trend ($Z = 2.75$ with $\alpha = 0.01$) with a slope of 0.01 mg/L per year. The Harris well, however, shows no significant concentration trend since 1991 ($\alpha > 0.1$). However, concentration distributions since 1991 suggest passage of a slug of selenium in the Harris well, with concentrations increasing from 1991 to 1994, then decreasing from 1994 to 2002. To better characterize the latter concentration trend, selenium concentrations were analyzed from 1994 to 2002. The S statistic indicates a significant decreasing concentration trend (S = -30 with α = 0.001). Because n is less than 10, Sen's Q could not be calculated.

Chloride

Chloride concentrations in Mormon A Spring exhibit a significant decreasing concentration trend since 1991 (Z = -1.99 with $\alpha = 0.05$) with a slope of -4.3 mg/L per year. The Harris well, however, shows no significant concentration trend since 1991 ($\alpha > 0.1$).

Molybdenum

Molybdenum concentrations in Mormon A Spring do not exhibit a significant concentration trend since 1991 ($\alpha > 0.1$). However, molybdenum in the Harris well show a significant increasing concentration trend for molybdenum (Z = 2.19 with $\alpha = 0.05$) with a slope of 0.001 mg/L per year. It should be noted that molybdenum concentrations observed in the last two years at the Harris well are lower than concentrations observed since 1995, possibly indicating the beginning of a decreasing trend.

Sulfate

Sulfate concentrations in Mormon A Spring exhibit a significant increasing concentration trend since 1991 (Z = 2.61 with $\alpha = 0.01$) with a slope of approximately 28.4 mg/L per year. However, over the past seven years, sulfate concentrations appear to be stabilizing. Calculation of S from 1996 to 2002 resulted in a stable (not significant) concentration trend ($\alpha>0.1$). Harris well does not exhibit a significant concentration trend ($\alpha > 0.1$).

NW Pond Wells

In the Northwest Pond wells (TW-16 and TW-17 in the UBZ, and TW-18 in the LBZ), cadmium, chloride, molybdenum, and sulfate are stable or decreasing in all wells. Fluoride is decreasing in TW-16 and TW-17, but increasing in TW-18. Manganese is decreasing in TW-16 and stable in TW-18, but increasing in TW-17. Nitrate and selenium are stable in all three wells.

Cadmium

Cadmium concentrations in TW-16 show a statistically significant decreasing concentration trend ($\alpha = 0.01$) since 1991, with a slope of -0.01 mg/L per year. TW-17 and TW-18 show no significant concentration trend and, thus, have remained stable since 1991. TW-18 has remained stable at non-detected concentrations through this period.

Fluoride

Fluoride concentrations in TW-16 and TW-17 exhibit significant decreasing trends (Z = -2.75 and –2.42, respectively, with α = 0.01 and 0.05) with a slope of -0.13 and -0.06 mg/L per year since 1991. TW-18 shows a slight, but significant increasing concentration trend (Z = 2.42, $\alpha = 0.05$) with a slope of 0.02 mg/L per year since 1991.

Manganese

Manganese concentrations in TW-16 exhibit a significant decreasing trend ($Z = -2.63$ with $\alpha = 0.01$) since 1991, with a slope of approximately -0.006 mg/L per year. TW-17, however, shows a significant increasing concentration trend since 1991 ($Z = 3.83$ with $\alpha = 0.001$) with a slope of 0.08 mg/L per year.

Nitrate as N

In all three NW Pond wells (TW-16, TW-17, and TW-18), no significant concentration trends are exhibited ($\alpha > 0.1$ for all wells), with TW-17 and TW-18 containing mostly non-detected concentrations of nitrate as N.

Selenium

All three Northwest Pond wells (TW-16, TW-17, and TW-18) do not exhibit significant concentration trends ($\alpha > 0.1$ for all wells).

Chloride

Since 1991, TW-16 and TW-18 do not exhibit a significant concentration trend ($\alpha > 0.1$ for both wells). TW-17, however, exhibits a decreasing concentration trend ($Z = -3.13$ with $\alpha = 0.01$) with a slope of -8.0 mg/L per year.

Molybdenum

Since 1992, TW-16 and TW-17 show a significant decreasing concentration trend ($Z = -2.49$ and –2.66, respectively, with $\alpha = 0.05$ and 0.01, respectively), both with slopes of -0.002 mg/L per year. TW-18 has mainly non-detected concentrations of molybdenum since 1992, so no significant concentration is apparent.

Sulfate

Sulfate concentrations in TW-16 and TW-18 show no significant concentration trend ($\alpha > 0.1$) and appear to be statistically stable since 1991. TW-17, however, exhibits a significant decreasing concentration trend ($Z = -2.91$ with $\alpha = 0.01$) with a slope of approximately -5.5 mg/L per year.

Old Underflow Solids Pond Area Wells

In the old Underflow Solids Pond Area wells (TW-37 in the UBZ and TW-45 in the LBZ), cadmium, fluoride, manganese, nitrate, chloride, and molybdenum are stable or decreasing in all wells. Selenium and sulfate are stable in all four wells.

Cadmium

Cadmium concentrations in TW-37 show no significant concentration trend, thus they have remained stable since 1991. TW-45 exhibits a significant decreasing concentration trend ($Z = -2.41$ with $\alpha = 0.05$) since 1991, with a slope of -0.001 mg/L per year.

Fluoride

Well TW-45 show no significant concentration trends and, thus, have been statistically stable since 1991. TW-37 exhibits a significant decreasing concentration trend ($Z = -2.06$ with $\alpha = 0.05$) with a slope of approximately -0.32 mg/L per year.

Manganese

Well TW-37 in the Underflow Solids Pond Area show no significant concentration trends since 1991 ($\alpha \geq 0.1$). TW-45, however, exhibits a significant decreasing concentration trend ($Z = -2.54$ with $\alpha = 0.05$) with a slope of -0.02 mg/L per year since 1991.

Nitrate as N

Nitrate as N concentrations in TW-37 do not exhibit any significant concentration trends ($\alpha > 0.1$ for all three wells). TW-45 shows a significant decreasing concentration trend ($Z = -2.06$ with $\alpha = 0.05$) with a slope of approximately -0.02 mg/L per year.

Selenium

Selenium concentration trends in TW-37 and TW-45 do not exhibit any significant trends ($\alpha > 0.1$ for all wells).

Chloride

Since 1991, TW-37 and TW-45 exhibit significant decreasing concentration trends ($Z = -2.47$ and –3.85, respectively, with $\alpha = 0.05$ and 0.001, respectively) with slopes of approximately -3.5 and -3.0 mg/L per year, respectively.

Molybdenum

TW-37 and TW-45 both exhibit significant decreasing concentration trends since 1991 ($Z = -2.65$ and –2.73. respectively, with $\alpha = 0.01$ for both wells) with slopes of approximately -0.03 and -0.004 mg/L per year.

Sulfate

Since 1991, TW-37 and TW-45 do not show a significant concentration trend ($\alpha > 0.1$).

Old Hydroclarifier Wells

In the Old Hydroclarifier wells (TW-40 in the UBZ and TW-44 in the LBZ), cadmium, nitrate, molybdenum, and sulfate are stable in both wells. Fluoride and chloride are stable in TW-40, but increasing in TW-44. Manganese is decreasing in TW-40 and stable in TW-44. Selenium is increasing in TW-40, but stable in TW-44.

Cadmium

No significant concentration trends were computed for either TW-40 or TW-44 since 1991.

Fluoride

TW-40 shows no significant trend in fluoride concentrations since 1991. TW-44, however, exhibits a slight, but significant ($Z = 2.89$ with $\alpha = 0.01$) increase in fluoride concentrations with a slope of approximately 0.02 mg/L per year since 1991.

Manganese

Manganese concentrations in TW-40 show a significant decreasing trend ($Z = -2.96$ with $\alpha = 0.01$) with a slope of approximately -0.04 mg/L per year. TW-44 does not exhibit a significant decreasing trend ($\alpha > 0.1$)

Nitrate as N

TW-40 and TW-44 show no significant trends in nitrate as N concentrations since 1991 ($\alpha > 0.1$ for both wells).

Selenium

Selenium concentrations in TW-40 exhibit a significant increasing concentration trend ($Z = 2.65$ with $\alpha = 0.01$) with a slope of approximately 0.08 mg/L per year. TW-44 exhibits no significant concentration trend ($\alpha > 0.1$).

Chloride

Chloride concentrations in TW-40 do not exhibit a significant concentration trend ($\alpha > 0.1$). However, chloride concentrations in TW-44 exhibit a significant increasing concentration trend ($Z = 2.75$ with $\alpha = 0.01$) with a slope of 1.3 mg/L per year.

Molybdenum

Molybdenum concentrations in TW-40 do not exhibit a significant concentration trend ($\alpha > 0.1$). In TW-44, the 1992 concentration is a non-detected value, but with a higher detection limit that subsequent years, leading to a false "decreasing" concentration trend. When the 1992 value was removed from the statistical analysis, no significant concentration trend was exhibited ($\alpha > 0.1$).

Sulfate

Both TW-40 and TW-44 show no significant concentration trend for sulfate ($\alpha > 0.1$).

Springs South of Plant

In the springs south of the plant (Calf Spring and Homestead Spring), cadmium, manganese, nitrate, and molybdenum are stable in both springs. Fluoride, selenium, and chloride are stable in Calf Spring, but increasing in Homestead Spring. Sulfate is increasing in both springs.

Cadmium

Both Calf Spring and Homestead Spring show stable, non-detected concentrations of cadmium. No significant trend was computed for either spring.

Fluoride

Since 1991, Calf Spring shows no significant concentration trend for fluoride. Homestead Spring, however, exhibits a significant increasing fluoride concentration trend ($Z = 2.91$ with $\alpha = 0.01$) with a slope of 0.02 mg/L per year since 1991.

Manganese

Manganese concentrations in both Calf Spring and Homestead Spring show no significant concentration trends since 1991 ($\alpha > 0.1$).

Nitrate as N

Since 1991, nitrate as N concentrations show no significant concentration trends in either Calf or Homestead Springs ($\alpha > 0.1$ for both springs).

Selenium

Selenium concentrations in Calf Spring show no significant concentration trend ($\alpha > 0.1$). However, selenium in Homestead Spring exhibits a significant increasing concentration trend ($Z = 1.99$ with $\alpha = 0.05$) with a slope of approximately 0.002 mg/L per year since 1991.

Chloride

Chloride concentrations in Calf Spring show no significant concentration trend ($\alpha > 0.1$). However, chloride in Homestead Spring exhibits a significant increasing concentration trend ($Z = 2.47$ with $\alpha = 0.05$) with a slope of approximately 0.74 mg/L per year since 1991.

Molybdenum

Molybdenum concentrations in both Calf Spring and Homestead Spring show no significant concentration trend ($\alpha > 0.1$), with all data points in Homestead Spring being non-detected.

Sulfate

Both Calf Spring and Homestead Spring exhibit significant increasing concentration trends since 1991 ($Z = 2.80$ and 3.02, respectively, and $\alpha = 0.01$ for both) with slopes of -33.5 and -3.9 mg/L per year, respectively.

5.3.2.1.5 Summary of Statistical Analyses

All wells showed stable (no significant trend) or decreasing concentration trends since 1991/1992 with the following exceptions:

Cadmium

- None

Fluoride

- Production Wells: PW-02, PW-03, PW-04

- South Fenceline Wells: TW-35
- Southern Boundary Wells: TW-53, TW-55, TW-56
- Harris Well
- NW Pond Wells: TW-18
- Old Hydroclarifier Wells: TW-44
- Springs South of Plant: Homestead Spring

Manganese

- NW Pond Wells: TW-17

Nitrate as N

- None

Selenium

- Mormon A Spring
- Old Hydroclarifier Wells: TW-40
- Springs South of Plant: Homestead Spring

Chloride

- Old Hydroclarifier Wells: TW-44
- Springs South of Plant: Homestead Spring

Molybdenum

- Southern Boundary Wells: TW-53
- Harris Well

Sulfate

- Mormon A Spring
- Springs South of Plant: Calf Spring, Homestead Spring

5.4 Evaluation of Extent of Constituent Plumes

Isopleth maps for the constituents of concern and additional constituents were created from the June 2002 data to evaluate changes, if any, in the extent of the constituent plumes. The 2002 plumes are compared to those presented in the Phase II RI (Golder 1995) based on 1993 water quality data. The plumes based on the 1993 data are shown on Figures 7a through 14a. The plumes based on the 2002 water quality data are presented on Figures 7b through 14b.

5.4.1 Cadmium in Upper Basalt Zone

Visual comparison of the cadmium plume in UBZ-4 shows that the plume is decreasing in concentration but increasing slightly in areal extent (Figures 7a and 7b). Results of statistical analyses support visual observations, with the production wells downgradient of the old sources exhibiting decreasing concentration trends, with present concentrations less than the remediation goals (RGs) in PW-01 and PW-02, and decreasing concentrations in PW-03. TW-40 in the Old Hydroclarifier area shows a possibly decreasing, but statistically insignificant, concentration trend.

The cadmium plume in UBZ-2 has extended beyond the plant fenceline since 1993. Concentrations in the source area appear to be relatively stable in extent and concentration profile. This is supported by statistical analyses that show wells near the old Underflow Solids Ponds and the South Fenceline areas having stable or insignificant concentration trends.

5.4.2 Fluoride in Upper Basalt Zone

The 2002 fluoride plume in UBZ-4 appears to be relatively similar to the 1993 plume. Concentrations in the old source area at the Old Hydroclarifier appear to be stable, supported by statistical analysis at TW-40. Concentrations downgradient of the old source area appear to be increasing due to capture by the plant wells, while concentrations upgradient of the old source are decreasing. These observations are supported by statistical analyses at the production wells (increasing trends at PW-01, PW-02, and PW-03) and Northwest Pond area (decreasing trends at TW-16 and TW-17) suggesting that natural attenuation and containment by pumping are performing as expected.

In UBZ-2, the areal extent of the fluoride plume is relatively stable, with decreasing concentrations. Concentrations in the old source area at the old UFS Pond are decreasing, consistent with natural attenuation and supported by statistical analysis at TW-37 showing a decreasing concentration trend. Downgradient concentrations suggest migration of the plume with groundwater flow, shown by stable or insignificant concentration trends at the South Fenceline. Increasing concentration trends at the Southern Boundary suggest passage of the fluoride plume into this area, consistent with natural attenuation. Based on these observations, natural attenuation appears to be performing as expected.

5.4.3 Manganese in Upper Basalt Zone

The UBZ-4 manganese plume in the Old Hydroclarifier area has significantly decreased in areal extent and concentration profile (Figures 9a and 9b) as concentrations in the Old Hydroclarifier wells and plant wells have decreased to non-detect levels. This is supported by statistical analysis at TW-40 showing a decreasing concentration trend. However, the old source at the Northwest Ponds area appears to continue to be providing manganese to groundwater, as concentrations in this plume appear to be increasing (supported by statistical analysis at TW-17 showing an increasing concentration trend).

The manganese plume in UBZ-2 appears to be stable, with concentrations in the old source area (old Underflow Solids Ponds area) showing stable trends (TW-37) and downgradient concentrations showing stable trends (based on statistical analyses at TW-22 and TW-24, as well as at the South

Fenceline and Southern Boundary wells). These observations are consistent with the expectations of retardation of manganese in the UBZ.

5.4.4 Nitrate as N in Upper Basalt Zone

The nitrate plume in the UBZ-4 zone associated with the Northwest Pond and Old Hydroclarifier has decreased in areal extent and in concentration (Figures 10a and 10b). This is consistent with the continued containment by the plant production wells. The nitrate plume on the east side of the plant in the UBZ-3 and UBZ-4 zones has decreased in areal extent and concentration as the plume from the Kerr-McGee plant passes through the area.

The nitrate plume in the UBZ-2 zone has decreased in areal extent and concentration, consistent with a conservative constituent migrating through the UBZ-2 zone. This is supported by statistical analyses showing stable or decreasing nitrate concentrations in the old UFS pond well (TW-37), fence line wells, and southern boundary wells.

5.4.5 Selenium in Upper Basalt Zone

In UBZ-4, the selenium plume is increasing slightly in areal extent downgradient of the source area, and decreasing in areal extent upgradient of the Old Hydroclarifier are as a result of capture by the plant production wells. Concentrations in the source area at the Old Hydroclarifier appear to be increasing, supported by statistical analysis at TW-40 showing an increasing concentration trend (Figures 11 and 11a).

In UBZ-2, the selenium plume is generally stable and concentrations in the old UFS pond source area are also stable, supported by statistical analysis at TW-37 showing a stable or statistically insignificant concentration trend. Downgradient concentrations are stable or decreasing (supported by statistical analyses at the South Fenceline and Southern Boundary wells), with the exception of the springs south of the plant, Mormon A and Homestead Springs, which exhibit increasing concentration trends suggesting transport of the plume into these areas. These observations are consistent with natural attenuation.

5.4.6 Chloride in Upper Basalt Zone

The extent of the chloride plumes in UBZ-4 appears to be relatively stable (Figures 12 and 12a), with concentrations staying stable or decreasing as supported by statistical analyses, consistent with capture by the plant production wells.

The extent of the chloride plume in the UBZ-2 appears to be decreasing in the source area, consistent with natural attenuation and confirmed by statistical analysis of chloride concentrations in TW-37 at the old Underflow Solids Pond. The plume extent at the southern boundary wells appears to be stable, with the chloride concentration decreasing in these wells, consistent with natural attenuation.

5.4.7 Molybdenum In Upper Basalt Zone

The areal extent of the molybdenum plume in UBZ-4 is stable. Molybdenum concentrations in the UBZ-4 plume are stable or decreasing (Figures 13a and 13b), consistent with the statistical analyses. The molybdenum plume inside the plant boundary adjacent to the Kerr-McGee site in UBZ-4 (TW-33) and in UBZ-3 downgradient of TW-12 and TW-56 is decreasing in concentration and areal extent, consistent with the migration of the molybdenum plume from Kerr-McGee operations onto the Monsanto site.

The molybdenum plume extent in UBZ-2 is generally stable, and concentrations in the source area (old Underflow Solids Pond) and plume are either stable or decreasing, with the exception of TW-53 in the Southern Boundary area and in Harris well.

5.4.8 Sulfate in Upper Basalt Zone

Visual comparison of the sulfate plumes in 1993 and 2002 suggests that the areal extents of the plumes in UBZ-2 and UBZ-4 have remained stable (Figures 14a and 14b). Statistical analyses of concentrations support this observation, with most points exhibiting stable or decreasing trends consistent with natural attenuation in UBZ-2 and capture by the plant production wells in UBZ-4. The plume on the east side of the plant originating from Kerr-McGee has decreased in areal extent and concentration as a result of migration of the plume with groundwater flow. The springs south of the plant (Mormon A, Calf, and Homestead), however, exhibit increasing concentration trends, suggesting movement of the plume downgradient, consistent with natural attenuation.

5.5 Evaluation of Groundwater Modeling Projections

5.5.1 Original Solute Transport Model

A groundwater solute transport model was developed as part of the Phase II RI for the Monsanto plant to predict the fate and transport of constituents in groundwater in the vicinity of the plant (Golder 1993; Golder 1995). This model (termed the "RI Model") is described in detail in Section 2.3 and Appendix L-2 of the Phase II RI.

The RI Model was developed for the old Underflow Solids Ponds area, the portion of the plant west of the Monsanto Fault where there is potential for off-site transport of constituents in groundwater (UBZ-2), as this plume is not contained by the plant pumping wells. The RI Model projected concentrations over time at three endpoints south of the plant (the southern plant boundary, the estimated discharge point of the plume into Soda Creek, and the estimated discharge point of the plume into Bear River). Projections were calculated for constituent transport for a period of over 100 years. Although plumes are present in UBZ-4, originating from the Old Hydroclarifier and the Northwest Pond, modeling was not conducted for this area because pumping in the production wells contains the plumes in UBZ-4 and prevents offsite migration of the constituents.

The following section summarizes the RI Model.

5.5.1.1 RI MODEL

The RI Model was developed for the UBZ-2 area (old Underflow Solids Pond area) to evaluate the concentration of the constituents of concern at locations downgradient of the plant (Golder 1993; Golder 1995). The model was developed using a modified two-dimensional analytical equation based on the mass balance for a non-decaying dissolved solute (Dominico 1987). The model incorporates solute transport by advection and dispersion. The model also accounts for retardation of the solute when appropriate. The old UFS ponds were assumed to have a constant source concentration while the ponds were in operation, followed by a declining source after closure. The Dominico model does not account for a decaying source term. Superposition techniques were used account for the decaying source concentrations following closure of the ponds.

The aquifer hydraulic properties used in the RI model were based on a regional groundwater flow model that was constructed for the Monsanto site and surrounding area. The model used the following aquifer properties:

- Hydraulic conductivity: 400 ft/d;
- Porosity: 30%; and
- Hydraulic gradient: 0.0075 ft/ft.

Using these parameters, the groundwater velocity is 10 ft/d.

The source constituent concentrations while the old UFS ponds were in use were not known. The source term concentrations for the time when the ponds were in use were estimated using an exponential decay function based on the observed decline in constituent concentrations in monitoring well TW-37 following pond closure (Golder 1993). The predicted source concentrations and rate of decay are summarized on Table 5. Fluoride was modeled using a constant source concentration following closure of the ponds because fluoride concentrations following closure of the pond were relatively stable following an initial sharp decline.

The RI Model was used to evaluate concentrations of the constituents of concern at the following locations:

- Approximately 500 feet south of the plant fence line, at the approximate location of TW-54 and TW-55, or about 5,000 feet south of the old UFS ponds;
- Approximately 8,500 feet south of the old UFS ponds, at the approximate discharge point of the plume to Soda Creek in the event the plume were to follow a pathway to Soda Creek; and
- Approximately 18,500 feet south of the old UFS ponds, at the approximate discharge location of the plume to the Bear River if the plume followed a pathway to the Bear River.

The RI Model predicted that:

- Concentrations for conservative constituents such as chloride at the southern boundary wells would rise rapidly at the onset of pond usage in 1964, reaching a plateau from 1968 to 1986, while the ponds were in service. The peak concentrations for conservative constituents would occur about four years later at Soda Creek and about eight years later at the Bear River;
- Concentrations for conservative constituents would start to decline in 1986 following closure of the ponds. Concentrations of conservative constituents at the fence line would decline to background levels over a period of 20 to 30 years following closure of the ponds. The start of the decline occurs about four and eight years later, respectively, at Soda Creek and the Bear River;
- Concentrations for cadmium, the most highly retarded constituent, would reach a maximum concentration at the fenceline in about 1994. The maximum cadmium concentrations would occur at Soda Creek and the Bear River in about 2004 and 2034, respectively.

Since the modeling was completed, approximately ten years of additional groundwater monitoring data are available to compare with the model results. These comparisons are included in the next section.

Comparison of RI Model Results and Water Quality Data

This section presents a comparison of the RI Model results and the groundwater quality data for chloride (a conservative plume tracer) and the constituents of concern collected at the site over the past ten years. Plots of the predicted and observed concentrations at the source well (TW-37), plant fence line wells (TW-20 and TW-39), and the southern boundary wells (TW-54 and TW-55) are included in Attachment C. Table 6 summarizes the predicted and observed concentrations in 2002.

5.5.1.2 Chloride

The RI Model assumed a chloride source concentration of 364 mg/L while the ponds were in operation, plus a background chloride concentration of 16 mg/L. The decay function used in the RI Model for chloride in TW-37 matches well with the actual chloride measurements made since 1993 (Attachment C, Figure C-1).

However, the RI Model overpredicts the chloride concentration at the plant fence line wells (TW-20 and TW-39) between 1985 and 1990 and then underpredicts the chloride concentrations between 1990 and 2002 (Figure C-2). The model predicts a concentration of about 25 mg/L in 2002. Observed concentrations in TW-20 and TW-37 were about 100 mg/L. The RI Model predicts the chloride concentrations well at TW-55 and underpredicts the concentration at TW-54.

5.5.1.3 Fluoride

The RI Model assumed a constant source concentration for fluoride of 40 mg/L while the old UFS ponds were in service (1964 to 1984) and a constant concentration of 17 mg/L after 1984, when the ponds were taken out of service. The observed concentrations at the underflow solids ponds (TW-37) ranged from about 14 to 16 mg/L between about 1992 and 1998 (Attachment C, Figure C-4). In 1998, fluoride concentrations in TW-37 decreased to about 12 mg/L, and have remained relatively constant since. Therefore, the RI Model overpredicts the concentrations at the source. Fluoride concentrations at the source area are controlled by the solubility of calcium fluorite (a secondary source) in the aquifer below the old UFS ponds.

The RI model overpredicts the fluoride concentrations at the plant fence line and at the southern boundary as a result of the constant source concentration of 17 mg/L following pond closure (Figures C-5 and C-6). At the downgradient locations, the RI Model predicts a fluoride concentration of 17 mg/L. The fluoride concentration in the fence line wells is currently about 2 to 4 mg/L. In the southern boundary wells, the fluoride concentration is currently about 0.6 to 3 mg/L (Table 6).

5.5.1.4 Nitrate

The RI Model assumed a nitrate source concentration of 11.9 mg/L while the old UFS ponds were in service and background concentration of 0.96 mg/L. The observed concentrations at the old UFS ponds (TW-37) ranged from about 25 mg/L to 6 mg/L between 1985 and 1989 (Figure C-7). Nitrate concentrations ranged from about 6 to 10 mg/L after 1989. The RI Model underpredicts the nitrate concentration at the source. This is likely due to underestimation of the background nitrate concentrations, which are about 2 mg/L in TW-57. Concentrations of about 4 mg/L have been observed in other wells upgradient of the plant, such as TW-29 and PW-04.

The RI Model over-predicts the nitrate concentration at the plant fence line wells (TW-20 and TW-39) prior to 1990 and under-predicts the nitrate concentrations following that time similar to the chloride history (Figure C-8). The model predicts a concentration of about 2 mg/L; the observed concentrations are presently about 4 to 7 mg/L (TW-20 and TW-39). The model-predicted nitrate concentrations at the southern boundary wells (TW-54 and TW-55) and the observed concentrations are both about 2 mg/L (Figure C-9).

5.5.1.5 Selenium

The RI Model assumed a selenium concentration of 1.51 mg/L while the old UFS ponds were in service. Groundwater quality data for selenium at the old UFS ponds (TW-37) prior to 1991 was found to be in error (Golder 1995). The model slightly underpredicts the present concentration at the old UFS ponds at about 0.1 mg/L, while the observed concentrations are about 0.4 mg/L (Figure C-10).

In the plant fence line wells (TW-20 and TW-39), the present observed selenium concentrations are about 0.1 mg/L (Figure C-11), ignoring the abberant measurement from TW-20 in 2002. The RI Model slightly overpredicts the concentration at about 0.15 mg/L. The model also overpredicts the present selenium concentration at the southern boundary wells (TW-54 and TW-55), where the observed selenium concentrations are about 0.02 to 0.1 mg/L (Figure C-12). The RI Model predicts concentrations of about 0.15 mg/L.

5.5.1.6 Manganese

The RI Model used a source concentration of 4.95 mg/L while the old UFS ponds were in service. Manganese concentrations in TW-37 have declined since the closure of the UFS ponds (Figure C-13). Since about 1995, manganese concentrations have been fairly stable in TW-37 at between about 0.5 and 1 mg/L. The RI Model predicts a present manganese source concentration of about 0.2 mg/L, underpredicting the observed concentrations. This may be due to solubility control of manganese by manganese oxyhydroxides in the aquifer or the redox conditions in the aquifer.

Manganese concentrations at the plant fence line wells (TW-20 and TW-39) are presently low (generally at the analytical detection limit for manganese of 0.001 to 0.06 mg/L) (Figure C-14). Similar concentrations are observed at the southern boundary wells (TW-54 and TW-55) (Figure C-15). The RI Model predicts the present manganese concentration to be about 0.004 mg/L at the plant fence line wells and southern boundary wells.

5.5.1.7 Cadmium

The RI Model used a source concentration of 1.41 mg/L for cadmium while the ponds were in service. Cadmium concentrations in TW-37 decreased from 1985 through about 1991 (Figure C-16). Since 1991, cadmium concentrations have been relatively stable at about 0.4 to 0.5 mg/L. This suggests that cadmium concentrations are controlled by the solubility of cadmium minerals such as otavite (cadmium carbonate). The RI Model predicts a present cadmium source concentration of about 0.8 mg/L (assuming no solubility control). Therefore, if no solubility control is assumed, the RI model overpredicts the cadmium concentration at TW-37. The RI Model was also was run assuming solubility control of cadmium. This model predicts a present cadmium concentration of less than 0.005 mg/L, underpredicting the actual concentration.

At the plant fence line wells (TW-20 and TW-39), the RI Model predicts a present cadmium concentration of about 0.06 mg/L with no solubility control (Figure C-17). The present observed concentration is between about 0.005 and 0.015 mg/L. At the southern boundary wells (TW-54 and TW-55), the present cadmium concentrations are about 0.001 to 0.002 mg/L (Figure C-18). The RI

Model predicts a present concentration of about 0.7 mg/L with no solubility control. Therefore, the model overpredicts cadmium concentrations assuming no solubility control.

If solubility control of cadmium is assumed, the RI Model predicts concentrations at the plant fence line wells and southern boundary wells of about 0.002 mg/L.

5.5.2 Revised Solute Transport Model

As described above, the selected remedy for groundwater at the Monsanto plant, per the ROD, is natural attenuation until constituent concentrations are at or below remediation goals. One of the elements of the five-year review, per the ROD, is to compare modeled concentrations against measured groundwater concentrations to determine whether there is a significant difference. If there is a significant difference, the ROD states that the model and the need for additional groundwater remedial actions should be re-evaluated.

The solute transport model (RI Model) used as the basis for the ROD was developed using groundwater monitoring data over a period of five years (1991 to 1995). Due to continued groundwater monitoring at the Monsanto plant, there are groundwater and outfall data available for a period of twelve years (1991 to 2002).

A revised solute transport model ("GoldSim Model") was developed for this five-year review to provide a more accurate projection of groundwater concentrations in the UBZ-2 zone south of the Monsanto plant. The RI Model was revised to account for the observed changes in groundwater quality since the contaminant transport model was developed in 1993 and re-interpretation of the source area history and groundwater quality data from the monitoring wells. The groundwater quality changes result from decreases in constituent concentrations since 1993 and stabilization of concentrations for selected constituents such as fluoride, cadmium, and magnesium. The additional monitoring data and re-interpretation of the source areas also provided information to refine the groundwater velocities in the vicinity of the old UFS Ponds. The source concentrations were also revised based on the additional groundwater quality data collected since 1993.

The RI Model was revised using GoldSim (2002), a graphical, probabilistic modeling tool. GoldSim was used to evaluate the concentrations of the constituents of concern at the plant fence line (Wells TW-20 and TW-39), at the southern boundary wells (TW-54 and TW-55), at Mormon A Spring and the Harris Well, and at the downgradient discharge location to Soda Creek. A GoldSim model was first constructed to verify the results of the analytical modeling conducted in 1993. The GoldSim model uses the same input parameters as the earlier model to simulate the results at the southern boundary wells. The concentrations predicted by the GoldSim model are plotted along with the concentrations predicted by the 1993 model and the constituent concentrations at the southern boundary wells (Attachment C, Figures C-3, C-6, C-9, C-12, C-15, and C-18). The GoldSim model replicated the results of the earlier modeling well. Therefore, GoldSim was used to construct a new model incorporating the data collected since 1993 and the revised interpretations of the source area histories and aquifer hydraulic properties.

Evaluation of Data Collected Since 1993

This section describes the evaluation of the data collected since 1993 and the revised interpretations of the source concentrations and source history for the constituents of concern, plume history at downgradient wells, and aquifer properties.

5.5.2.1 Source Concentrations and History

About ten years of additional groundwater quality data are available for the old UFS ponds (Well TW-37) and downgradient wells. The additional groundwater monitoring indicates the following at the source area:

- The source area concentrations for the constituents of concern have declined since the ponds were closed;
- Concentrations of chloride and nitrate have declined to near background levels; and
- Concentrations of manganese, fluoride, selenium, and cadmium have declined since the ponds were closed and have stabilized indicating solubility control of the constituent concentrations.

The source area concentrations, rate of decline, and stabilization were also revised based on the time history of the constituents of concern. The concentrations and rate of decline used in the old and revised models are summarized on Table 7. Table 7 also includes the stabilized source concentrations used in the Goldsim model.

5.5.2.2 Aquifer Properties

The aquifer properties (hydraulic conductivity and hydraulic gradient) used in the RI Model were based on the results of a regional groundwater flow model constructed of the Monsanto site and surrounding area. The results of the regional model indicated the hydraulic conductivity of the basalt aquifer was 400 ft/d and the hydraulic gradient was about 0.0075 ft/ft. Assuming a porosity of 0.3, the groundwater velocity was determined to be 10 ft/d.

The hydraulic conductivity and gradient were re-evaluated using data collected since 1993 and the observed passage of the core of the chloride plume from the old UFS ponds at the fence line and southern boundary wells. The hydraulic gradient was estimated to be 0.0065 ft/ft, based on groundwater level measurements made in May 2002 in TW-57, TW-37, TW-20, and TW-54 (Golder 2002).

The hydraulic conductivity was estimated based on the arrival of the peak concentrations of chloride at TW-20 and TW-54. Using the arrival of peak chloride concentrations at these wells (1992 in TW-20 and 1994 in TW-54) and a distance of 900 feet between these wells, a groundwater velocity of 1.2 ft/d is determined. Assuming a hydraulic gradient of 0.0065 and a porosity of 0.3, the hydraulic conductivity is estimated to be 55 ft/d. The hydraulic conductivity was calibrated in the GoldSim model to match the arrival of the chloride plume at the fenceline and southern boundary wells. The best match was obtained using a hydraulic conductivity of 40 ft/d. The groundwater velocity, using the revised hydraulic conductivity and gradient, and assuming a porosity of 0.3, is about 1 ft/d, rather than 10 ft/d used in the RI Model.

5.5.2.3 Old UFS Pond Source History

The old UFS source history was re-interpreted based on the observed chloride concentration history at the fence line wells and at the southern boundary wells. Based on the observed chloride concentration history of downgradient wells and observations during the GoldSim model calibration process and the revised aquifer hydraulic properties, it appears that historical releases from the old UFS ponds occurred over an approximate five year period, rather than over the life of the ponds, which was about 20 years. The revised source area history for the old UFS ponds is summarized as:

- 1964 to 1979 No releases to groundwater flow system
- 1979 to 1984 Constant mass load release to groundwater flow system
- After 1984 Ponds taken out of service, no releases. Concentrations decrease exponentially.

The old and revised source area histories are shown on Figure 15.

Distribution Coefficients

The distribution coefficients (Kd) for manganese and cadmium were re-evaluated as the manganese plume from the UFS ponds has not been observed at the downgradient wells. The distribution coefficient for manganese used in the RI Model was 0.2. This is the minimum value for manganese distribution coefficients reported in the literature, which includes 16.5 ml/g (Batelle 1989) and a range of 0.2 to 10,000 ml/g (Dragun 1988). No site-specific manganese distribution coefficient data are available. The value of 10 ml/g chosen is therefore conservative and reasonable for the Monsanto site. The manganese distribution coefficient cannot be confirmed until the plume arrives at the downgradient wells.

The RI model used a distribution coefficient of 1.25 ml/g for cadmium. The cadmium plume from the old UFS Ponds has not been observed at the downgradient wells. No site-specific cadmium distribution coefficient data are available. Literature values for distribution coefficients include 14.9 ml/g (Batelle 1989), a range of 1.3 to 27 ml/g (Dragun 1988), and a range of 8 to 4,000 ml/g (EPA 1999). The value of 1.25 ml/g used in the RI Model is therefore a minimum value. The value of 10 ml/g chosen is therefore conservative and reasonable for the Monsanto site. Cadmium was modeled with a distribution coefficient of 10 ml/g.

The other constituents of concern (selenium, nitrate, and fluorite) are transported conservatively at the site. Therefore, no distribution coefficients were applied to these constituents.

GoldSim Input Parameters

5.5.2.4 Constituent Loads

The source concentrations when the old UFS ponds were active were estimated using the observed concentrations at TW-37 and the estimated decay rates. The source concentrations and decay rate used in the RI Model, and the revised source concentrations and decay rates used in the Goldsim Model are summarized on Table 7.

Speciation modeling conducted as part of the RI using groundwater quality data collected at TW-37 indicated that the concentrations of cadmium and fluoride may be controlled by the solubility of cadmium or fluoride minerals in the aquifer such as otavite (cadmium carbonate) or fluorite that originated from seepage from the old UFS ponds. The concentration of manganese may also be controlled by the solubility of manganese oxides or by redox conditions in the aquifer. Selenium concentrations also appear to have reached quasi-steady state. Therefore, to account for solubility control for these constituents, a minimum constant concentration was assumed following exponential decline to that concentration (Figure 15). The minimum concentrations were based on the observed quasi-steady state concentrations in TW-37 and are as follows:

- Cadmium: 0.35 mg/L;
- Manganese: 0.7 mg/L;
- Fluoride: 6 mg/L; and
- Selenium: 0.05 mg/L.

Nitrate (6 mg/L) and chloride (16 mg/L) concentrations have also reached quasi-steady state conditions in TW-37. This likely reflects the background concentration of nitrate and chloride in the aquifer. Nitrate concentrations in well TW-57, located offsite and upgradient of the UFS ponds area, are about 2 mg/L. Higher nitrate concentrations of about 4 to 5 mg/L have been observed at other wells upgradient of the plant site (TW-48 and PW-04). A background concentration of 4 mg/L was used for nitrate, and a background concentration of 16 mg/L was used for chloride.

5.5.2.5 Hydrogeologic Data

The upper basalt zone aquifer at the UFS pond site was assumed to be 30 feet thick, with a hydraulic conductivity of 40 ft/d and a hydraulic gradient of 0.0065 ft/ft. The porosity of the aquifer was assumed to be 0.3 (Table 8). The dispersivity was estimated based on published information (Appelo and Postma 1994). The longitudinal dispersivity was estimated to be 10 percent of the flowpath length. The vertical and horizontal transverse dispersivities were assumed to be equal to 1% and 0.1% of the longitudinal dispersivity, respectively, considering the relatively narrow aquifer zones resulting from faulting and the thin interflow zones.

Flow in the aquifer downgradient of the old UFS Ponds was simulated as pipe flow in GoldSim. The GoldSim model setup and old UFS Pond source concentrations and mass loading history equations are included in Attachment D.

5.5.3 Results of GoldSim Modeling

The results of the GoldSim modeling are included in Attachment D as plots of the observed constituent concentrations and the model-predicted values. The model predicted concentrations and the actual concentrations from the 2002 sampling event for the constituents of concern are tabulated on Table 9. The results are discussed below.

5.5.3.1 Chloride

Chloride has not been identified as a constituent of concern at the Monsanto site. Chloride is conservative in the site groundwater meaning it travels at the average linear groundwater velocity. Chloride concentrations in the source area and downgradient wells were used to calibrate the hydraulic properties of the model and the source history.

It is estimated that the revised chloride source concentration while the old UFS ponds were in operation was 400 mg/L (Figure D-1). The GoldSim model predicts the chloride plume peak reached the plant fence line between about 1988 and 1992 (Figure D-3). The chloride peak in these wells occurred between about 1989 and 1991. The present chloride concentration is predicted to be about 60 mg/L, slightly lower than the observed concentrations of about 100 mg/L. At the southern boundary wells, the GoldSim model predicts that the chloride plume peak reaches wells TW-54 and TW-55 between about 1990 and 1994 (Figure D-4). Sampling started in these wells in 1992. Chloride concentrations were highest in these wells between 1992 and 1994. The present chloride concentration at these wells is about 40 to 100 mg/L. The model predicts a present concentration of about 60 mg/L.

The GoldSim model predicts the chloride plume peak to arrive at the Harris Well and Mormon A Spring between about 1993 and 1995 (Figure D-5). The chloride peak was observed in Mormon A Spring between about 1992 and 1995. An earlier peak was observed between about 1980 and 1984 that is likely not related to the old UFS ponds. The chloride peak occurred between about 1994 and 1996 in the Harris Well. The present chloride concentration at these locations is about 100 mg/L; the GoldSim model predicts a concentration of about 60 mg/L.

The GoldSim model predicts the chloride plume peak to reach a point 10,000 feet downstream from the old UFS Ponds between about 1997 and 1999 (Figure D-6). This point represents the downgradient discharge location to Soda Creek. The peak of the chloride plume was observed at Homestead Spring between about 1998 and 2000. The present concentration there is about 25 mg/L, lower than the predicted concentration of 50 mg/L.

The GoldSim model predicts the chloride concentrations and time history at the point of compliance wells downgradient of the old UFS ponds well. The model predicts that the chloride concentrations at the downgradient wells will continue to decline, reaching background concentrations of 16 mg/L in the fence line wells in about 2020 and in the Southern Boundary Wells in 2023. The GoldSim model does not match the arrival of a chloride plume at Mormon A Spring and the Harris Well in the mid 19080's. It is believed that this plume represents seepage from the former sewage evaporation ponds and not the plume from the old UFS ponds.

5.5.3.2 Fluoride

Fluoride is a constituent of concern at the Monsanto site with a remediation goal of 4 mg/L. Fluoride is transported conservatively in groundwater at the Monsanto site. The source concentration used for fluoride is shown on Figure D-7. It is estimated the fluoride concentration while the old UFS Ponds were in operation was 31 mg/L.

The GoldSim model predicts the fluoride plume peak reached the fenceline wells between 1988 and 1992, with peak concentrations of about 11 to 12 mg/L (Figure D-9). The peak fluoride concentrations observed at this time were about 6 to 8 mg/L, however, the fenceline wells were not sampled for fluoride between the end of 1988 and the end of 1991. The GoldSim model predicts fluoride concentrations will be below the remediation goal of 4 mg/L by 2006 at the fence line wells. Fluoride concentrations are presently lower than the remediation goal at about 2 to 3.5 mg/L in wells TW-20 and TW-39.

The GoldSim model predicts a fluoride plume peak concentration of about 8 mg/L at the southern boundary wells (Figure D-10) and at the Harris Well and Mormon Spring (Figure D-11) between about 1990 and 1994. Observed concentrations were about 2 to 4 mg/L in Mormon A Spring and about 1 mg/L in the Harris Well. Fluoride concentrations at these locations are predicted to be below the remediation goal in 2002. The present fluoride concentration at these locations is about 1 to 3 mg/L.

The GoldSim model predicts fluoride concentrations to reach a maximum of about 3 mg/L, below the remediation goal, between 1997 and 1999 at the downstream discharge point (Figure D-12). The present concentration at the discharge location (Homestead Spring) is less than 1 mg/L, lower than the predicted value of 2.4 mg/L.

The GoldSim model predicts the fluoride concentrations and time history at the point of compliance wells downgradient of the old UFS ponds well. The model predicts that the fluoride concentrations at the downgradient wells will continue to decline, reaching steady-state concentrations in the fence line wells in about 2020 and in the Southern Boundary Wells in 2023. The steady state concentrations are below the remedial goals and reflect the constant source concentration from dissolution of fluoride minerals in the aquifer mass. The GoldSim model does not match the arrival of a fluoride plume at Mormon A Spring and the Harris Well that occurred in the mid 1980's. It is believed that this plume represents seepage from the former sewage evaporation ponds and not the plume from the old UFS ponds.

5.5.3.3 Nitrate

The remediation goal for nitrate is 10 mg/L (as nitrogen). Nitrate is transported conservatively at the Monsanto site. Nitrate is also present at background levels of about 2 to 4 mg/L in the site groundwater.

It is estimated that the old UFS ponds source concentration for nitrate while the ponds were in operation was 13.4 mg/L (including a background concentration of 4 mg/L). The source concentration history used for nitrate is shown on Figure D-13. The GoldSim model predicts the nitrate plume peak to arrive at the fence line wells between about 1988 and 1992. The GoldSim model predicts nitrate to reach concentrations of about 8 mg/L at that time (Figure D-15). The maximum concentration at the fence line wells is less than the remediation goal at all times. The present nitrate concentration at the fence line wells is about 4 to 7 mg/L, similar to the predicted value of 6 mg/L. At the southern boundary wells (Figure D-16) and the Harris Well and Mormon Spring (Figure D-17), the GoldSim model predicts nitrate concentrations reach a maximum between 1990 and 1994. Maximum concentrations at these locations are about 5 to 7 mg/L, below the remediation goal or 10 mg/L (as N). The present nitrate concentrations at these wells is about 1 to 6 mg/L, in comparison to the predicted value of about 6 mg/L

At the downstream discharge location, the GoldSim model predicts nitrate concentrations to peak at about 5 mg/L between 1997 and 1999 (Figure D-18). The present concentration at Homestead Spring is about 7 mg/L. The GoldSim model predicts a concentration of about 5 mg/L.

The GoldSim model predicts the nitrate concentrations and time history at the point of compliance wells downgradient of the old UFS ponds well. The model predicts that the nitrate concentrations at the downgradient wells will continue to decline, reaching background concentrations of 4 mg/L in the fence line wells in about 2020 and in the Southern Boundary Wells in 2023. The GoldSim model does not match the arrival of a nitrate plume at Mormon A Spring and the Harris Well in the mid 1980's. It is believed that this plume represents seepage from the former sewage evaporation ponds and not the plume from the old UFS ponds.

5.5.3.4 Selenium

The remediation goal for selenium is 0.05 mg/L. The old UFS pond source concentration is shown on Figure D-19. Selenium data prior to 1991 was found to not meet QA requirements. Selenium concentrations declined from a projected maximum of 1.4 mg/L following closure of the old UFS ponds. Based on the present observed concentration of selenium in TW-37 and the observed concentrations in the downgradient wells at the fence line and southern boundary, the selenium concentration at the source area is projected to reach a quasi-steady state concentration of about 0.05 mg/L.

The GoldSim model predicts the selenium concentration at the plant fence line wells reaches a maximum of about 0.6 mg/L between about 1988 and 1992 (Figure D-21). The concentrations decrease after 1992 and are predicted to decrease below the remediation goal of 0.05 mg/L by 2020. The present selenium concentration at the fence line wells is about 0.1 to 0.3 mg/L, while the GoldSim model predicts a concentration of about 0.28 mg/L.

The GoldSim model predicts selenium concentrations reach a maximum concentration of about 0.45 mg/L at the south boundary wells (Figure D-22) between 1990 and 1994. The selenium concentration decreases after 1994, and is predicted to fall below the remedial goal by 2020. The present selenium concentration at the southern boundary wells is about 0.02 to 0.1 mg/L. In comparison, the GoldSim model predicts a present concentration of about 0.28 mg/L. The GoldSim model predicts the peak of the selenium plume at the Harris Well and Mormon Springs (Figure D-23) between about 1991 and 1994. The predicted concentration at that time is about 0.35 mg/L. The present selenium concentration at these locations ranges from 0.02 mg/L to 0.34 mg/L, while the GoldSim model predicts a concentration of about 0.25 mg/L.

At the discharge to Soda Creek, the GoldSim model predicts the peak of the selenium plume to arrive between about 1997 and 1999, with a maximum concentration of about 0.17 mg/L. The present selenium concentration at Homestead Spring is about 0.02 mg/L. The GoldSim model predicts a present concentration of about 0.16 mg/L (D-24).

The GoldSim model predicts the selenium concentrations and time history at the point of compliance wells downgradient of the old UFS ponds fairly well. The model overpredicts the downgradient concentrations. This is likely due to the lack of selenium groundwater quality data at the old UFS ponds until 1991, complicating the interpretation of the source history for selenium.

5.5.3.5 Manganese

The remediation goal for manganese is 0.18 mg/L. The old UFS pond source concentration history for manganese is shown on Figure D-25. It is estimated that the manganese source concentration declined from a maximum of 4.95 mg/L to a quasi-steady state concentration of about 0.7 mg/L. Manganese was modeled with a distribution coefficient of 10 ml/g. In comparison, the RI model used a distribution coefficient of 0.2 ml/g for manganese.

The GoldSim model was run for 200 years, from 1964 to 2164. The model predicts that the peak of the manganese plume will not arrive at the fence line by the end of the model simulation in 2164. The predicted concentration at that time is about 0.003 mg/L, well below the remediation goal of 0.18 mg/L. The GoldSim model predicts the present manganese concentration at the plant fence line to be less than 0.001 mg/L. Manganese is presently below detection at the plant fence lines (Figure D-27).

The GoldSim model predicts the peak of the manganese plume will not arrive at the other downgradient locations (southern boundary wells, Mormon A Spring, Harris Wells, or Soda Creek discharge) by the end of the model simulation in 2164. The GoldSim model predicts current manganese concentrations at these locations to be less than 0.001 mg/L (Figures D-28 through D-30). The present concentrations at these locations are less than the detection limit (0.01 to 0.06 mg/L).

The GoldSim model predicts manganese concentrations to be at very low levels (less than 0.0001 mg/L) at the downgradient wells. Manganese concentrations at these locations are generally less than the laboratory detection limit. Therefore, the model could not be calibrated to downgradient data and it is difficult to determine whether the model will accurately predict the behavior of manganese in the future.

5.5.3.6 Cadmium

The remediation goal for manganese is 0.005 mg/L. The projected source concentration history for manganese is shown on Figure D-31. The cadmium source concentration is projected to have declined from a maximum of 1.4 mg/L to a quasi-steady state concentration of about 0.4 mg/L.

The GoldSim model predicts very low (less than 0.00001 mg/L) present cadmium concentrations at the fence line, southern boundary wells, Harris Well, and Mormon Spring. However, the present cadmium concentrations at these locations are variable (Table 6) ranging from less than 0.002 mg/L to 0.0176 mg/L. The elevated cadmium concentrations are due to the presence of cadmium chloride and cadmium sulfate complexes while the old UFS ponds were active (see Geochemical Modeling Memorandum in Appendix E).

The GoldSim model predicts that the peak of the cadmium plume will not arrive at the fence line before at least 2164 (the model was run for 200 years from 1964 to 2164). The predicted concentration in 2064 at the fence line wells is less than 0.001 mg/L (Figures D-33). The predicted cadmium concentrations at the downgradient locations (southern boundary wells, Mormon A Spring, Harris Well, and Soda Creek Discharge) are also all less than 0.001 mg/L (Figures D-34 through D-36). The GoldSim model predicts the present cadmium concentration at all locations downgradient of the old UFS ponds to be less than 0.0001 mg/L. The present cadmium concentrations at the fence line wells ranges from 0.006 mg/L to 0.12 mg/L. The present cadmium concentrations are generally less than 0.001 mg/L in the southern boundary wells and Homestead Spring. The present cadmium concentration is about 0.15 mg/L in Mormon A Spring, and less than 0.001 mg/L in the Harris Well.

The GoldSim model predicts that the cadmium plume originating from the old UFS ponds is highly retarded and cadmium concentrations are predicted to remain below the remediation goals at the compliance points. However, elevated cadmium concentrations were observed at the plant fence line wells and Mormon A Spring between about 1985 and the present time. A cadmium plume peak was observed in the fence line wells coincident with the chloride (and sulfate) peak between about 1990 and 1994. The arrival of cadmium at the same time as chloride is not consistent with a highly retarded constituent such as cadmium. It appears that these elevated concentrations are the artifact of the transport of cadmium as chloride and sulfate complexes while elevated chloride and sulfate concentrations were present in the UBZ-2 groundwater. These complexes can be expected to migrate conservatively in groundwater. The chloride and sulfate concentrations in the UBZ-2 groundwater are continuing to decrease from historic levels following closure of the old UFS ponds. As the old UFS ponds are no longer a source for chloride and sulfate, cadmium concentrations will decrease in these downgradient wells to levels expected from the transport of a retarded species of cadmium. Over the long term, cadmium present in groundwater from the dissolution of otavite (cadmium carbonate) in the aquifer below the old UFS ponds will occur as free cadmium ions [Cd2+], which will be subject to the adsorption process and will be highly retarded. Therefore, future cadmium concentrations downgradient are predicted to be similar to the GoldSim model predictions.

The GoldSim model predicts cadmium concentrations to be at very low levels (less than 0.0001 mg/L) at the downgradient wells. Cadmium concentrations at these locations are generally less than the laboratory detection limit or elevated due to cadmium complexes. Therefore, the model could not be calibrated to downgradient data and it is difficult to determine whether the model will accurately predict the behavior of cadmium in the future.

5.5.3.7 Discussion

The Goldsim Model predicts the following:

- Concentrations of fluoride and nitrate are below the remediation goals at the plant fence line and southern boundary wells;
- Concentrations of selenium are presently above the remedial goal at the fence line. Selenium concentrations are predicted to continue declining and meet the remediation goal in about 20 years. (Actual data suggests that the remediation goal may be met before this time, perhaps in 5 to 10 years); and
- Concentrations of manganese and cadmium at the fence line and southern boundary wells are generally below the remediation goal and are expected to remain so for the next 100 years. Based on the modeling, concentrations of cadmium and manganese at these locations may never exceed the remedial goal because of the high retardation for these metals.

6.0 TECHNICAL ASSESSMENT

In the EPA document "Comprehensive Five-Year Review Guidance" (EPA 2001) that provides guidance for conducting Five-Year Reviews, it is recommended that three questions be answered in the Technical Assessment. These include:

- Question A: Is the remedy functioning as intended by the decision documents?
- Question B: Are the exposure assumptions, toxicity data, cleanup levels, and remedial action objectives (RAOs) used at the time of the remedy still valid?
- Question C: Has any other information come to light that could call into question the protectiveness of the remedy?

6.1 Attainment of Question A

This section describes the effectiveness of the chosen remedies for groundwater in the UBZ-2 and UBZ-4 zones. The chosen remedy in the UBZ-2 zone is monitored natural attenuation. The chosen remedy in the UBZ-4 zone is also monitored natural attenuation. In the UBZ-4 region, pumping of the plant production wells controls the offsite migration of affected groundwater. Institutional controls are also in place for groundwater in the UBZ-2 and UBZ-4 zones.

6.1.1 Institutional Controls

Institutional controls are in place in the UBZ-4 zone (Figure 2) to restrict the use of groundwater that may not meet the remedial goals. The institutional controls in place include the following:

- Monsanto has purchased property downgradient of the plant site, including properties with wells that were impacted by the site releases. Access to these properties is controlled and the properties will not be developed. No wells will be developed on these properties and access to the springs on these properties is restricted.
- Monsanto supplied drinking water from the Soda Springs municipal system to the one downgradient residence with a domestic well that was impacted by the site. The domestic well is no longer used for water supply.

The institutional controls in place south of the plant are an appropriate remedy and are functioning as intended. Affected groundwater from this area is not being used for domestic purposes, and controls are in place to prevent future development of groundwater in this area.

6.1.2 UBZ-2 Monitored Natural Attenuation

Monitored natural attenuation is the chosen remedy in the UBZ-2 zone (Figure 2). Monsanto monitors groundwater quality annually in the point of compliance wells and springs in this region, and also monitors water quality in several other wells and springs in the UBZ-2 zone. The groundwater quality for the constituents of concern in the UBZ-2 zone is summarized in Tables 3 and 4, and below:

- Nitrate and fluoride currently meet the remedial goals in all point of compliance wells and show generally stable or decreasing concentrations. Fluoride is increasing in several of the down-gradient wells but remains below the remediation goal;

- Manganese meets the remedial goals at all point of compliance wells and has generally stable or decreasing concentrations in the wells in the UBZ-2 zone. Manganese in TW-34 is the result of the upwelling of sodic water from the LBZ that contains naturally occurring elevated manganese (Golder, 1995). Manganese is highly retarded and the manganese plume may not arrive at the point of compliance wells in concentrations that exceed the remedial goal;
- Selenium concentrations exceed the remedial goal in several of the fence line and southern boundary wells (TW-20, TW-39, and TW-54) and in the Harris Well and Mormon Spring. The selenium concentrations in these wells are generally stable or declining and modeling indicates the concentrations of selenium should fall below the remedial goal within 20 years or less; and
- Cadmium meets the remedial goals at all point of compliance wells except for TW-20, TW-39 and TW-54. Exceedances at these wells are believed to be temporary as a result of cadmium-chloride or cadmium sulfate complexes related to elevated chloride and sulfate concentrations following closure of the old UFS ponds. Cadmium is generally stable or decreasing in the remaining wells in the UBZ-2 zone. Cadmium is highly retarded and once the chloride plume has dissipated, the cadmium plume is not expected to reach the point of compliance wells in the UBZ-2 zone in concentrations that exceed the remedial goal.

Based on the results of the annual groundwater sampling and transport modeling, concentrations of the constituents of concern that are not retarded either currently meet the remedial goals or are anticipated to meet them within the next 20 years. The concentrations of highly retarded constituents (manganese and cadmium) may never reach the point of compliance wells at concentrations that exceed the remedial goals.

Monitored natural attenuation is an appropriate remedy for the UBZ-2 zone. Monsanto has committed to continue the annual monitoring of the point of compliance wells and other wells and springs in the UBZ-2 region.

6.1.3 UBZ-4 Region

Monitored natural attenuation plus containment using the plant production wells is the chosen remedy in the UBZ-4 zone (Figure 2). Monsanto monitors groundwater quality annually in the point of compliance wells (plant production wells) in this region, and also monitors water quality in several other wells and springs in the UBZ-4 zone. The groundwater quality of the constituents of concern in the UBZ-4 zone is summarized as follows:

- Fluoride and nitrate, the most mobile (conservative) constituents, meet remedial goals in the point of compliance wells. Nitrate is stable in all of the production wells. Fluoride is stable in PW-01, and increasing in PW-02 and PW-03;
- Selenium concentrations exceed the remedial goal in PW-01, but selenium concentrations are generally stable;
- Manganese concentrations meet the remedial goals in all of the plant production wells, and are stable;
- Cadmium concentrations meet the remedial goals in PW-02 and PW-03. Cadmium concentrations exceed the remedial goal in PW-01, however, cadmium concentrations

have a significant decreasing concentration trend. Cadmium is highly retarded and may take tens of years to meet the remedial goal.

Based on the results of the annual groundwater sampling, concentrations of the constituents of concern that are not retarded and manganese currently meet the remedial goals. The concentrations of cadmium, a highly retarded constituent, may take years to meet remedial goals. However, the continuous pumping of the plant production wells contains affected groundwater and prevents offsite migration.

Monitored natural attenuation in conjunction with containment by the plant production wells and institutional controls are appropriate remedies for the UBZ-4 zone. Monsanto has committed to continue the annual monitoring of the point of compliance wells and other wells and springs in the UBZ-4 region.

6.1.4 Attainment of Question A

Based on the results of the annual water quality monitoring and transport modeling, the chosen remedies for groundwater in the UBZ-2 and UBZ-4 regions are functioning as intended and are therefore appropriate remedies.

6.2 Attainment of Question B

This section describes any changes in the factors that were considered in the ROD for the constituents of concern for groundwater. The constituents of concern identified in the ROD are cadmium, selenium, fluoride, nitrate, and manganese. The remediation goals for the constituents of concern are the MCLs under the Safe Drinking Water Act for cadmium, fluoride, nitrate, and selenium, and a risk-based concentration for manganese.

6.2.1 Changes in Standards and To Be Considereds (TBCs)

The remedial goals for cadmium, selenium, nitrate, and fluoride are the MCLs under the Safe Drinking Water Act as follows:

- Cadmium: 0.005 mg/L
- Selenium: 0.05 mg/L;
- Nitrate: 10 mg/L (as nitrogen); and
- Fluoride: 4 mg/L.

The MCLs for these constituents have not changed since the RI was completed in 1995. Therefore, the remedial goals for these constituents remain valid and protective for groundwater at the Monsanto site.

The remedial goal for manganese is 0.18 mg/L. The remedial goal for manganese is a risk-based concentration. There have been no changes in the exposure pathways or toxicity values for manganese. Therefore, the remedial goal for manganese remains valid and protective for the Monsanto site.

6.2.2 Changes in Exposure Pathways, Toxicity, and Other Contaminant Characteristics

This section describes the changes, if any, in exposure pathways, toxicity, and other contaminant characteristics that could affect the choice of remedy of the remedial goals of the remedy.

6.2.2.1 Exposure Pathways

There have been no changes in potential exposure pathways in the vicinity of the site since the completion of RI activity:

- The land use and the proposed land use in the vicinity of the site, including downgradient of the plant site, have not changed;
- Institutional controls are in place and functioning as intended;
- There are no newly identified or changed human health or ecological routes of exposure or receptors;
- There are no newly identified contaminants or sources of contamination at the site. All previously identified sources of contamination have been closed and are no longer ongoing sources of contamination;
- There have been no unanticipated deleterious byproducts of the remedy since it was instituted, and none are anticipated; and
- There have been no changes in the physical conditions of the site that would affect the transport of the contaminants or the protectiveness of the remedy. The revised contaminant transport modeling included in this report used a lower groundwater velocity. This change was the result of evaluation of additional water quality data collected since the RI was completed in 1995 and resulted in a better calibration of the model to the observed water quality. Therefore, the model is predicting the long-term water quality more accurately. These changes do not affect the protectiveness of the remedy.

6.2.2.2 Toxicity

There have been no changes in the toxicity of the constituents of concern since the ROD was issued.

6.2.2.3 To Be Considereds

There were no To Be Considereds identified in the ROD.

6.3 Attainment of Question C

The protectiveness of the chosen remedy for groundwater at the site is appropriate given the following:

- Concentrations of the constituents of concern in groundwater are either generally stable or decreasing and projected to meet RGs within about 20 years for most constituents;
- There are no known groundwater users downgradient of the site;
- Institutional controls for groundwater are in place and functioning as intended;

- There are no changes in the land use or planned land use for property purchased by Monsanto for institutional controls, and access to groundwater resources (wells and springs) on these properties is controlled;
- Transport modeling indicates that highly retarded constituents (cadmium and manganese) may not reach the point of compliance wells at concentrations that exceed the remedial goals; and
- Monsanto has committed to long-term monitoring of groundwater quality and operation of the production wells to control the offsite migration of affected groundwater.

6.4 Technical Assessment Summary

According to the data reviewed and the transport modeling, the remedy is functioning as intended by the ROD. The concentrations of the constituents of concern are either stable or declining. The remedial goals for nitrate and fluoride are being met at the points of compliance. Cadmium occurs above the RGs in several fence line and southern boundary wells. These exceedences are likely related to greater cadmium solubility due to the formation of cadmium chloride or cadmium sulfate complexes from elevated chloride and sulfate concentrations following closure of the old UFS ponds. Chloride and sulfate concentrations are declining and once these plumes have dissipated, cadmium transport will be dominated by the distribution coefficient (highly retarded). Manganese only exceeds the RG in TW-34 (a well completed in a transition zone between the UBZ and LBZ that contains naturally elevated manganese). The use of this well as a point of compliance should be discontinued. Well TW-35 is completed in a similar zone and should also be discontinued. Selenium concentrations exceed the RG in the fence line and southern boundary wells. Concentrations at these locations are generally declining or stable. The transport modeling indicates selenium should meet the RGs in 20 years.

There have been no changes in the physical conditions at the site, the methods used to develop the risk assessment, or the toxicity factors for the constituents of concern.

6.5 Issues

No issues requiring further investigation of the groundwater at the Monsanto site or action were discovered during the course of the 5-year review.

6.6 Recommendations and Follow-Up Actions

The following are recommendations for the continued performance of the implemented remedies for groundwater at the Monsanto site:

- The present groundwater monitoring program should be maintained;
- The present annual groundwater quality reports should be continued; and
- The effectiveness of the chosen remedies should be re-evaluated in the next 5-year report.

6.7 Protectiveness Statement

Based on the information review conducted as part of the 5-year review process, the remedies contained in the ROD for groundwater at the Monsanto Soda Springs Site are functioning as intended and are protective of human health and the environment.

7.0 REFERENCES

Appelo, C.A.J., and Postma, D., 1994, Geochemistry, Groundwater and Pollution, A.A. Balkema, Netherlands.

Batelle, 1989, Chemical Databases for the Multimedia environmental Pollutant Assessment System (MEPAS), Version 1, Batelle memorial institute.

Dominico, P.A., An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species, Journal of Hydrology, Vol. 91, p. 49-58.

Dragun, James, 1988. The Soil Chemistry of Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring, Maryland.

Gilbert, R.O., 1987, Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, New York, 320 p.

Golder Associates, Inc., 1985, Report to Monsanto Industrial Chemical Company on Hydrogeological Investigation, Soda Springs Plant Site, Soda Springs, Idaho, Volumes 1-3, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington,

Golder Associates, Inc., 1992, Phase I Remedial Investigation/Feasibility Study, Preliminary Site Characterization Summary Report for the Soda Springs Elemental Phosphorus Plant, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington, April 23, 1992.

Golder Associates Inc., 1993, Phase II Remedial Investigation Memorandum on Fate and Transport Modeling, Monsanto Elemental Phosphorus Plant, Soda Springs, Idaho, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington, October 5, 1993.

Golder Associates, Inc., 1995, Phase II Remedial Investigation Report for the Soda Springs Elemental Phosphorus Plant, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington, November 21, 1995.

Golder Associates Inc., 1998, Groundwater Conditions at the Soda Springs Plant, Soda Springs, Idaho, Draft 1998 Summary Report, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington.

Golder Associates Inc., 1999, Groundwater Conditions at the Soda Springs Plant, Soda Springs, Idaho, Draft 1999 Summary Report, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington.

Golder Associates Inc., 2000, Groundwater Conditions at the Soda Springs Plant, Soda Springs, Idaho, Draft 2000 Summary Report, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington.

Golder Associates Inc., 2001, Groundwater Conditions at the Soda Springs Plant, Soda Springs, Idaho, Draft 2001 Summary Report, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington.

Golder Associates Inc., 2002, Groundwater Conditions at the Soda Springs Plant, Soda Springs, Idaho, Draft 2002 Summary Report, prepared for Monsanto Chemical Company by Golder Associates, Inc., Redmond, Washington.

GoldSim, 2002, GoldSim Version 7.51.2, GoldSim Technology Group, Division of Golder Associates Inc.

Kendall, M.G., 1975, Rank Correlation Methods, 4th ed., Charles Griffin, London.

Mann, H.B., 1945, Non-Parametric Tests Against Trend, Econometrica, 13, pp. 245-259.

Salmi, T., A. Maatta, P. Anttila, T. Ruoho-Airola, and T. Amnell, 2002, Detecting Trends of Annual Values of Atmospheric Pollutants by the Mann-Kendall Test and Sen's Slope Estimates-The Excel Template Application MAKESENS, No. 31, Finnish Meteorological Institute, Helsinki, Finland, 35 pp.

Sen, P.K., 1968, Estimates of the regression coefficient based on Kendall's tau, Journal of the American Statistical Association, 63, pp. 1379-1389.

U.S. Environmental Protection Agency, 1997, Record of Decision, Monsanto Chemical Company Superfund Site, Caribou County, Idaho, U.S. Environmental Protection Agency Region 10, Office of Environmental Cleanup, Seattle, Washington, April 30, 1997.

U.S. Environmental Protection Agency, 1999, Understanding Variation in Partition Coefficient, Kd, Values, Volume II: Review of Geochemistry and Available Kd values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium, (3H), and Uranium, Office of Radiation and Indoor Air and Office of Environmental Restoration, U.S. Environmental Protection Agency, Washington D.C., August 1999.

U.S. Environmental Protection Agency, 2001, Comprehensive Five-Year Review Guidance, Office of Emergency and Remedial Response U.S. Environmental Protection Agency, Washington D.C., June 2001

TABLES

TABLE 4a

Summary of Cadmium Statistical Analyses

Cadmium (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	-2.15	-0.004	Significant	⇩
	PW-02	12	-3.02	-0.001	Significant	⇩
	PW-03	12	-2.89	-0.0004	Significant	⇩
	PW-04	12	-0.74	0.000	Not Significant	⬄
South Fenceline Wells	TW-20	12	-3.30	-0.001	Significant	⇩
	TW-34	12	-1.26	0.000	Not Significant	⬄
	TW-35	12	-0.85	0.000	Not Significant	⬄
	TW-39	11	-0.82	0.000	Not Significant	⬄
Southern Boundary Wells	TW-53	11	-0.86	0.000	Not Significant	⬄
	TW-54	11 (10)	-1.26 (-2.37)	0.000 (-2.41E-04)	Not Significant (Significant)	⬄(⇩)
	TW-55	11	-1.20	0.000	Not Significant	⬄
	TW-56	11	-1.20	0.000	Not Significant	⬄
Springs	MORMON A SPRING	12	0.55	0.000	Not Significant	⬄
	HARRIS WELL	12	-1.00	0.000	Not Significant	⬄
NW Pond Wells	TW-16	12	-2.91	-0.011	Significant	⇩
	TW-17	11	-0.23	0.000	Not Significant	⬄
	TW-18	11	-1.24	0.000	Not Significant	⬄
Underflow Solids Pond Area Wells	TW-22	12	0.69	0.001	Not Significant	⬄
	TW-24	11	0.78	0.003	Not Significant	⬄
	TW-37	12 (11)	-1.65 (-1.02)	-0.011 (-0.00667)	Not Significant	⬄
	TW-45	12	-2.41	-0.001	Significant	⇩
Old Hydroclarifier Wells	TW-40	11	-0.93	-0.35	Not Significant	⬄
	TW-44	12	-0.21	0.000	Not Significant	⬄
Springs South of Plant	CALF SPRING	11	-0.94	0.000	Not Significant	⬄
	HOMESTEAD SPRING	12	-1.26	0.000	Not Significant	⬄

Note: Results in parenthesis indicate results from calculation with anomalous values removed.

TABLE 3

2002 Results Compared to Remediation Goals

Point of Compliance	Cadmium (mg/L)	Q	Fluoride (mg/L)	Manganese (mg/L)	Q	Nitrate as N (mg/L)	Q	Selenium (mg/L)	Q
Remediation Goals	**0.005**		**4**	**0.18**		**10**		**0.05**	
PW-01	0.041		0.95	0.06	U	4.5		0.061	
PW-02	0.003		0.64	0.06	U	3.4		0.010	
PW-03	0.0025		0.66	0.06	U	3.4		0.010	
SODA UP*	0.003		0.67	0.07		1.4		0.005	U
SODA DN**	0.002	U	0.99	0.086		1.3		0.030	
TW-20	0.0069		1.8	0.06	U	6.9		0.30	
TW-34	0.002	U	0.71	0.19		1.1		0.013	
TW-35	0.002	U	0.60	0.17		0.05	U	0.005	U
TW-39	0.012		3.4	0.06	U	3.8		0.087	
TW-53	0.002	U	2.8	0.06	U	5.1		0.091	
TW-54	0.0176		2.6	0.06	U	1.0		0.34	
TW-55	0.002	U	0.69	0.06	U	2.9		0.017	
HARRIS WELL	0.002	U	3.1	0.06	U	5.8		0.11	

Note: Results in shaded areas indicate remediation goal is exceeded.

*SODA UP - Soda Creek upstream of effluent outfall.

**SODA DN - Soda Creek downstream of effluent outfall.

TABLE 4c

Summary of Manganese Statistical Analyses

Manganese (1991-2002)	**Compliance Point**	**Total # Values (n)**	**Z-Test (or S-Test if n<10) Result**	**Median Slope (mg/L per year)**	**Conclusion**	**General Trend**
Production Wells	PW-01	10	0.00	0.000	Not Significant	⇔
	PW-02	12	-0.07	0.000	Not Significant	⇔
	PW-03	12	0.00	0.000	Not Significant	⇔
	PW-04	12	0.00	0.000	Not Significant	⇔
South Fenceline Wells	TW-20	12	-0.14	0.000	Not Significant	⇔
	TW-34	12	-0.75	-0.005	Not Significant	⇔
	TW-35	12	1.10	0.002	Not Significant	⇔
	TW-39	12	-0.29	0.000	Not Significant	⇔
Southern Boundary Wells	TW-53	11	0.63	0.001	Not Significant	⇔
	TW-54	11	0.47	0.000	Not Significant	⇔
	TW-55	11	-0.16	0.000	Not Significant	⇔
	TW-56	11	0.00	0.000	Not Significant	⇔
Springs	MORMON A SPRING	12	-0.44	0.000	Not Significant	⇔
	HARRIS WELL	12	-0.07	0.000	Not Significant	⇔
NW Pond Wells	TW-16	12	-2.63	-0.006	Significant	⇩
	TW-17	11	3.83	0.078	Significant	▨
	TW-18	11	1.87	0.007	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	12	0.07	0.009	Not Significant	⇔
	TW-24	11	-0.62	-0.009	Not Significant	⇔
	TW-37	12	-1.85	-0.046	Not Significant	⇔
	TW-45	12	-2.54	-0.017	Significant	⇩
Old Hydroclarifier Wells	TW-40	11	-2.96	-0.039	Significant	⇩
	TW-44	12	0.34	0.001	Not Significant	⇔
Springs South of Plant	CALF SPRING	11	-1.63	0.000	Not Significant	⇔
	HOMESTEAD SPRING	12	1.37	0.001	Not Significant	⇔

Note: Shaded cells indicate a significant increasing concentration trend

Summary of Fluoride Statistical Analyses

Fluoride (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	-0.54	-0.014	Not Significant	⇔
	PW-02	12	2.95	0.030	Significant	▨
	PW-03	12	2.15	0.025	Significant	▨
	PW-04	12	3.10	0.020	Significant	▨
South Fenceline Wells	TW-20	12	-3.50	-0.53	Significant	⇩
	TW-34	12	0.75	0.0097	Not Significant	⇔
	TW-35	12	2.00	0.018	Significant	▨
	TW-39	12	-3.10	-0.18	Significant	⇩
Southern Boundary Wells	TW-53	11	2.96	0.28	Significant	▨
	TW-54	11	-2.02	-0.28	Significant	⇩
	TW-55	11	3.67	0.034	Significant	▨
	TW-56	11	3.05	0.025	Significant	▨
Springs	MORMON A SPRING	12	0.62	0.063	Not Significant	⇔
	HARRIS WELL	12	2.34	0.31	Significant	▨
NW Pond Wells	TW-16	12	-2.75	-0.13	Significant	⇩
	TW-17	11	-2.42	-0.064	Significant	⇩
	TW-18	11	2.42	0.018	Significant	▨
Underflow Solids Pond Area Wells	TW-22	12	-0.34	-0.024	Not Significant	⇔
	TW-24	11	0.16	0.089	Not Significant	⇔
	TW-37	12	-2.06	-0.32	Significant	⇩
	TW-45	12	-1.10	-0.010	Not Significant	⇔
Old Hydroclarifier Wells	TW-40	11	-0.16	-0.044	Not Significant	⇔
	TW-44	12	2.89	0.021	Significant	▨
Springs South of Plant	CALF SPRING	11	0.86	0.11	Not Significant	⇔
	HOMESTEAD SPRING	12	2.91	0.023	Significant	▨

Note: Shaded cells indicate a significant increasing concentration trend

TABLE 4e

Summary of Selenium Statistical Analyses

Selenium (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	0.89	0.002	Not Significant	⇔
	PW-02	12	0.00	0.000	Not Significant	⇔
	PW-03	12	-0.27	0.000	Not Significant	⇔
	PW-04	12	0.76	0.0001	Not Significant	⇔
South Fenceline Wells	TW-20	12 (11)	-1.17 (-1.71)	-0.020 (-0.03)	Not Significant	⇔
	TW-34	12	1.86	0.001	Not Significant	⇔
	TW-35	12	1.25	0.00025	Not Significant	⇔
	TW-39	12	-0.82	-0.012	Not Significant	⇔
Southern Boundary Wells	TW-53	11	-1.71	-0.017	Not Significant	⇔
	TW-53 (1994 to 2002)[a]	9	-32	NA	Significant	⇩
	TW-54	11 (10)	-1.87 (-2.68)	-0.027 (-0.036)	Not Significant	⇔/⇩
	TW-55	11	-3.89	-0.019	Significant	⇩
	TW-56	11	0.08	0.000	Not Significant	⇔
Springs	MORMON A SPRING	12	2.75	0.013	Significant	▨
	HARRIS WELL	12	-0.89	-0.016	Not Significant	⇔
	HARRIS (1994 to 2002)[a]	9	-30.00	NA	Significant	⇩
NW Pond Wells	TW-16	12	0.14	0.002	Not Significant	⇔
	TW-17	11	0.47	0.000	Not Significant	⇔
	TW-18	11	0.63	0.000	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	12	0.41	0.005	Not Significant	⇔
	TW-24	11	0.00	0.001	Not Significant	⇔
	TW-37	12	-1.03	-0.019	Not Significant	⇔
	TW-45	12	-0.49	-0.002	Not Significant	⇔
Old Hydroclarifier Wells	TW-40	11	2.65	0.081	Significant	▨
	TW-44	12	-0.15	0.000	Not Significant	⇔
Springs South of Plant	CALF SPRING	11	-0.78	-0.010	Not Significant	⇔
	HOMESTEAD SPRING	12	1.99	0.002	Significant	▨

[a] Short series calculations made to observe trends following passage of elevated concentrations. Slope could not be calculated because n < 10.

Note: Shaded cells indicate a significant increasing concentration trend
Results in parenthesis indicate results from calculation with anomalous values removed.

Summary of Nitrate as N Statistical Analyses

Nitrate (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	-1.89	-0.060	Not Significant	⇔
	PW-02	12	-0.62	-0.058	Not Significant	⇔
	PW-03	12	-1.51	-0.088	Not Significant	⇔
	PW-04	12	1.18	0.037	Not Significant	⇔
	TW-20	12	-2.26	-0.33	Significant	⇩
	TW-34	12	1.58	0.026	Not Significant	⇔
	TW-35	12	-0.14	0.000	Not Significant	⇔
	TW-39	12	0.83	0.47	Not Significant	⇔
	TW-39 (1997 to 2002) [a]	6	-0.12	NA	Significant	⇩
Southern Boundary Wells	TW-53	11	-0.78	-0.17	Not Significant	⇔
	TW-54	11	-2.11	-0.47	Significant	⇩
	TW-55	11	-0.47	-0.007	Not Significant	⇔
	TW-56	11	0.16	0.040	Not Significant	⇔
Springs	MORMON A SPRING	12	1.71	0.17	Not Significant	⇔
	HARRIS WELL	12	0.48	0.25	Not Significant	⇔
NW Pond Wells	TW-16	12	-1.17	-0.12	Not Significant	⇔
	TW-17	11	-1.04	-0.005	Not Significant	⇔
	TW-18	11	-1.57	-0.006	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	12	1.17	0.29	Not Significant	⇔
	TW-24	11	0.86	0.17	Not Significant	⇔
	TW-37	12	0.62	0.051	Not Significant	⇔
	TW-45	12	-2.06	-0.015	Significant	⇩
Old Hydroclarifier Wells	TW-40	11	-0.70	-0.99	Not Significant	⇔
	TW-44	12	-0.82	-0.007	Not Significant	⇔
Springs South of Plant	CALF SPRING	11	1.25	0.40	Not Significant	⇔
	HOMESTEAD SPRING	12	1.58	0.17	Not Significant	⇔

[a] Short series calculations made to observe trends following passage of elevated concentrations. Slope could not be calculated because n < 10.

Note: Shaded cells indicate a significant increasing concentration trend

Summary of Molybdenum Statistical Analyses

Molybdenum (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	9	-22.00	N/A	Significant	⇩
	PW-02	11	0.86	0.001	Not Significant	⇔
	PW-03	11	-2.89	-0.005	Significant	⇩
	PW-04	11	0.00	0.000	Not Significant	⇔
South Fenceline Wells	TW-20	11	-3.58	-0.007	Significant	⇩
	TW-34	11	-0.69	0.000	Not Significant	⇔
	TW-35	11	0.00	0.000	Not Significant	⇔
	TW-39	11	-1.40	-0.003	Not Significant	⇔
Southern Boundary Wells	TW-53	11	3.27	0.007	Significant	▨
	TW-54	11	-2.34	-0.006	Significant	⇩
	TW-55	11	-0.69	0.000	Not Significant	⇔
	TW-56	11	-1.57	-0.001	Not Significant	⇔
Springs	MORMON A SPRING	11	0.23	0.001	Not Significant	⇔
	HARRIS WELL	11	2.19	0.004	Significant	▨
NW Pond Wells	TW-16	11	-2.49	-0.002	Significant	⇩
	TW-17	11	-2.66	-0.002	Significant	⇩
	TW-18	10	0.00	0.000	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	11	-0.78	-0.004	Not Significant	⇔
	TW-24	11	0.62	0.060	Not Significant	⇔
	TW-24 (1997 to 2002)[a]	6	-13.00	NA	Significant	⇩
	TW-37	11	-2.65	-0.031	Significant	⇩
	TW-45	11	-2.73	-0.004	Significant	⇩
Old Hydroclarifier Wells	TW-40	10	-0.36	-0.001	Not Significant	⇔
	TW-44	11 (10)	-2.05 (-1.64)	-0.001 (-0.0005)	Significant (Not Significant)	⇩/⇔
Springs South of Plant	CALF SPRING	10	-0.36	-0.001	Not Significant	⇔
	HOMESTEAD SPRING	11	-0.69	0.000	Not Significant	⇔

[a] Short series calculations made to observe trends following passage of elevated concentrations. Slope could not be calculated because n < 10.

Note: Shaded cells indicate a significant increasing concentration trend
Results in parenthesis indicate results from calculation with anomalous values removed.

TABL

Summary of Chloride Statistical Analyses

Chloride (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	-2.50	-5.7	Significant	⇩
	PW-02	12	0.89	1.1	Not Significant	⇔
	PW-03	12	-0.82	-0.21	Not Significant	⇔
	PW-04	12	1.32	0.17	Not Significant	⇔
South Fenceline Wells	TW-20	12	-2.47	-7.4	Significant	⇩
	TW-34	12	-0.75	-0.60	Not Significant	⇔
	TW-35	12	-2.20	-1.2	Significant	⇩
	TW-39	12	-3.36	-6.8	Significant	⇩
Southern Boundary Wells	TW-53	11	-0.47	-2.6	Not Significant	⇔
	TW-53 (1994 to 2002) [a]	9	-20.00	NA	Significant	⇩
	TW-54	11	-2.49	-13	Significant	⇩
	TW-55	11	-2.80	-3.9	Significant	⇩
	TW-56	11	-1.95	-2.3	Not Significant	⇔
Springs	MORMON A SPRING	12	-1.99	-4.3	Significant	⇩
	HARRIS WELL	12	0.27	0.94	Not Significant	⇔
NW Pond Wells	TW-16	12	-1.10	-0.47	Not Significant	⇔
	TW-17	11	-3.13	-8.0	Significant	⇩
	TW-18	11	0.63	0.1	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	12	0.21	1.2	Not Significant	⇔
	TW-24	11	-0.55	-1.0	Not Significant	⇔
	TW-37	12	-2.47	-3.5	Significant	⇩
	TW-45	12	-3.85	-3.0	Significant	⇩
Old Hydroclarifier Wells	TW-40	11	-1.09	-30	Not Significant	⇔
	TW-44	12	2.75	1.3	Significant	■
Springs South of Plant	CALF SPRING	11	-1.41	-3.3	Not Significant	⇔
	HOMESTEAD SPRING	12	2.47	0.74	Significant	■

[a] Short series calculations made to observe trends following passage of elevated concentrations. Slope could not be calculated because n < 10.

Note: Shaded cells indicate a significant increasing concentration trend

TABLE 5

RI Model Old UFS Source Area Concentrations

Constituent	t1 (year)	t2 (year)	c(t1) (mg/L)	c(t2) (mg/L)	Decay Rate (1/yr)	Predicted 1984 Concentration (mg/L)
Fluoride	1988	1992	17	17	0	40
Nitrate	1986	1992	9.1	4.04	0.135	11.9
Cadmium	1985	1992	1.22	0.44	0.146	1.4
Manganese	1987	1992	3	1.3	0.167	4.95
Selenium	-	Jun-92	-	0.52	0.13	1.51
Chloride	Jun-85	1992	259	59	0	364

Note: Decay rate for selenium based on average decay rate for aluminum, arsenic, cadmium, nickel, vanadium, and zinc.

t1: Year of first concentration

t2: Year of second concentration

c(t1): Concentration at time 1.

c(t2): Concentration at time 2.

Summary of Sulfate Statistical Analyses

Sulfate (1991-2002)	Compliance Point	Total # Values (n)	Z-Test (or S-Test if n<10) Result	Median Slope (mg/L per year)	Conclusion	General Trend
Production Wells	PW-01	10	-0.63	-2.4	Not Significant	⇔
	PW-02	12	1.58	2.7	Not Significant	⇔
	PW-03	12	0.21	0.88	Not Significant	⇔
	PW-04	12	1.03	1.3	Not Significant	⇔
South Fenceline Wells	TW-20	12 (11)	-1.79 (-2.73)	-29.5 (-32.8)	Not Significant (Significant)	⇔/⇩
	TW-34	12	0.00	0.000	Not Significant	⇔
	TW-35	12	0.83	0.66	Not Significant	⇔
	TW-39	12	1.65	21	Not Significant	⇔
Southern Boundary Wells	TW-53	11	0.62	7.4	Not Significant	⇔
	TW-54	11	-1.09	-25	Not Significant	⇔
	TW-55	11	-3.45	-11	Significant	⇩
	TW-56	11	-1.25	-2.6	Not Significant	⇔
Springs	MORMON A SPRING	12	2.61	28	Significant	▨
	MORMON (1996 to 2002)[a]	7	-4.00	NA	Significant	⇩
	HARRIS WELL	12	0.96	-28	Not Significant	⇔
NW Pond Wells	TW-16	12	0.21	0.72	Not Significant	⇔
	TW-17	11	-2.91	-5.5	Significant	⇩
	TW-18	11	0.55	0.50	Not Significant	⇔
Underflow Solids Pond Area Wells	TW-22	12	0.69	28	Not Significant	⇔
	TW-24	11	0.16	18	Not Significant	⇔
	TW-24 (1997 to 2002)[a]	6	-13.00	NA	Significant	⇩
	TW-37	12	-0.21	-1.5	Not Significant	⇔
	TW-45	12	-1.19	-4.1	Not Significant	⇔
Old Hydroclarifier Wells	TW-40	11	0.55	19	Not Significant	⇔
	TW-44	12	1.37	2.0	Not Significant	⇔
Springs South of Plant	CALF SPRING	11	2.80	34	Significant	▨
	HOMESTEAD SPRING	12	3.02	3.9	Significant	▨

[a] Short series calculations made to observe trends following passage of elevated concentrations. Slope could not be calculated because n < 10.

Note: Shaded cells indicate a significant increasing concentration trend

Results in parenthesis indicate results from calculation with anomalous values removed.

TABLE 7

Original and Revised Model UFS Ponds Source Concentrations

Constituent	RI Model						GoldSim Model						
	t1 (year)	t2 (year)	c(t1) (mg/L)	c(t2) (mg/L)	Decay Rate (1/yr)	Predicted 1984 Concentration (mg/L)	t1 (year)	t2 (year)	c(t1) (mg/L)	c(t2) (mg/L)	Decay Rate (1/yr)	Predicted 1984 Concentration (mg/L)	Stabilized Concentration (mg/L)
Fluoride	1988	1992	17	17	0	40	1985	1987	31	12	0.475	31.0	6
Nitrate	1986	1992	9.1	4.04	0.135	11.9	1985	1988	9.4	3.24	0.135	9.4	4[a]
Cadmium	1985	1992	1.22	0.44	0.146	1.4	1985	1994	1.22	0.4	0.146	1.4	0.4
Manganese	1987	1992	3	1.3	0.167	4.95	1987	1996	3	0.6	0.167	4.95	0.7
Selenium	-	Jun-92	-	0.52	0.13	1.51	1992	2001	0.493	0.389	0.130	1.4	0.05
Chloride	Jun-85	1992	259	59	0	364	1985	1996	259	39	0.23	400	16[a]

Notes:

a. Represents background concentration.

Background concentration of 4 mg/L and 16 mg/L not included for nitrate and chloride, respectively

Decay rate for selenium in RI Model based on average decay rate for aluminum, arsenic, cadmium, nickel, vanadium, and zinc.

t1: Year of first concentration

t2: Year of second concentration

c(t1): Concentration at time 1.

c(t2): Concentration at time 2.

TABLE 6

Predicted and Observed 2002 Concentrations - RI Model

Constituent	Location	Predicted Concentration (mg/L)	Observed Concentration[a] (mg/L)
Fluoride	Source (TW-37)	17	12.96
	Fence Line (TW-20, TW-39)	17	1.803 to 3.38
	Southern Boundary (TW-54, TW-55)	17	0.69 to 2.64
Nitrate	Source (TW-37)	0.83	3.79
	Fence Line (TW-20, TW-39)	1.97	6.08 to 6.95
	Southern Boundary (TW-54, TW-55)	1.99	1.04 to 2.91
Manganese	Source (TW-37)	0.19	0.01
	Fence Line (TW-20, TW-39)	0.43	0.01 to 0.80
	Southern Boundary (TW-54, TW-55)	0.45	0.01
Cadmium	Source (TW-37)	0.08/0.004[b]	0.397
	Fence Line (TW-20, TW-39)	0.03/0.67	0.0059 to 0.016
	Southern Boundary (TW-54, TW-55)	0.86/0.04	0.002
Selenium	Source (TW-37)	0.13	0.389
	Fence Line (TW-20, TW-39)	0.15	0.055 to 0.217
	Southern Boundary (TW-54, TW-55)	0.16	0.013 to 0.092

a. Concentration observed in 2001 (selenium) or 2002.

b. Solubility control/no solubility control

Summary of Predicted and Observed Concentrations in 2002

		Fence Line Wells			**Southern Boundary Wells**			**Mormon-Harris**			**Soda Creek Discharge**	
Constituent	Remediation Goal (mg/L)	Model Output (mg/L)	TW-20 (mg/L)	TW-39 (mg/L)	Model Output (mg/L)	TW-54 (mg/L)	TW-55 (mg/L)	Model Output (mg/L)	Harris Well (mg/L)	Mormon Spring (mg/L)	Model Output (mg/L)	Homestead Spring (mg/L)
Chloride	na	59.3	101.9	110.4	62.7	109.1	36.7	60.9	89.3	101.8	51.2	24.8
Fluoride	4	4.3	1.8	3.4	3.8	2.6	0.7	3.3	3.1	3.1	2.4	0.7
Nitrate	10	5.9	6.9	3.8	5.8	1.0	2.9	5.6	5.8	6.0	5.1	6.7
Selenium	0.05	0.32	0.30	0.09	0.30	0.34	0.02	0.26	0.11	0.27	0.17	0.02
Manganese	0.18	<0.00001	<0.06	<0.06	<0.00001	<0.06	<0.06	<0.00001	<0.06	<0.06	<0.00001	<0.06
Cadmium	0.005	<0.00001	0.0059	0.0120	<0.00001	0.0176	<0.002	<0.00001	<0.002	0.0149	<0.00001	<0.002

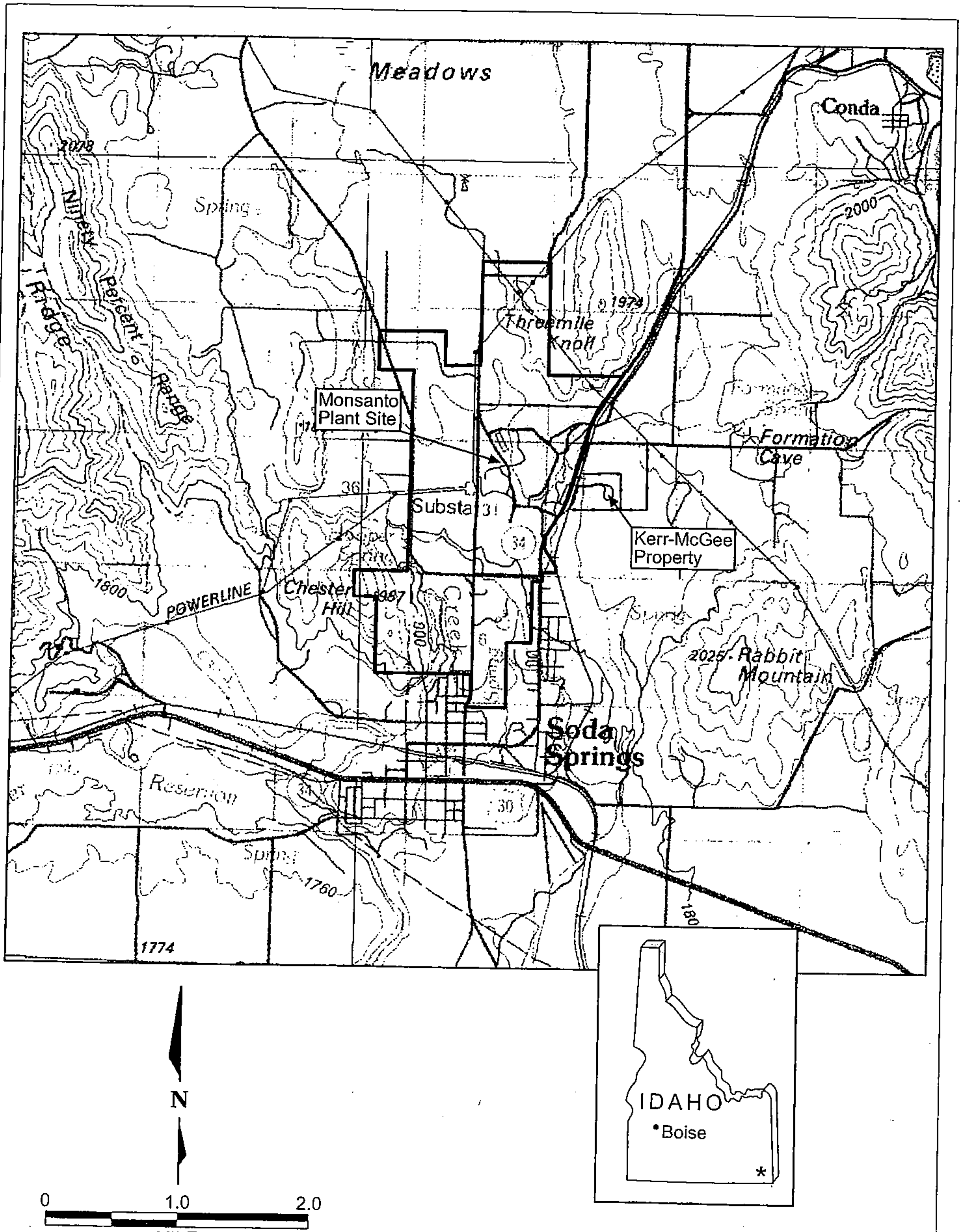
Notes:
All concentrations from May 2002 sampling.
na: Not Applicable
Exceedances of remediation goals shaded (model output and actual concentrations).

Summary of Model Input Parameters

Parameter	Units	RI Model	GoldSim Model
Hydraulic Conductivity	ft/d	400	40
Gradient	ft/ft	0.0075	0.0065
Porosity	-	0.3	0.3
Aquifer Length-Fence Line	ft	na	4,000
Aquifer Length-Southern Boundary	ft	5,000	5,000
Aquifer Length-Mormon/Harris	ft	na	6,000
Aquifer Length-Soda Creek Discharge	ft	na	10,000
Aquifer Width	ft	500	500
Aquifer Thickness	ft	30	30
Longitudinal Dispersivity	ft	231	0.1*aquifer length
Transverse Dispersivity (horizontal)	ft	3	0.1*Longitudinal Dispersivity
Transverse Dispersivity (vertical)	ft	na	0.01*Longitudinal Dispersivity
K_d Cadmium	ml/g	1.25	10
K_d Manganese	ml/g	0.2	10
Simulation Start Date	-	1964	1964

Note
Selenium, nitrate, fluoride, and chloride not retarded.
Aquifer length from UFS Ponds.
na: not included in RI Model

FIGURES



SOURCE: Topographic map of the USGS
Soda Springs Quadrangle (1:100,000) 1982.

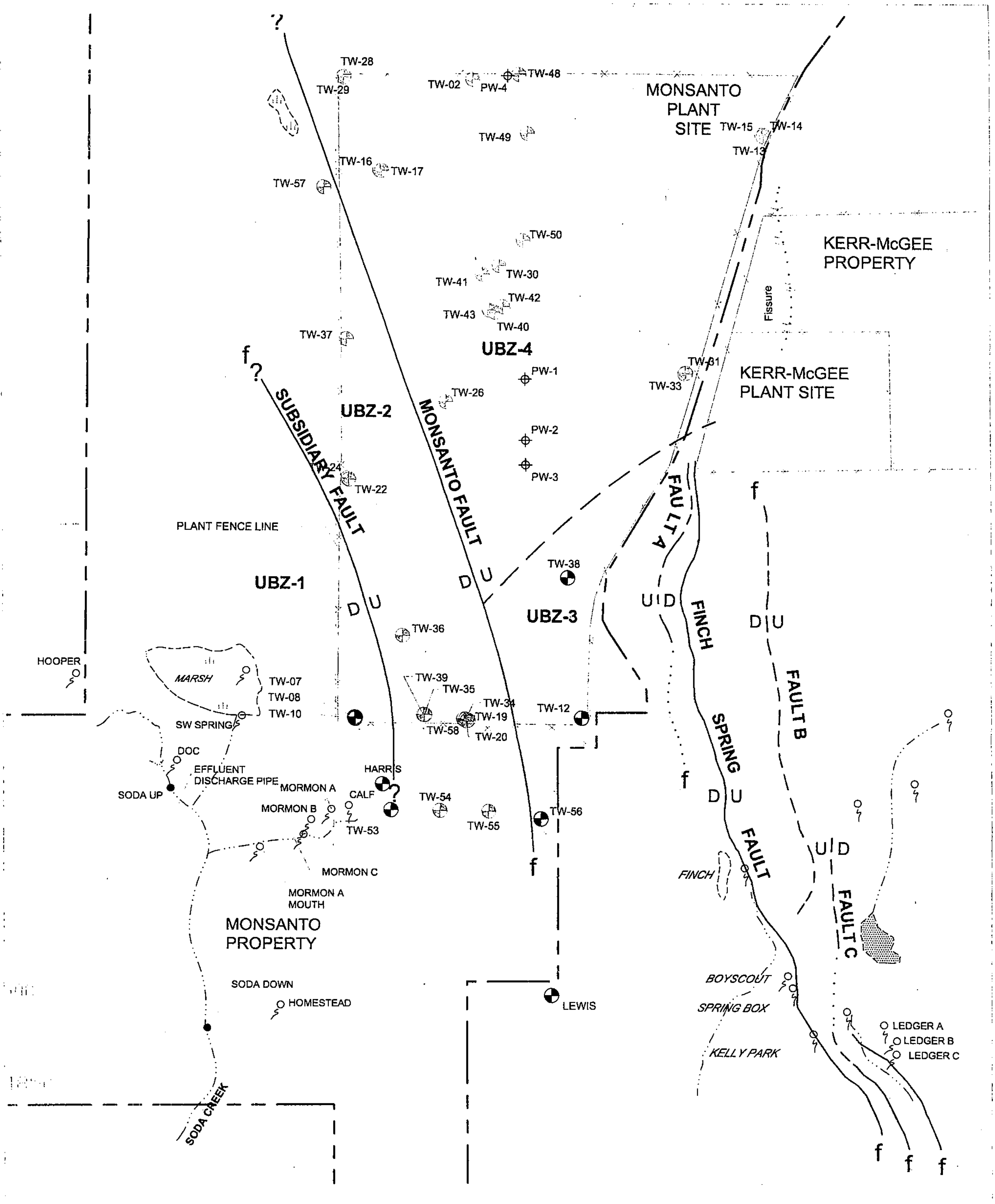
FIGURE **1**

MONSANTO PLANT VICINITY MAP

MONSANTO/PHASE 1 RI REPORT/ID

DRAWING NO. 9131101605fg01.fh9 DATE 04/08/03 DRAWN BY

Golder Associates



LEGEND

● TW-07	Monitoring well location and name in Groundwater Zone UBZ 1
TW-35	Monitoring well location and name in Groundwater Zone UBZ 2
● TW-35	Monitoring well location and name in Groundwater Zone UBZ 3
TW-38	Monitoring well location and name in Groundwater Zone UBZ 4
● SODA UP	Surface water sample location and name
⊕ PW-1	Production well location and name
○	Spring location
f — - — - ·	Fault (dashed where inferred)
UBZ-1	Groundwater Zones
— — —	Property Boundary

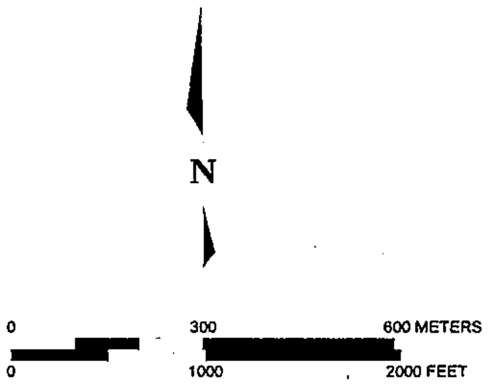


FIGURE **2**

LOCATION OF WELLS AND SPRINGS IN THE UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

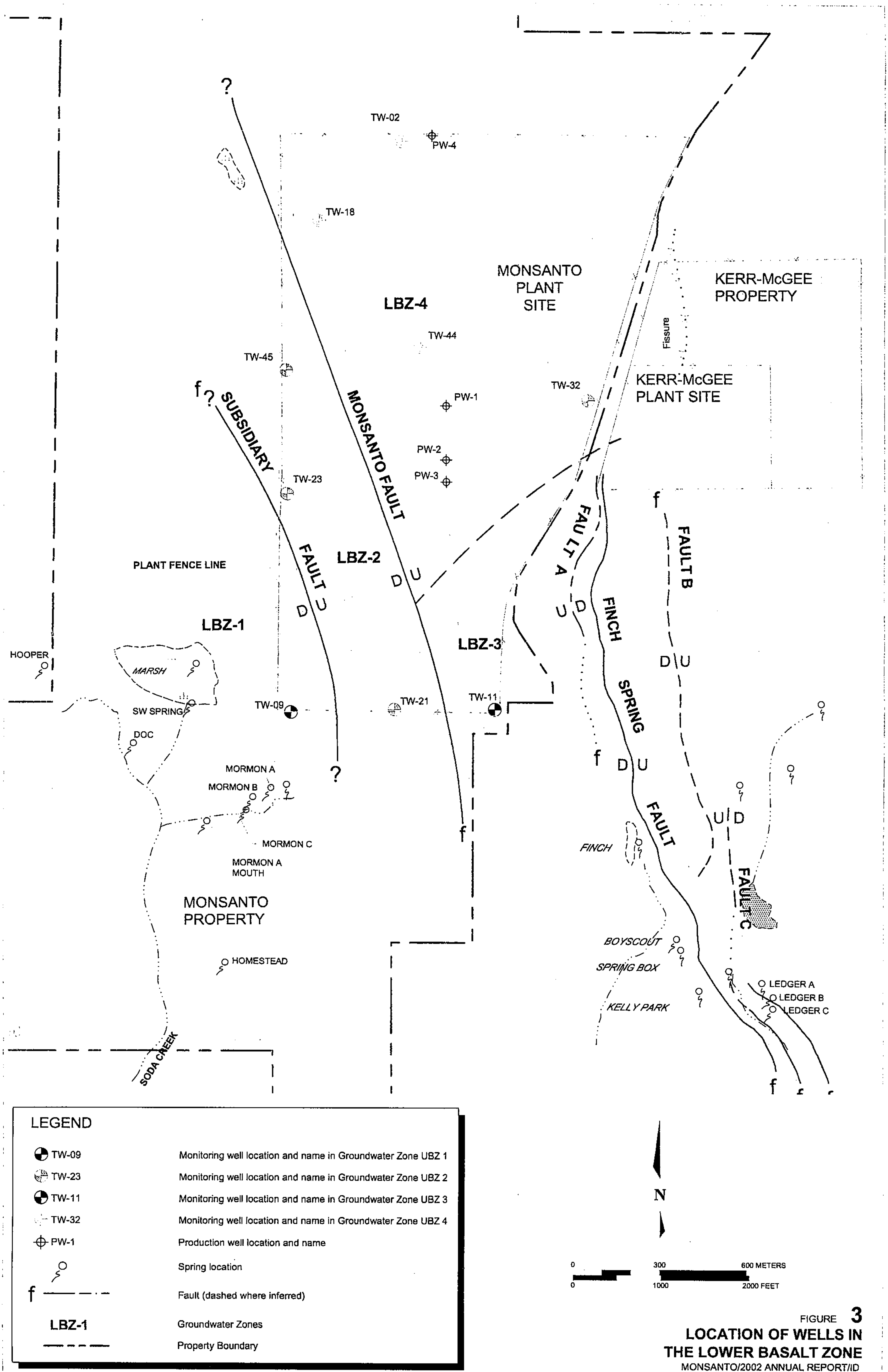


FIGURE 3

LOCATION OF WELLS IN THE LOWER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

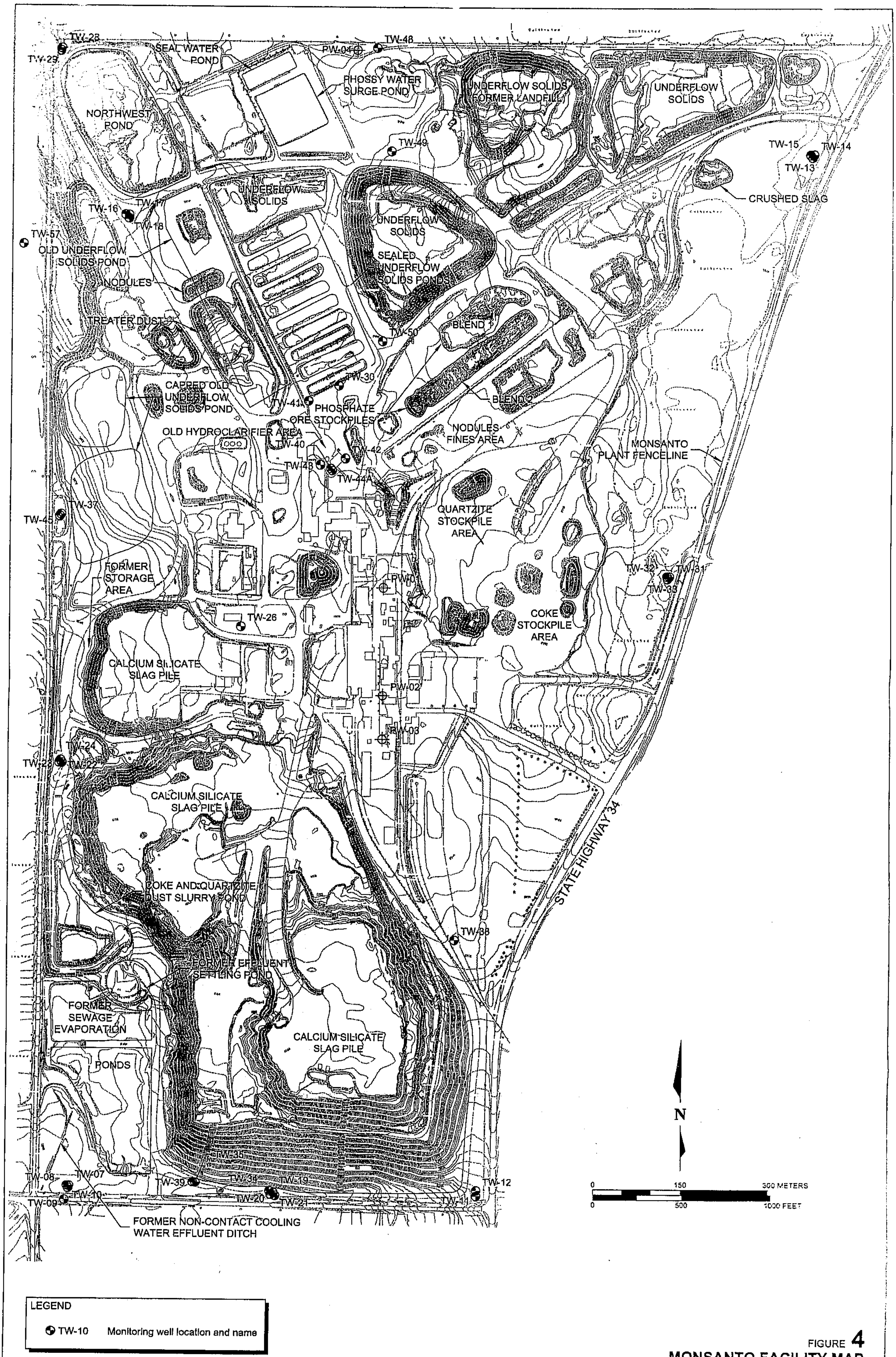


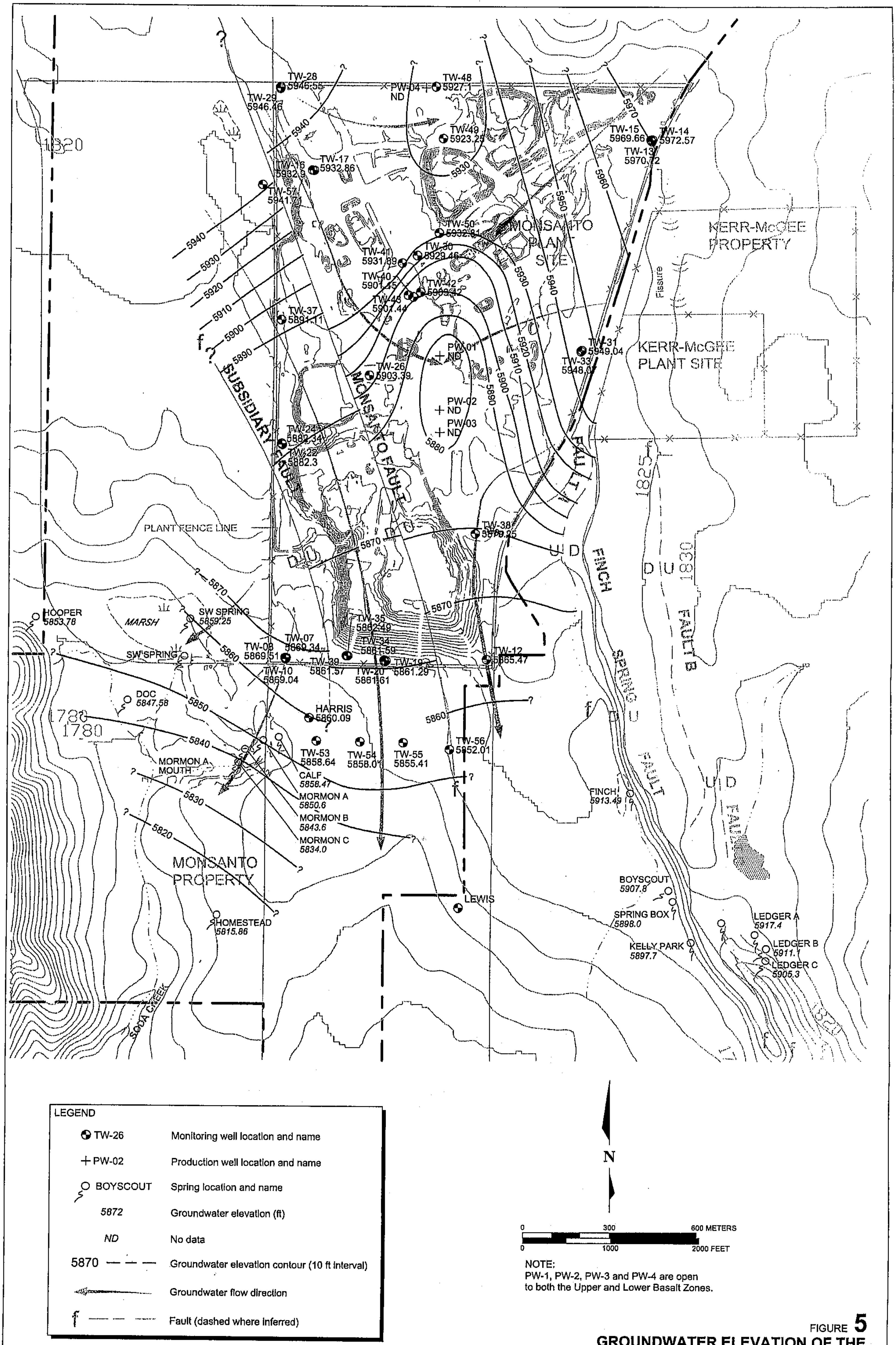
FIGURE 4

MONSANTO FACILITY MAP

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F17.dwg May 27, 2003 - 9:15am

Golder Associates



NOTE:
PW-1, PW-2, PW-3 and PW-4 are open to both the Upper and Lower Basalt Zones.

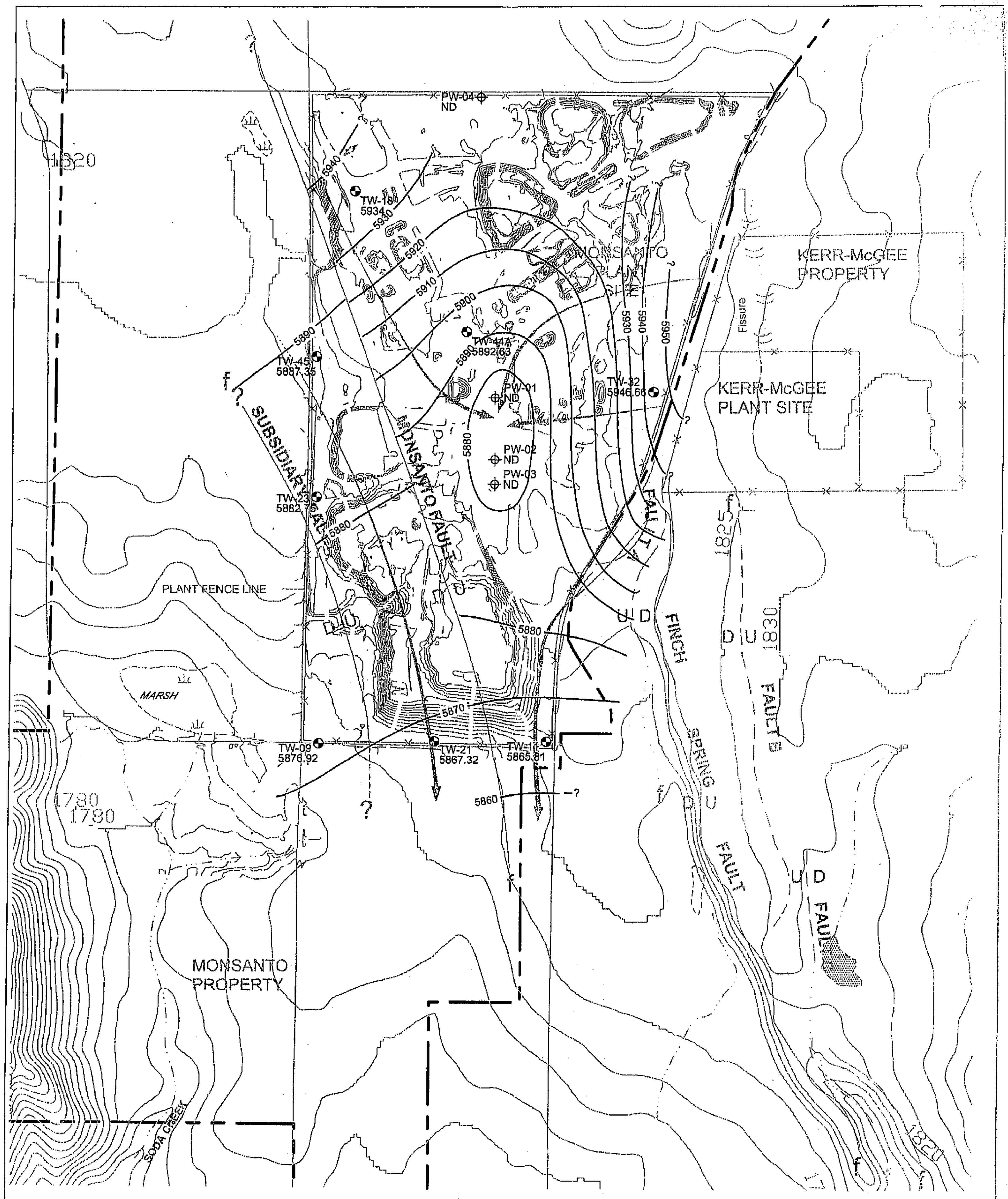
FIGURE **5**

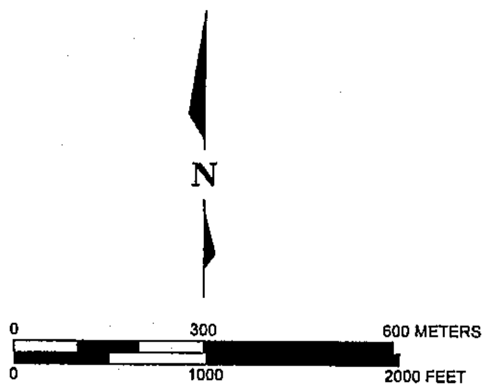
GROUNDWATER ELEVATION OF THE UPPER BASALT ZONE DURING JUNE 2002

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F18.dwg May 27, 2003 - 9:02am

Golder Associates





LEGEND

TW-26	Monitoring well location and name
PW-02	Production well location and name
5872	Groundwater elevation (ft)
ND	No data
5870 — — —	Groundwater elevation contour (10 ft interval)
◀——	Groundwater flow direction
f — — —	Fault (dashed where inferred)

NOTE:
PW-1, PW-2, PW-3 and PW-4 are open to both the Upper and Lower Basalt Zones.

FIGURE 6

GROUNDWATER ELEVATION OF THE LOWER BASALT ZONE DURING JUNE 2002

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F19.dwg May 27, 2003 – 10:09am

Golder Associates

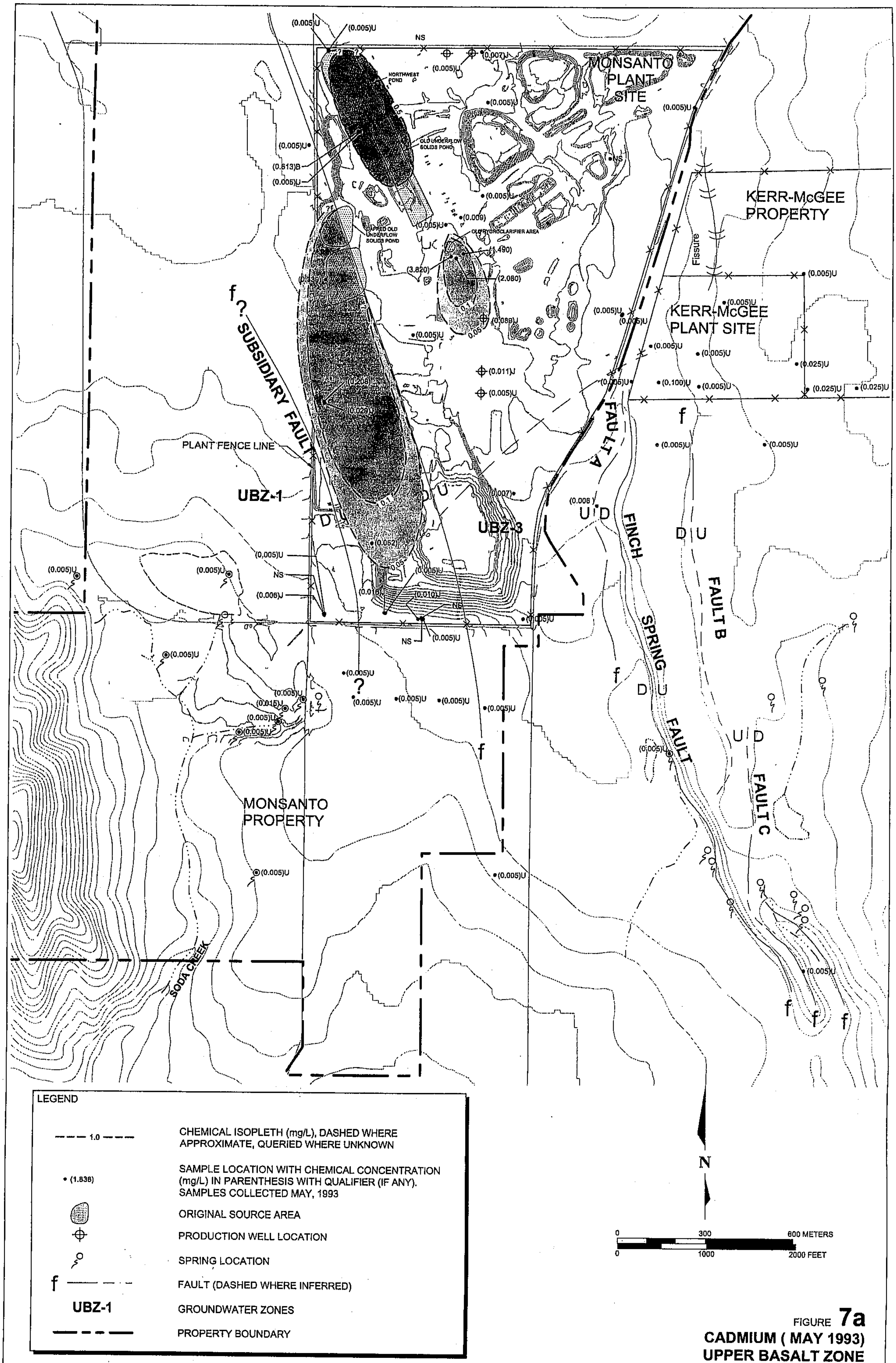


FIGURE **7a**

CADMIUM (MAY 1993)
UPPER BASALT ZONE
MONSANTO/PHASE I RI REPORT/ID

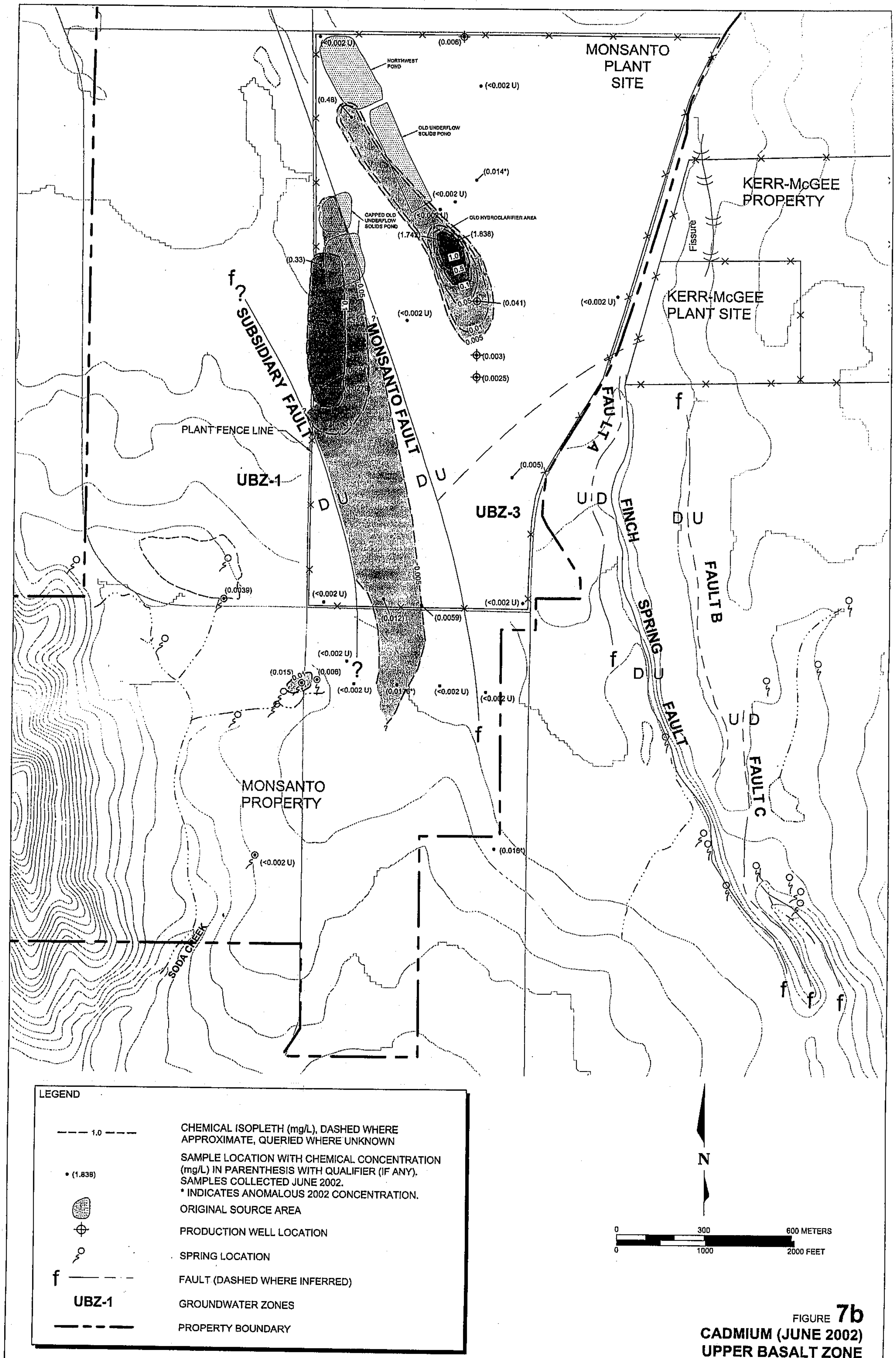


FIGURE **7b**

CADMIUM (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F02.dwg May 22, 2003 – 10:23am

Golder Associates

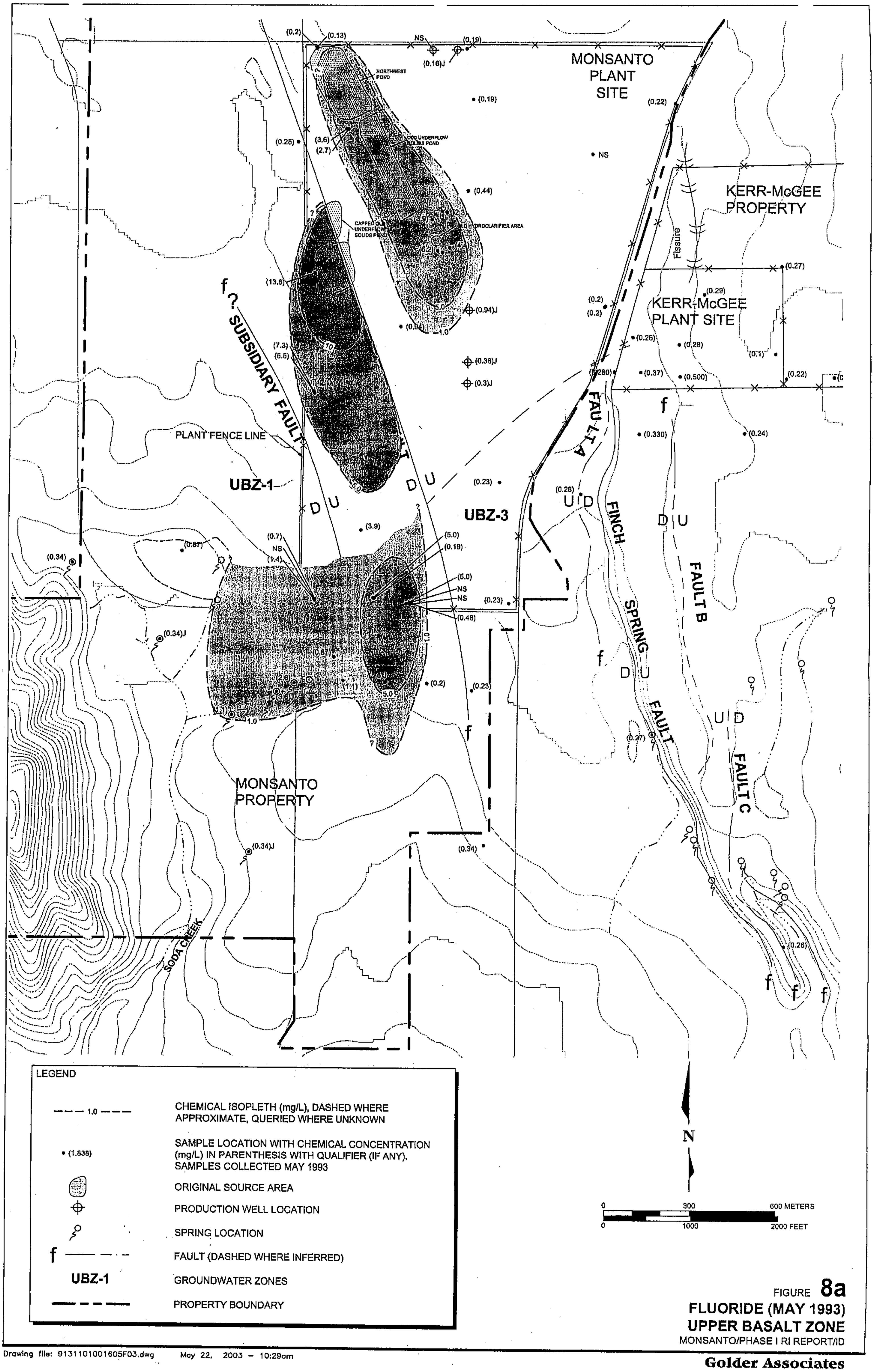
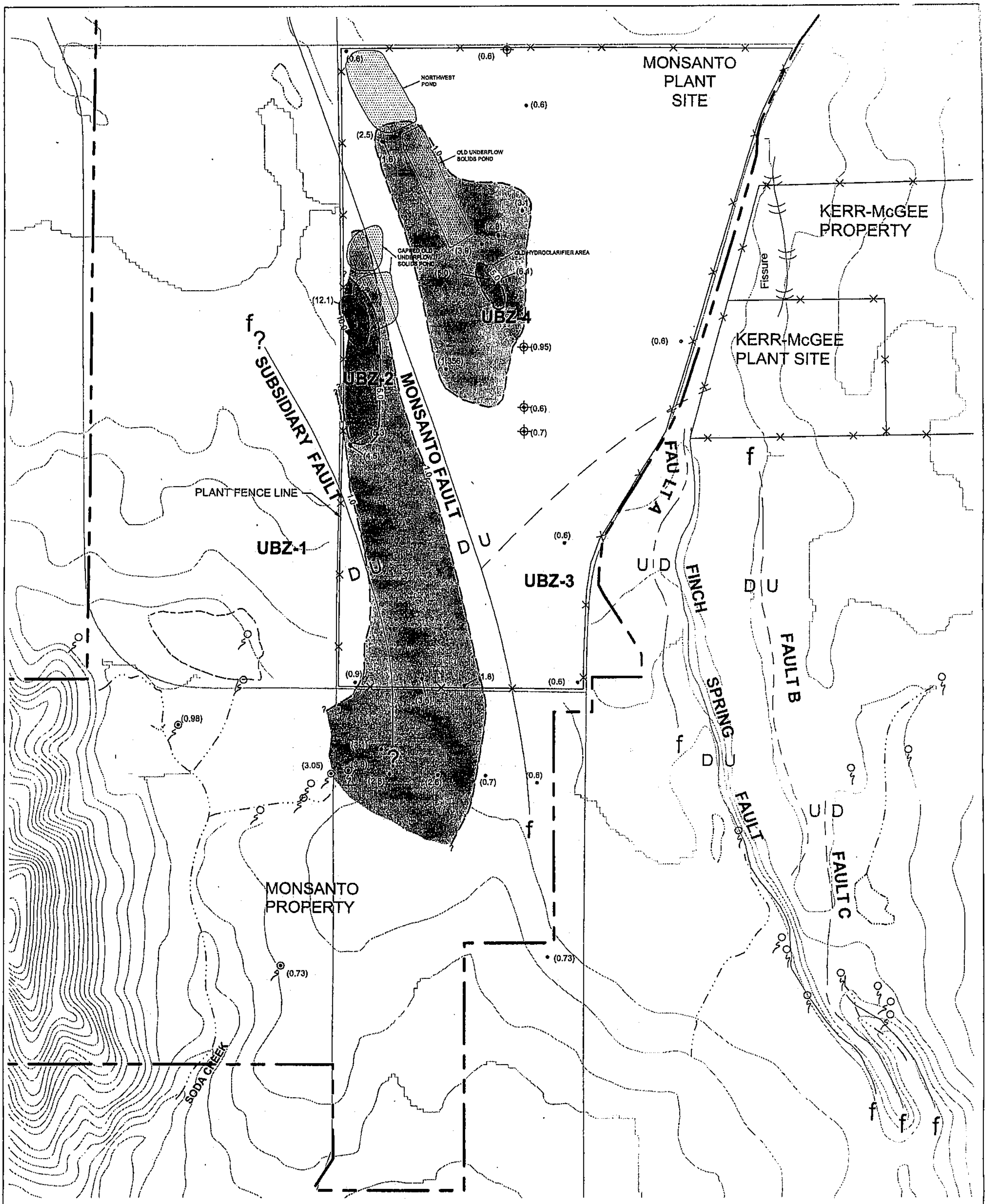


FIGURE **8a**

FLUORIDE (MAY 1993)

UPPER BASALT ZONE

MONSANTO/PHASE I RI REPORT/ID



LEGEND

— — 1.0 — — —	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.838)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 2002
▨	ORIGINAL SOURCE AREA
⌖	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f ——— — · —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
▬ ▬ ▬	PROPERTY BOUNDARY

N

0 300 600 METERS
0 1000 2000 FEET

FIGURE **8b**

FLUORIDE (JUNE 2002)
UPPER BASALT ZONE
MONSANTO/2002 ANNUAL REPORT/ID

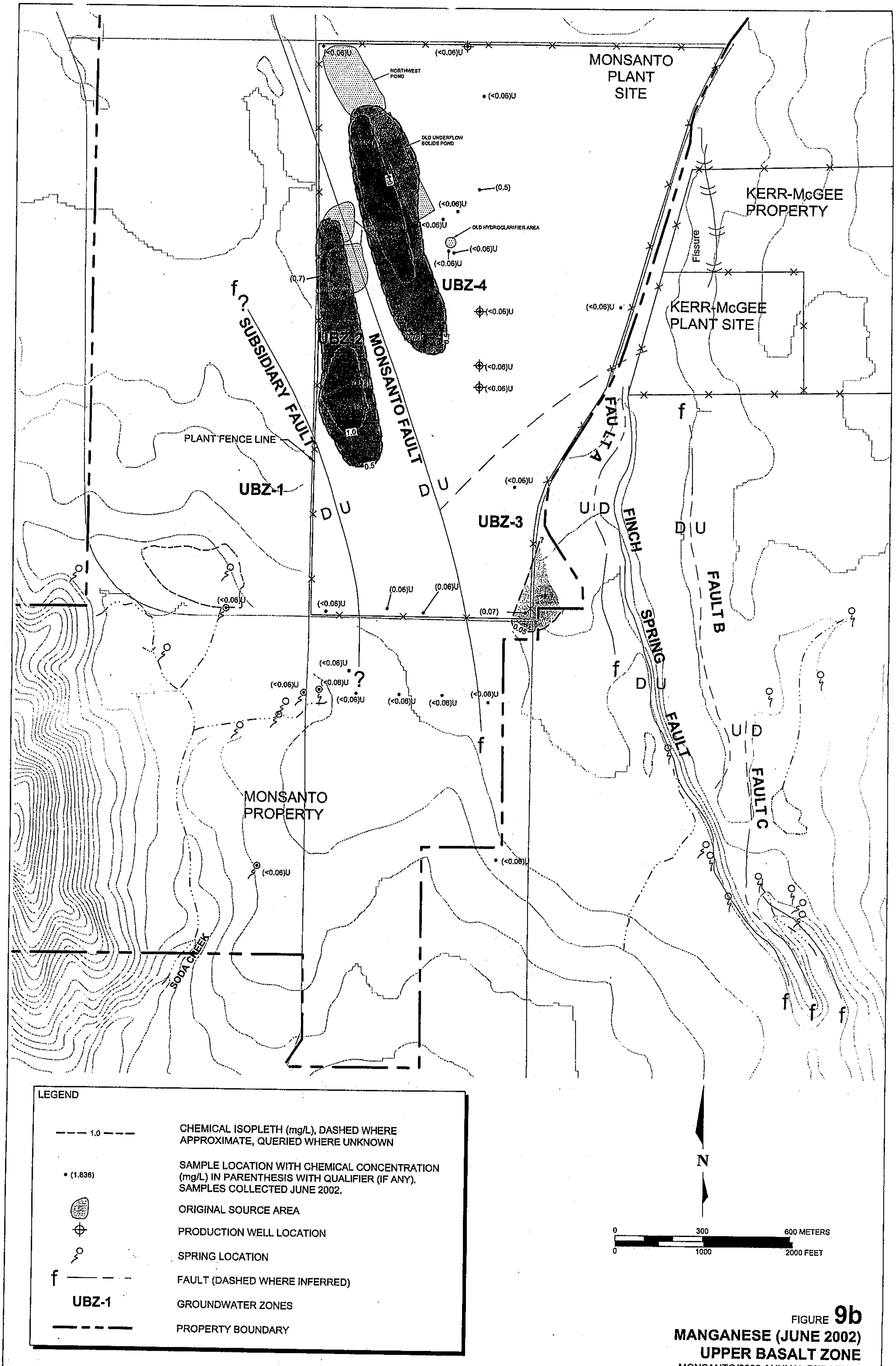


FIGURE **9b**

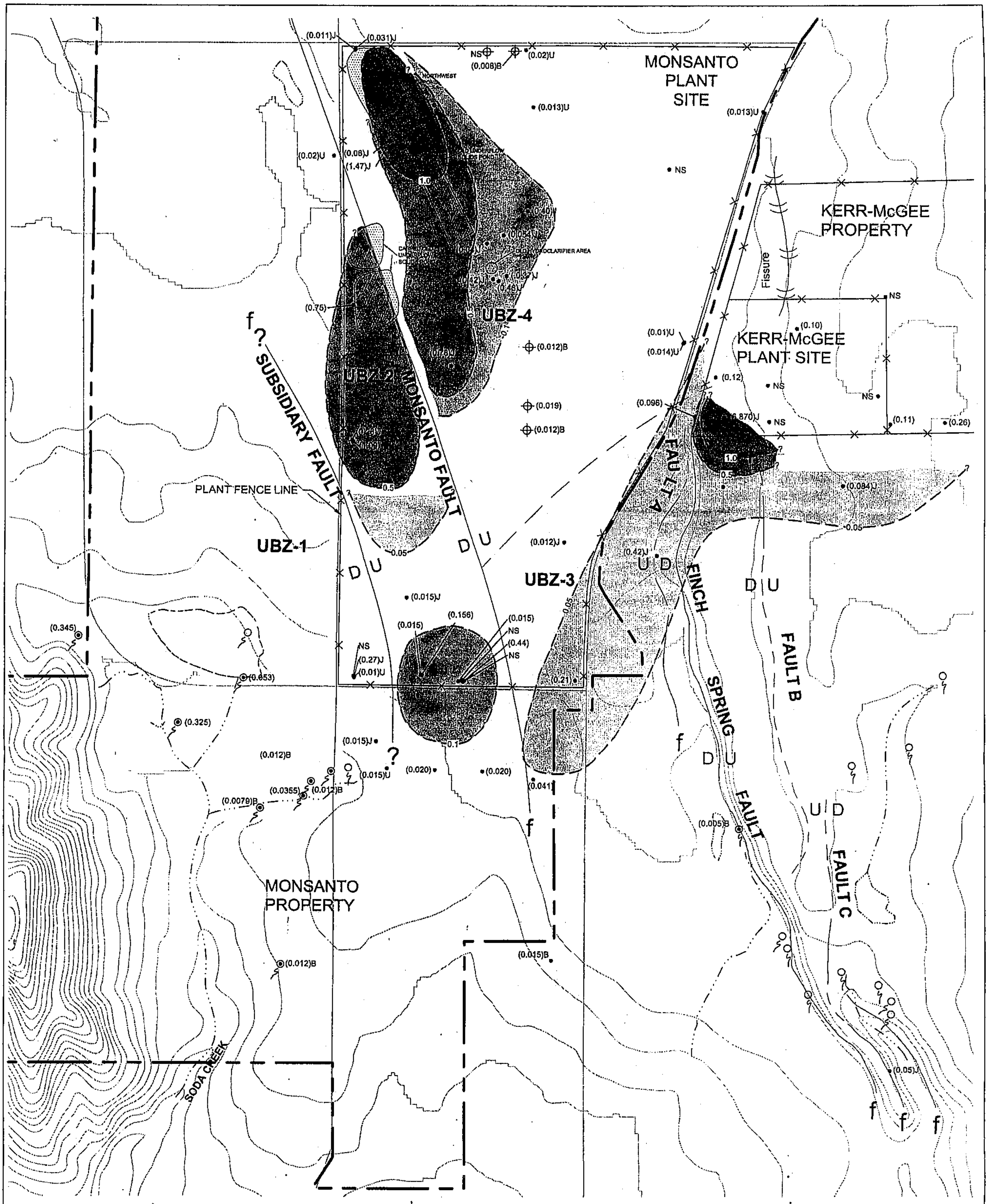
MANGANESE (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F06.dwg May 22, 2003 – 11:25am

Golder Associates



LEGEND

— — 1.0 — —	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.838)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 1993
▨	ORIGINAL SOURCE AREA
⊕	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f —— - —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
— — —	PROPERTY BOUNDARY

N

0 300 600 METERS
0 1000 2000 FEET

FIGURE 9a
MANGANESE (MAY 1993)
UPPER BASALT ZONE
MONSANTO/PHASE I RI REPORT/ID

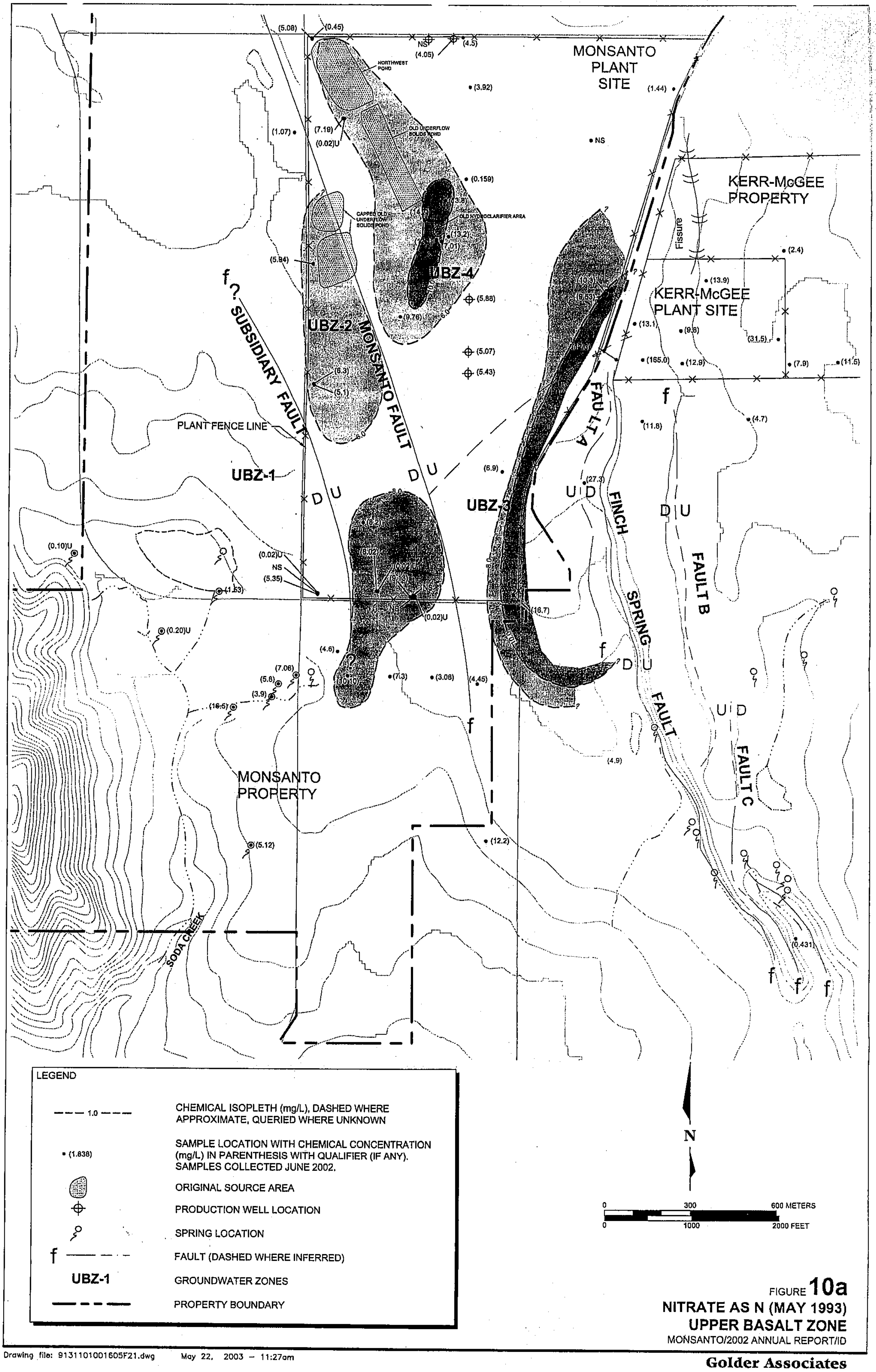
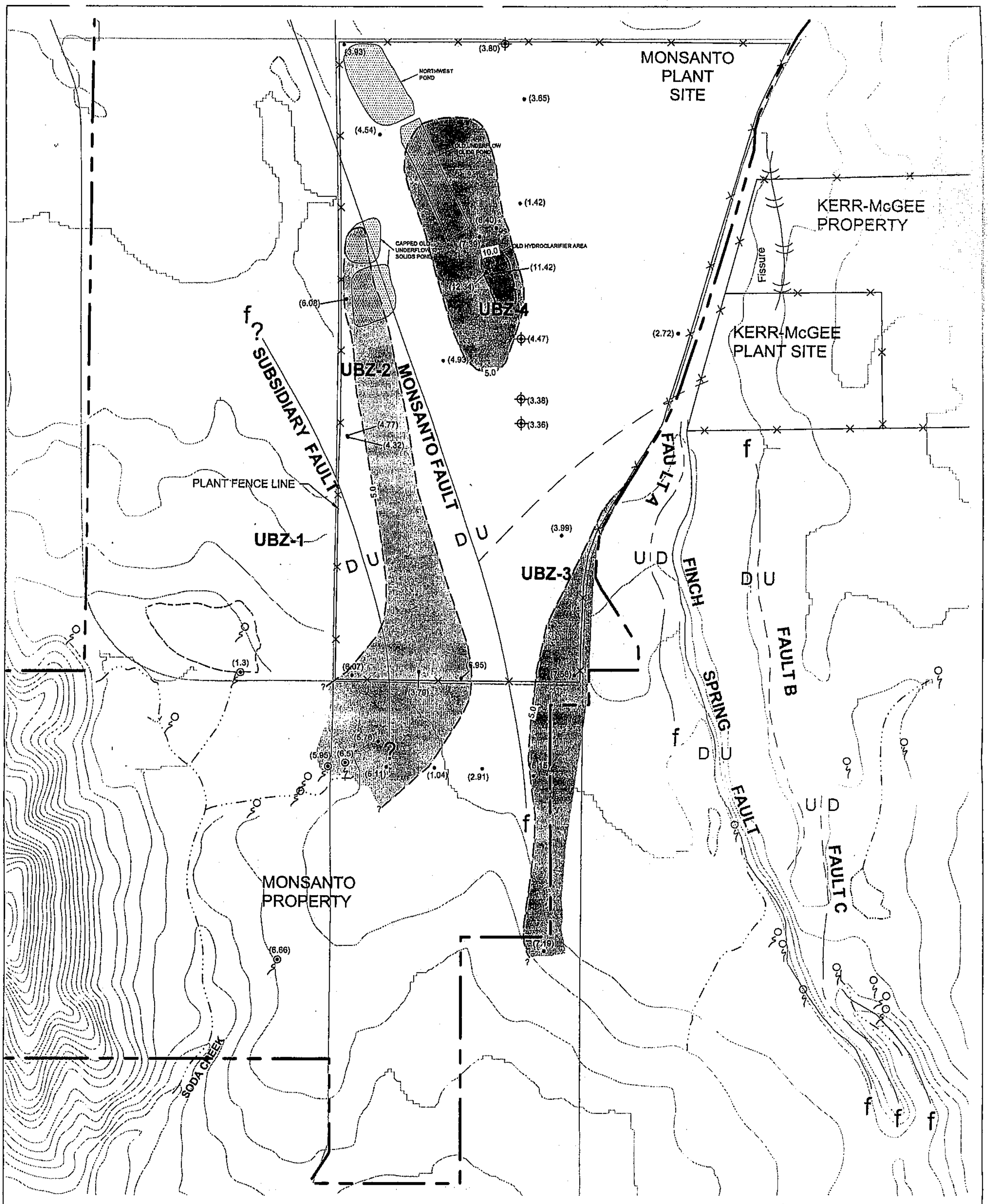


FIGURE **10a**

NITRATE AS N (MAY 1993)
UPPER BASALT ZONE
MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F21.dwg May 22, 2003 – 11:27am

Golder Associates



LEGEND

— — 1.0 — —	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.838)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 2002.
▨	ORIGINAL SOURCE AREA
⊕	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f — - —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
— — —	PROPERTY BOUNDARY

N

0 300 600 METERS

0 1000 2000 FEET

FIGURE **10b**

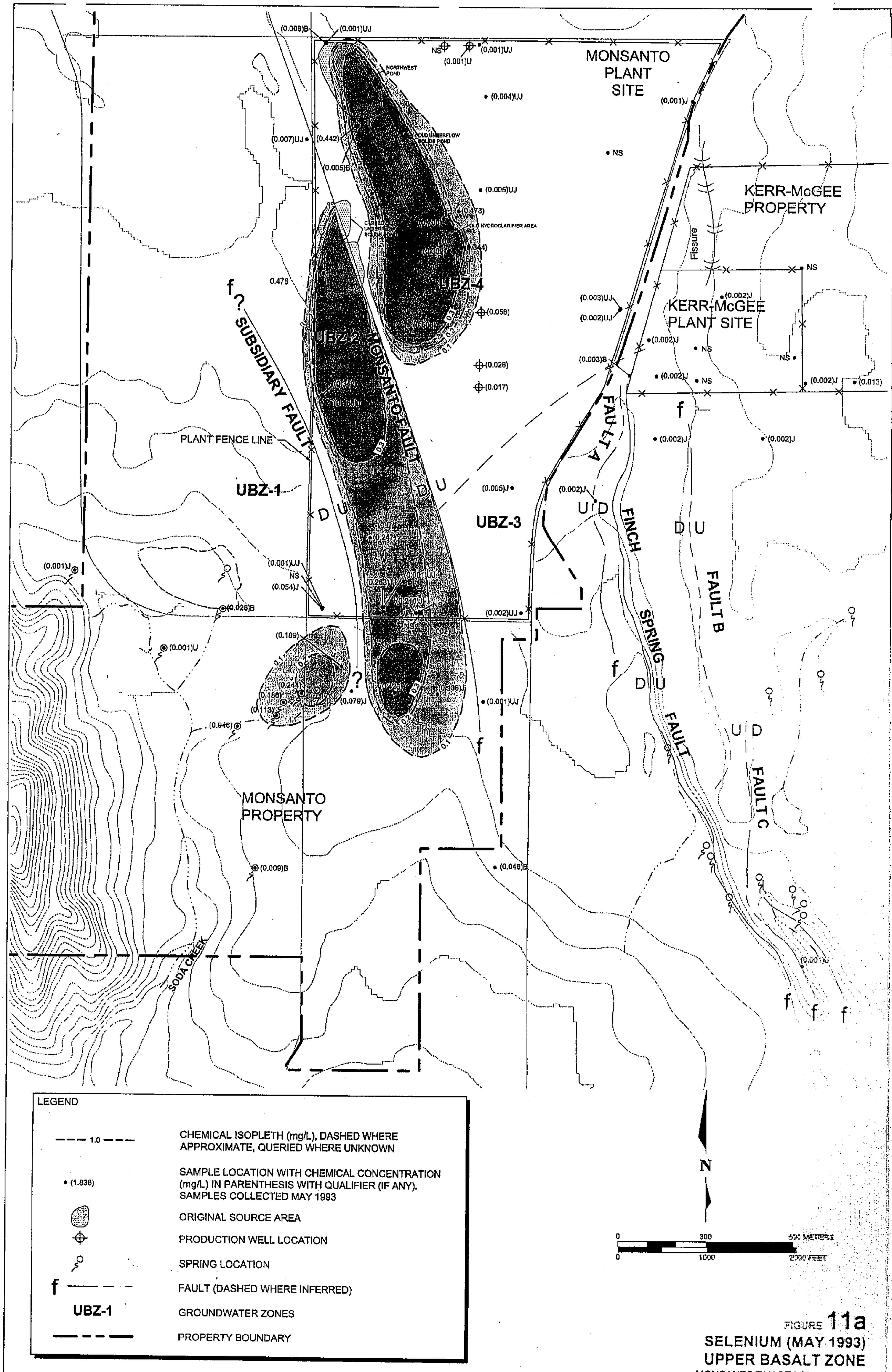
NITRATE AS N (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F07.dwg May 22, 2003 – 11:20am

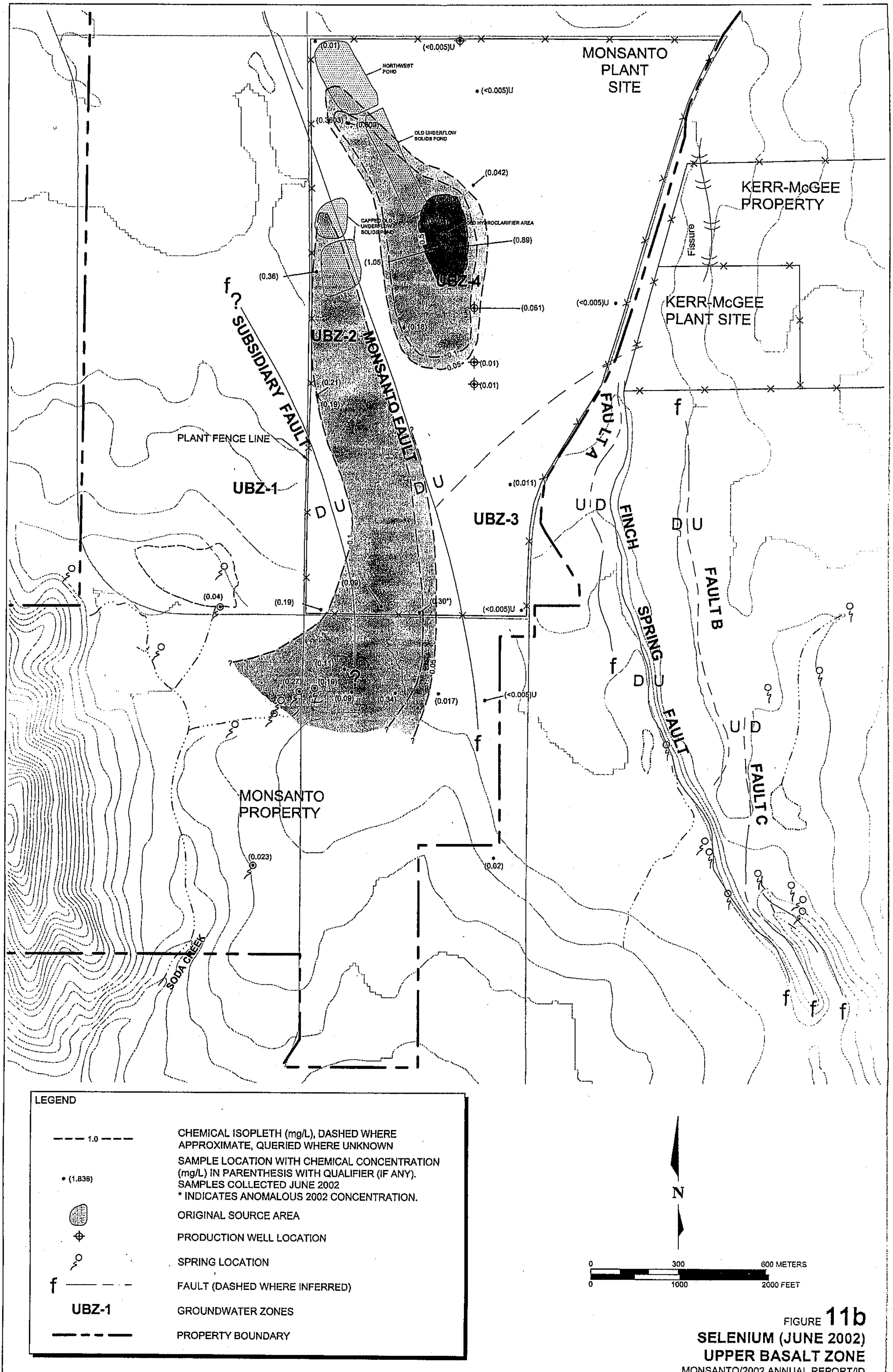
Golder Associates



LEGEND

--- 1.0 ---	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.638)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED MAY 1993
▨	ORIGINAL SOURCE AREA
⊕	PRODUCTION WELL LOCATION
♁	SPRING LOCATION
f — - —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
— — —	PROPERTY BOUNDARY

FIGURE 11a
SELENIUM (MAY 1993)
UPPER BASALT ZONE
MONSANTO/PHASE I RI REPORT/ID



LEGEND

——1.0——	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.838)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 2002 * INDICATES ANOMALOUS 2002 CONCENTRATION.
▨	ORIGINAL SOURCE AREA
⊕	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f —— — · —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
—— — ——	PROPERTY BOUNDARY

FIGURE **11b**

SELENIUM (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F09.dwg May 22, 2003 – 10:34am

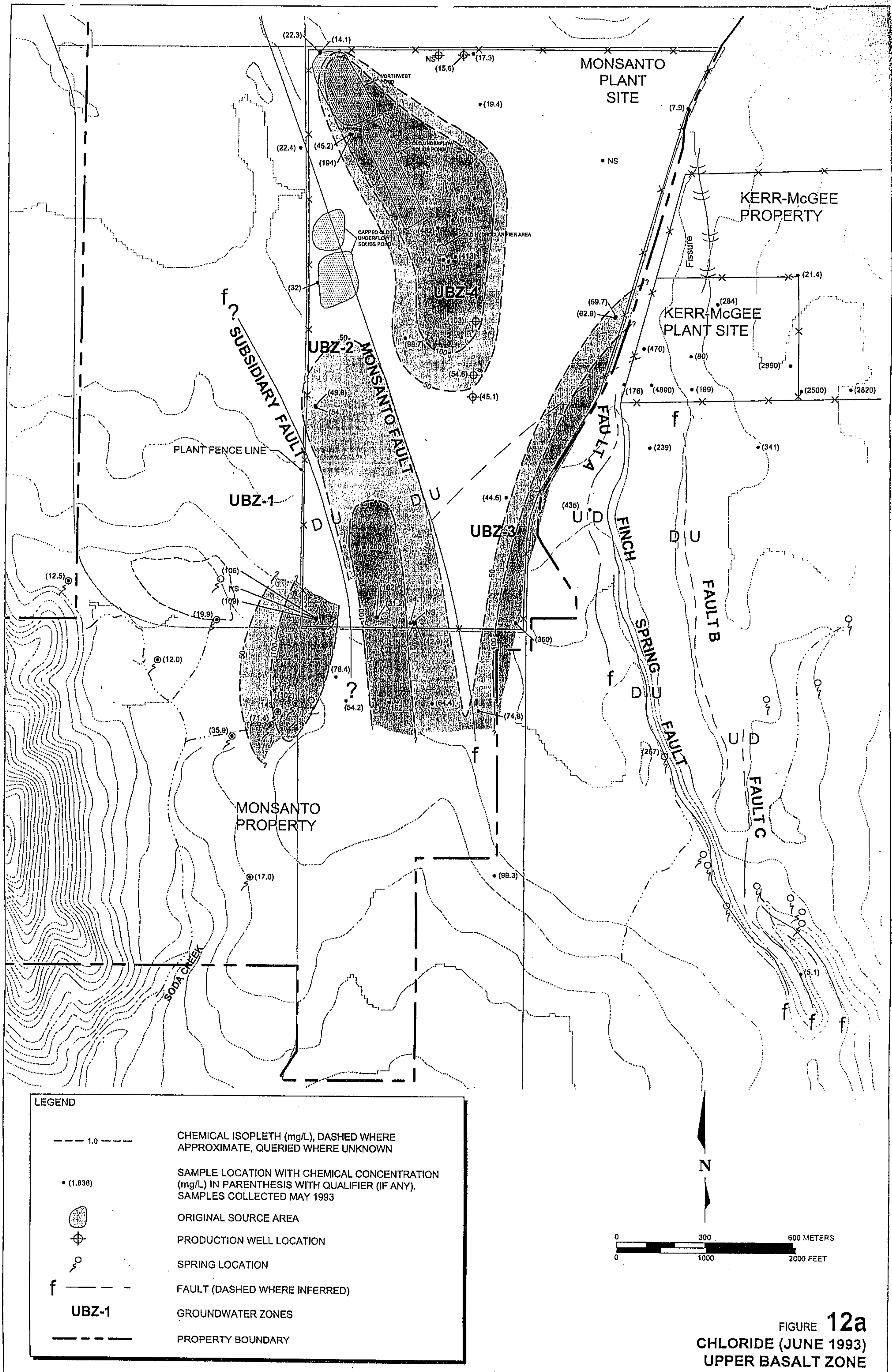
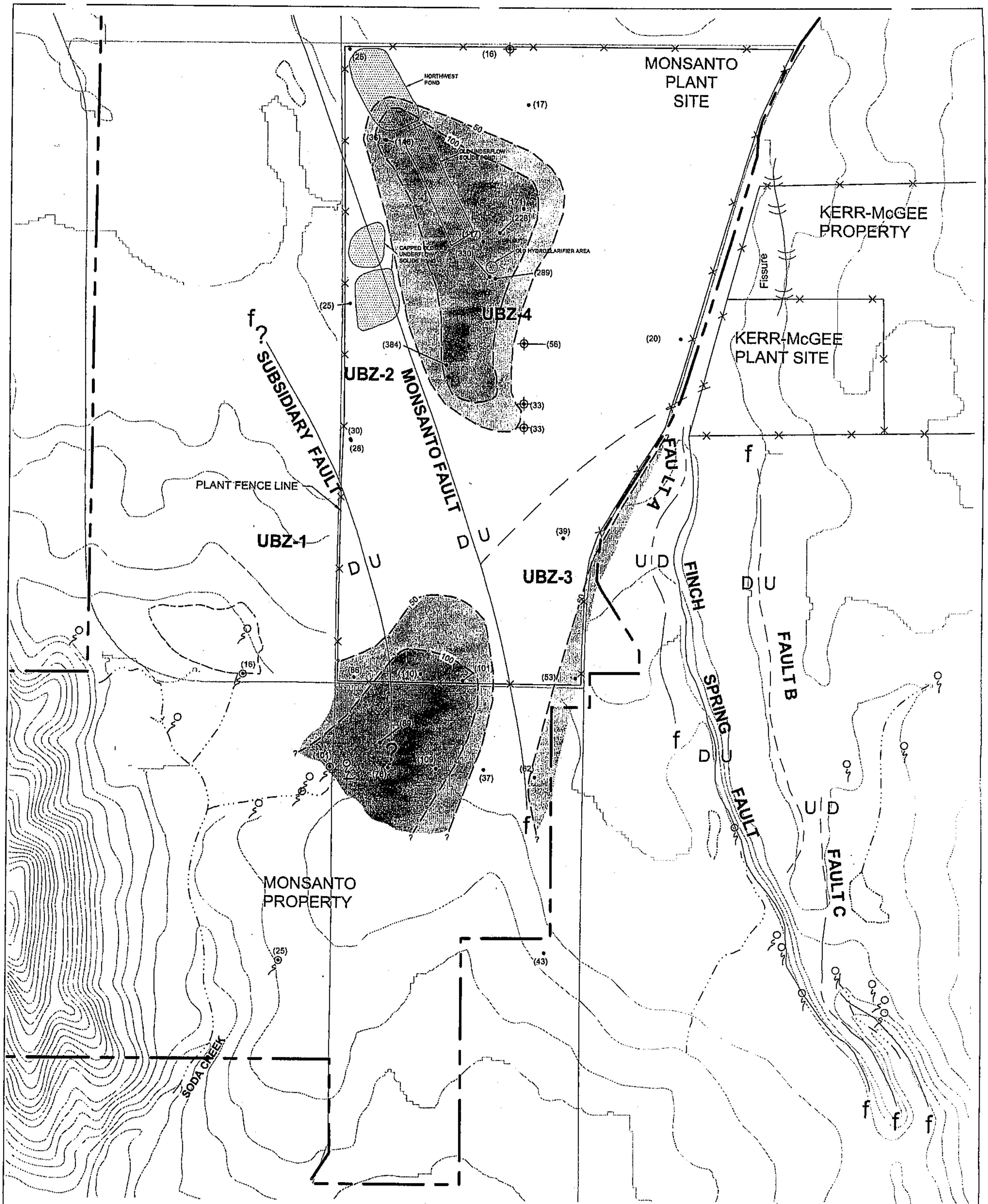


FIGURE **12a**

CHLORIDE (JUNE 1993)
UPPER BASALT ZONE
MONSANTO/PHASE I RI REPORT/ID



LEGEND

— — 1.0 — — —	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.838)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 2002.
▨	ORIGINAL SOURCE AREA
⌖	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f ——— — · —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
——— — — ———	PROPERTY BOUNDARY

N

0 300 600 METERS

0 1000 2000 FEET

FIGURE **12b**

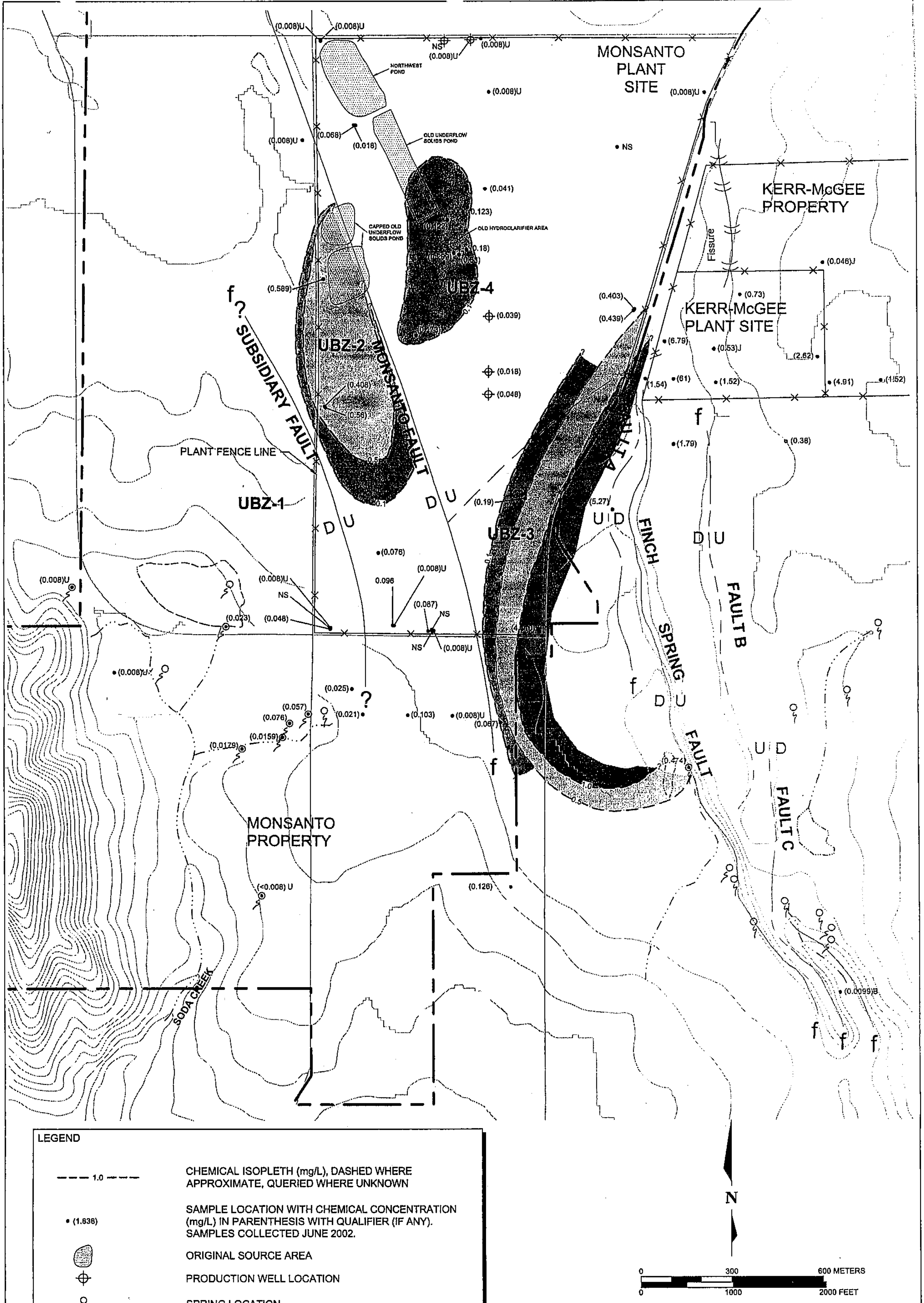
CHLORIDE (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F11.dwg May 22, 2003 – 10:36am

Golder Associates



LEGEND

— — 1.0 — —	CHEMICAL ISOPLETH (mg/L), DASHED WHERE APPROXIMATE, QUERIED WHERE UNKNOWN
• (1.836)	SAMPLE LOCATION WITH CHEMICAL CONCENTRATION (mg/L) IN PARENTHESIS WITH QUALIFIER (IF ANY). SAMPLES COLLECTED JUNE 2002.
▨	ORIGINAL SOURCE AREA
⊕	PRODUCTION WELL LOCATION
♀	SPRING LOCATION
f — - —	FAULT (DASHED WHERE INFERRED)
UBZ-1	GROUNDWATER ZONES
— — —	PROPERTY BOUNDARY

FIGURE 13a

MOLYBDENUM (MAY 1993)
UPPER BASALT ZONE
MONSANTO/2002 ANNUAL REPORT/ID

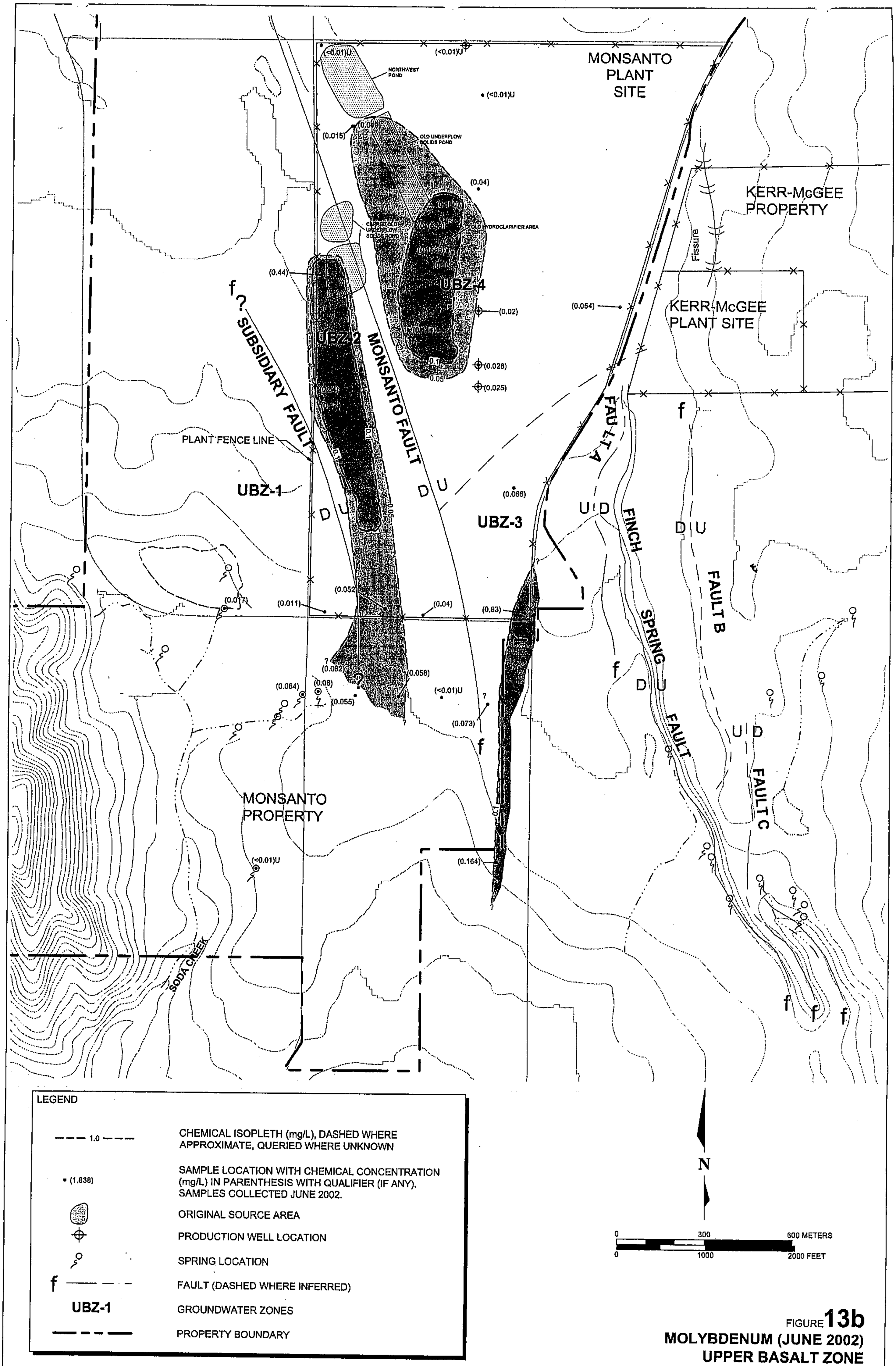


FIGURE **13b**

MOLYBDENUM (JUNE 2002)
UPPER BASALT ZONE
MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F12.dwg May 22, 2003 – 10:54am

Golder Associates

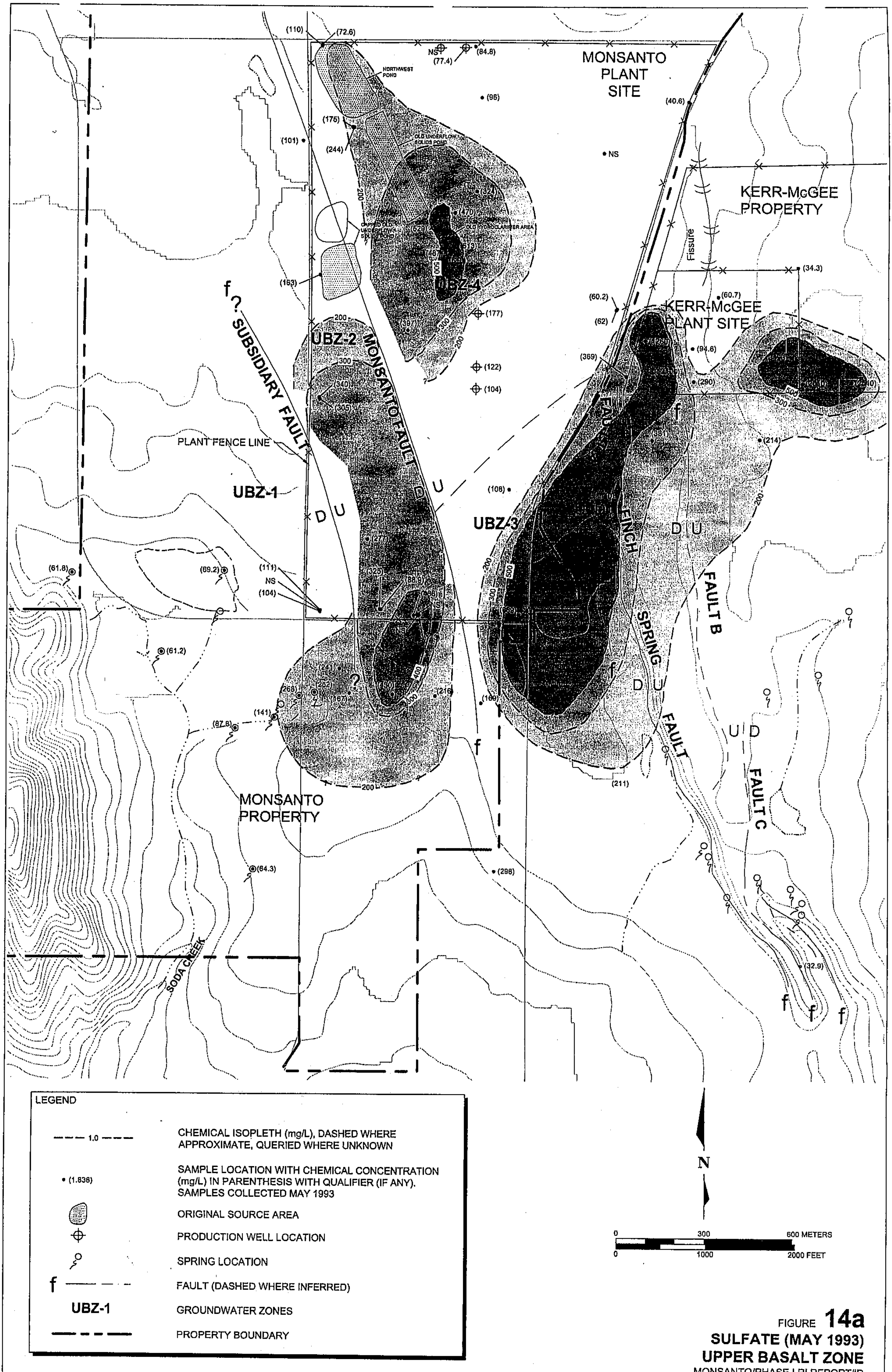


FIGURE **14a**

SULFATE (MAY 1993)

UPPER BASALT ZONE

MONSANTO/PHASE I RI REPORT/ID

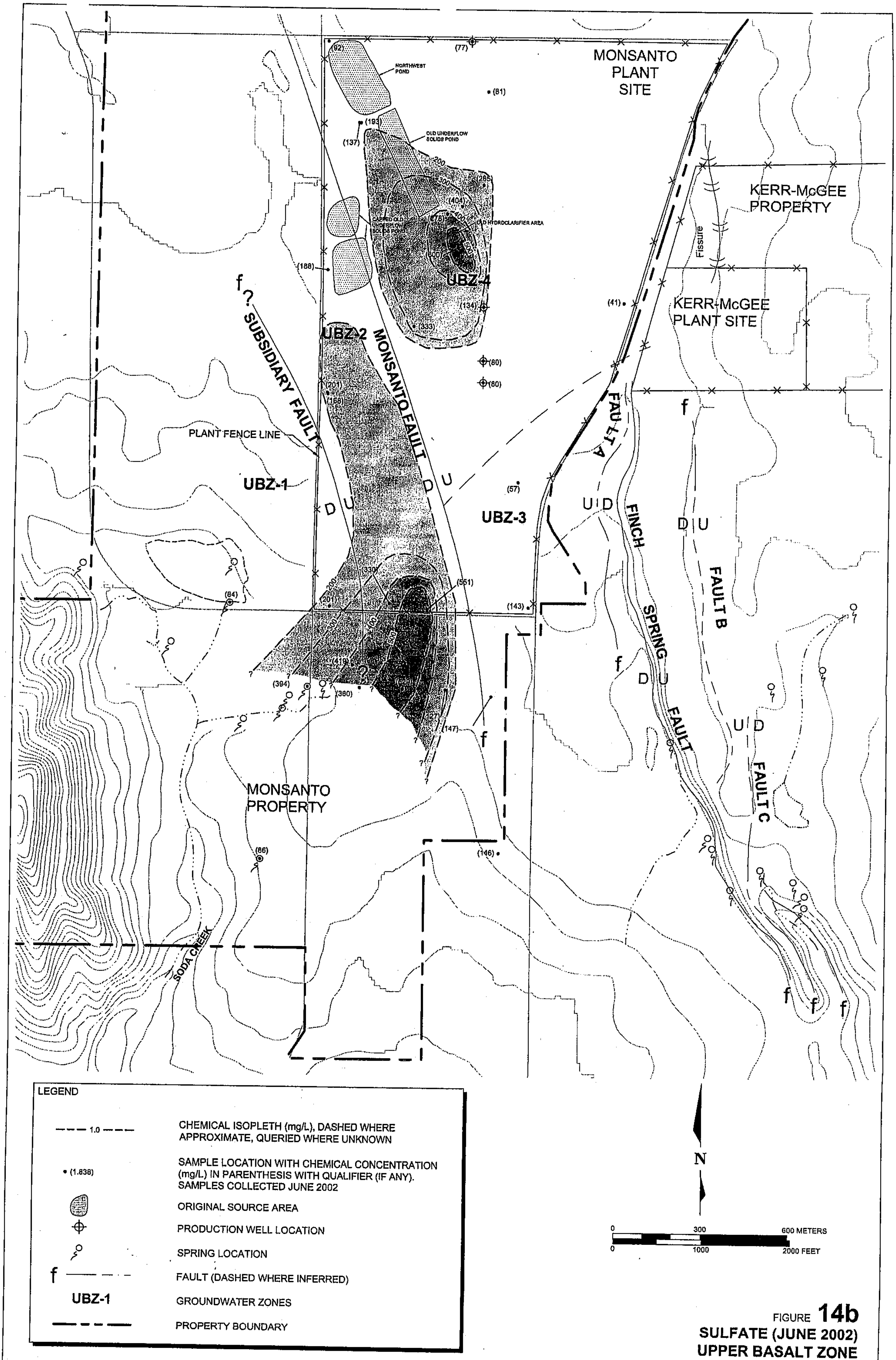


FIGURE **14b**

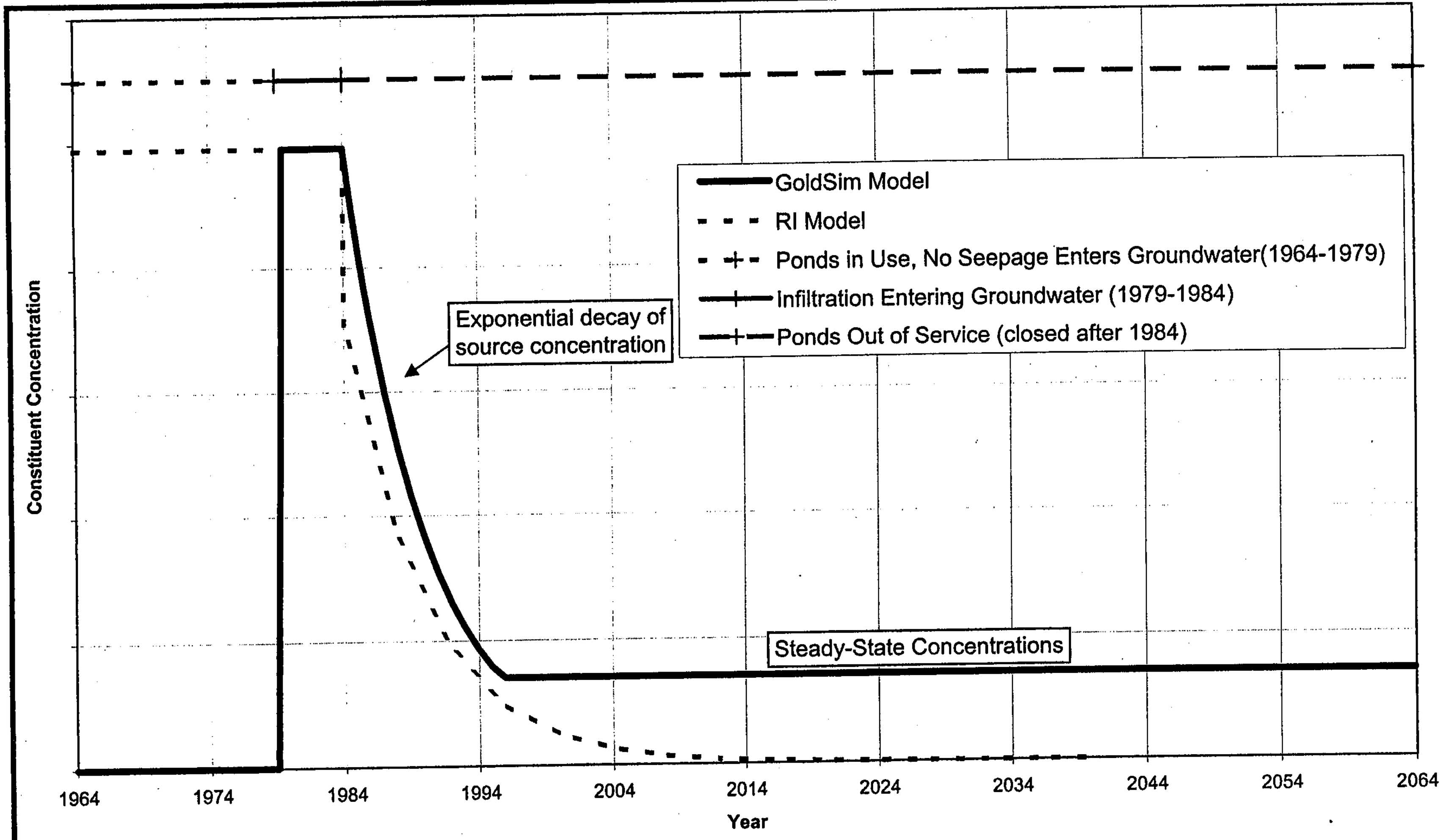
SULFATE (JUNE 2002)

UPPER BASALT ZONE

MONSANTO/2002 ANNUAL REPORT/ID

Drawing file: 9131101001605F14.dwg May 22, 2003 – 11:04am

Golder Associates



Golder Associates

Monsanto

Soda Springs Plant 5-Year Review

TITLE

UFS Ponds Source History Model

DRAWN	MPK	DATE	May 2003	JOB NO.	913-1101.605
CHECKED	DB	SCALE	na	DWG. NO.	na
REVIEWED	DB	FILE NO.	figure 15.xls	FIGURE NO.	15

ATTACHMENT A

THEORETICAL BACKGROUND OF STATISTICAL METHODS

Ilmanlaadun julkaisuja
Publikationer om luftkvalitet
Publications on air quality

No. 31

DETECTING TRENDS OF ANNUAL VALUES OF ATMOSPHERIC POLLUTANTS BY THE MANN-KENDALL TEST AND SEN'S SLOPE ESTIMATES
-THE EXCEL TEMPLATE APPLICATION MAKESENS

Timo Salmi
Anu Määttä
Pia Anttila
Tuija Ruoho-Airola
Toni Amnell

Ilmatieteen laitos
Meteorologiska Institutet
Finnish Meteorological Institute

Helsinki 2002

ISBN 951-697-563-1
ISSN 1456-789X
Painopaikka:Edita Oyj

Helsinki 2002

FINNISH METEOROLOGICAL INSTITUTE

Published by Finnish Meteorological Institute
Vuorikatu 24, P.O. Box 503
FIN-00101 Helsinki, Finland

Series title, number and report code of publication
Publications on Air Quality No. 31
Report code FMI-AQ-31
Date August 2002

Authors
Timo Salmi, Anu Määttä, Pia Anttila,
Tuija Ruoho-Airola and Toni Amnell

Name of project Air Quality Assessment in the Baltic countries as a consequence of local pollution and long range transport - a co-operation between Nordic and Baltic countries within the framework of the EMEP's 20 years Assessment

Commissioned by Nordic Council of Ministers

Title

Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates –the Excel template application MAKESENS

Abstract

An Excel template – MAKESENS – is developed for detecting and estimating trends in the time series of annual values of atmospheric and precipitation concentrations. The procedure is based on the nonparametric Mann-Kendall test for the trend and the nonparametric Sen's method for the magnitude of the trend. The Mann-Kendall test is applicable to the detection of a monotonic trend of a time series with no seasonal or other cycle. The Sen's method uses a linear model for the trend. The theory of the calculation, the user's manual and the macro code are presented. As an example the long term trends of precipitation and atmospheric concentrations of some compounds at the Virolahti air quality monitoring station of the Finnish Meteorological Institute are calculated and briefly discussed.

Publishing unit
Finnish Meteorological Institute, Air Quality Research

Classification (UDK)	Keywords
504.064 519.234	trend, Mann-Kendall test, Sen's method, annual time series, trend significance

ISSN and series title
1456-789X Publications on Air Quality

ISBN	Language
951-697-563-1	English

Sold by
Finnish Meteorological Institute / Library
P.O.Box 503, FIN-00101 Helsinki
Finland

Pages 35 Price

Note

Table of Contents

1 Introduction

An Excel template MAKESENS (Mann-Kendall test for trend and Sen's slope estimates) is developed for detecting and estimating trends in the time series of the annual values of atmospheric and precipitation concentrations. The need for this kind of simple and easy- to-use tool came up in the research project "Air quality Assessment in the Baltic countries as a consequence of local pollution and long range transport - a co-operation between Nordic and Baltic countries within the framework of EMEP's 20-years Assessment" financed by the Nordic Council of Ministers. This subproject is a contribution to the EMEP's (Evaluation of the Long-Range Transmission of Air Pollutants in Europe) twenty years of assessment work initiated by the EMEP's Task Force on Measurements and Modelling in Vienna October 2000 (TFMM 2000). This European-wide effort will assess the outcome of the emission control measures in Europe between 1980-2000, focusing on the significance of changes in concentrations and deposition in relation to emission changes.

The calculation of the Mann-Kendall test and the nonparametric Sen's method are briefly described here. We also present a detailed user's manual of MAKESENS, its macro code and some examples. In addition to the statistical calculations, MAKESENS also provides a simple graphical interface to assist the visual inspection of the time series and the statistical results. The details of the theories can be found in Gilbert (1987). Also Sirois (1998) gives an educative summary of the application of these methods in atmospheric chemistry studies.

2 Calculation of the Mann-Kendall test and the magnitude of the trend with the Sen's method in MAKESENS

MAKESENS performs two types of statistical analyses. First the presence of a monotonic increasing or decreasing trend is tested with the nonparametric Mann-Kendall test and secondly the slope of a linear trend is estimated with the nonparametric Sen's method (Gilbert 1987). These methods are here used in their basic forms; the Mann-Kendall test is suitable for cases where the trend may be assumed to be monotonic and thus no seasonal or other cycle is present in the data. The Sen's method uses a linear model to estimate the slope of the trend and the variance of the residuals should be constant in time. These methods offer many advantages that have made them useful in analysing atmospheric chemistry data. Missing values are allowed and the data need not conform to any particular distribution. Besides, the Sen's method is not greatly affected by single data errors or outliers.

2.1 Mann-Kendall test

The Mann-Kendall test is applicable in cases when the data values x_i of a time series can be assumed to obey the model

$$x_i = f(t_i) + \varepsilon_i \ , \qquad (1)$$

where $f(t)$ is a continuous monotonic increasing or decreasing function of time and the residuals ε_i can be assumed to be from the same distribution with zero mean. It is therefore assumed that the variance of the distribution is constant in time.

We want to test the null hypothesis of no trend, H_o, i.e. the observations x_i are randomly ordered in time, against the alternative hypothesis, H_1, where there is an increasing or decreasing monotonic trend. In the computation of this statistical test MAKESENS exploits both the so called S statistics given in Gilbert (1987) and the normal approximation (Z statistics). For time series with less than 10 data points the S test is used, and for time series with 10 or more data points the normal approximation is used.

2.1.1 Number of data values less than 10

The number of annual values in the studied data series is denoted by n. Missing values are allowed and n can thus be smaller than the number of years in the studied time series.

The Mann-Kendall test statistic S is calculated using the formula

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \operatorname{sgn}(x_j - x_k), \tag{2}$$

where x_j and x_k are the annual values in years j and k, $j > k$, respectively, and

$$\operatorname{sgn}(x_j - x_k) = \begin{cases} 1 & \text{if } x_j - x_k > 0 \\ 0 & \text{if } x_j - x_k = 0 \\ -1 & \text{if } x_j - x_k < 0 \end{cases}. \tag{3}$$

If n is 9 or less, the absolute value of S is compared directly to the theoretical distribution of S derived by Mann and Kendall (Gilbert, 1987). In MAKESENS the two-tailed test is used for four different significance levels α: 0.1, 0.05, 0.01 and 0.001. At certain probability level H_0 is rejected in favour of H_1 if the absolute value of S equals or exceeds a specified value $S_{\alpha/2}$, where $S_{\alpha/2}$ is the smallest S which has the probability less than $\alpha/2$ to appear in case of no trend. A positive (negative) value of S indicates an upward (downward) trend.

The minimum values of n with which these four significance levels can be reached are derived from the probability table for S as follows.

Significance level α	**required n**
0.1	≥ 4
0.05	≥ 5
0.01	≥ 6
0.001	≥ 7

The significance level 0.001 means that there is a 0.1% probability that the values x_i are from a random distribution and with that probability we make a mistake when rejecting H_0 of no trend. Thus the significance level 0.001 means that the existence of a monotonic trend is very probable. Respectively the significance level 0.1 means that there is a 10% probability that we make a mistake when rejecting H_0.

2.1.2 Number of data values 10 or more

If n is at least 10 the normal approximation test is used. However, if there are several tied values (i.e. equal values) in the time series, it may reduce the validity of the normal approximation when the number of data values is close to 10.

First the variance of S is computed by the following equation which takes into account that ties may be present:

$$VAR(S) = \frac{1}{18}\left[n(n-1)(2n+5) - \sum_{p=1}^{q} t_p(t_p-1)(2t_p+5) \right]. \tag{4}$$

Here q is the number of tied groups and t_p is the number of data values in the p^{th} group.

The values of S and $VAR(S)$ are used to compute the test statistic Z as follows

$$Z = \begin{cases} \dfrac{S-1}{\sqrt{VAR(S)}} & if\ S > 0 \\ 0 & if\ S = 0 \\ \dfrac{S+1}{\sqrt{VAR(S)}} & if\ S < 0 \end{cases} \tag{5}$$

The presence of a statistically significant trend is evaluated using the Z value. A positive (negative) value of Z indicates an upward (downward) trend. The statistic Z has a normal distribution. To test for either an upward or downward monotone trend (a two-tailed test) at α level of significance, H_0 is rejected if the absolute value of Z is greater than $Z_{1-\alpha/2}$, where

$Z_{1-\alpha/2}$ is obtained from the standard normal cumulative distribution tables. In MAKESENS the tested significance levels α are 0.001, 0.01, 0.05 and 0.1.

2.2 Sen's method

To estimate the true slope of an existing trend (as change per year) the Sen's nonparametric method is used. The Sen's method can be used in cases where the trend can be assumed to be linear. This means that $f(t)$ in equation (1) is equal to

$$f(t) = Qt + B \tag{6}$$

where Q is the slope and B is a constant.

To get the slope estimate Q in equation (6) we first calculate the slopes of all data value pairs

$$Q_i = \frac{x_j - x_k}{j - k}, \tag{7}$$

where $j>k$.

If there are n values x_j in the time series we get as many as $N = n(n-1)/2$ slope estimates Q_i. The Sen's estimator of slope is the median of these N values of Q_i. The N values of Q_i are ranked from the smallest to the largest and the Sen's estimator is

$$Q = Q_{[(N+1)/2]},\ \text{if } N \text{ is odd}$$

or (8)

$$Q = \frac{1}{2}\left(Q_{[N/2]} + Q_{[(N+2)/2]}\right),\ \text{if } N \text{ is even.}$$

A 100(1-α)% two-sided confidence interval about the slope estimate is obtained by the nonparametric technique based on the normal distribution. The method is valid for *n* as small as 10 unless there are many ties.

The procedure in MAKESENS computes the confidence interval at two different confidence levels; $\alpha = 0.01$ and $\alpha = 0.05$, resulting in two different confidence intervals.

At first we compute

$$C_\alpha = Z_{1-\alpha/2}\sqrt{VAR(S)}\,, \tag{9}$$

where *VAR(S)* has been defined in equation (4), and $Z_{1-\alpha/2}$ is obtained from the standard normal distribution.

Next $M_1 = (N - C_\alpha)/2$ and $M_2 = (N + C_\alpha)/2$ are computed. The lower and upper limits of the confidence interval, Q_{min} and Q_{max}, are the M_1th largest and the $(M_2 + 1)$th largest of the N ordered slope estimates Q_i. If M_1 is not a whole number the lower limit is interpolated. Correspondingly, if M_2 is not a whole number the upper limit is interpolated.

To obtain an estimate of B in equation (6) the *n* values of differences $x_i - Qt_i$ are calculated. The median of these values gives an estimate of B (Sirois 1998). The estimates for the constant B of lines of the 99% and 95% confidence intervals are calculated by a similar procedure.

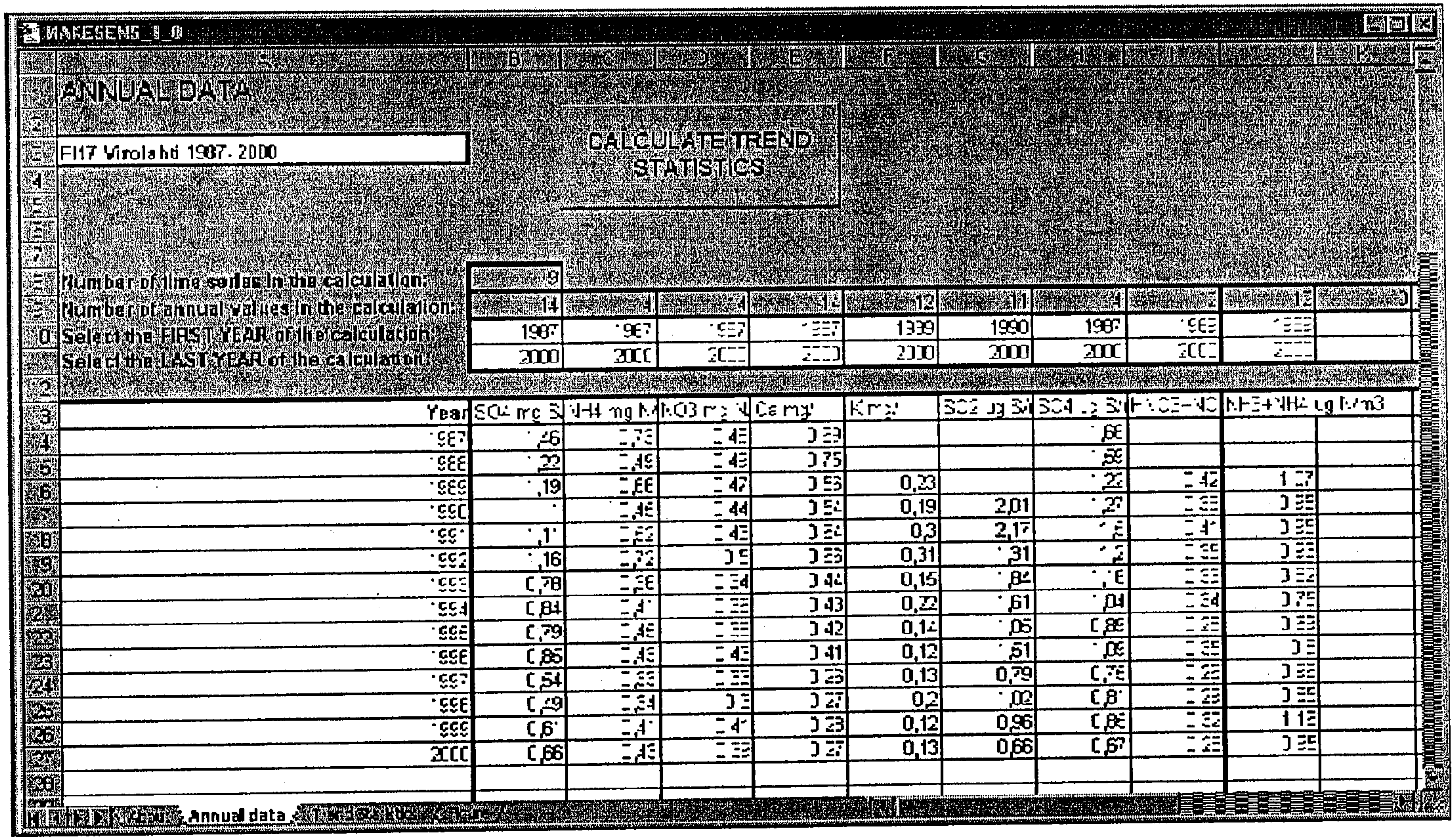
3 User's manual for MAKESENS

The MAKESENS template was created using Microsoft Excel 97 and the macros were coded with Microsoft Visual Basic. The template consists of four worksheets: **About, Annual data, Trend Statistics** and **Figure**. The **About** worksheet gives general information about the template. The data of time series are entered into the **Annual data** worksheet. The calculation macro can be activated by using the button **Calculate Trend Statistics** and the **Trend Statistics** worksheet contains the results. Finally, the original data and the statistics can be viewed numerically and visually in the **Figure** worksheet one time series at a time.

3.1 Entering the time series and other input values

All the input values are entered in the **Annual data** worksheet (see Figure 1). The years, the annual values and the names of the time series have to be typed or copied (**Paste Special/Values**) to the fixed places of the worksheet. The cells in the worksheet, in which the user may enter data have no shading. The other cells are protected and have grey shading.

- **A title to the whole data set** can be typed in cell **A3** . This title is also shown in cells **'Trend Statistics'!A3** and **'Figure'!B4.**
- **The names of the time series** are entered in cells **B13:Z13** starting from the column **B.** The maximum number of time series that can be entered is 25. The names are transposed into the cells **'Trend Statistics'!A6:A30.** The name of the time series is also shown in cell **'Figure'!C10** and as the title of Y-axis in the figure.
- Cell **A13** is reserved for the column title "Year".
- From cell **A14** downwards the user must enter an **increasing and continuous series of years**. The range of the years shall cover all the time series but excess years in the beginning or at the end are allowed. The number of years is limited to 100 but can be extended by changing the value of the constant **MaxData** in the macro code (Appendix 1).
- The **annual values** of each time series must be entered below the name of the time series according to the years in the column A. An empty cell indicates a missing value. The values of a time series or the entire table of annual data can also be copied from another table.



ANNUAL DATA

FI17 Virolahti 1987-2000

Number of time series in the calculation: 9

Number of annual values in the calculation:	14	4	4	[illegible]	12	11	4	[illegible]	[illegible]	0
Select the FIRST YEAR of the calculation:	1987	[illegible]	[illegible]	[illegible]	[illegible]	1990	1987	[illegible]	[illegible]	
Select the LAST YEAR of the calculation:	2000	[illegible]	[illegible]	[illegible]	[illegible]	2000	[illegible]	[illegible]	[illegible]	

Year	SO4 mg S	NH4 mg N	NO3 mg N	Ca mg/l	K mg/l	SO2 µg S	SO4 µg S	[illegible]	NH3+NH4 µg N/m3	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]	0,75			[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,23		[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,19	2,01	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,3	2,17	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,31	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	0,78	[illegible]	[illegible]	[illegible]	0,15	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	0,84	[illegible]	[illegible]	0,43	0,22	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	0,79	[illegible]	[illegible]	0,42	0,14	[illegible]	0,88	[illegible]	[illegible]	
[illegible]	0,85	[illegible]	[illegible]	0,41	0,12	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	0,54	[illegible]	[illegible]	[illegible]	0,13	0,79	[illegible]	[illegible]	[illegible]	
[illegible]	0,49	[illegible]	[illegible]	[illegible]	0,2	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,12	0,96	[illegible]	[illegible]	[illegible]	
2000	0,66	[illegible]	[illegible]	[illegible]	0,13	0,66	[illegible]	[illegible]	[illegible]	

Figure 1. The input data is entered to the **Annual data** worksheet of MAKESENS.

- **The first and the last year** to be handled in trend calculation must be entered in **rows 10 and 11**, above the names of the time series. Every time series must have its own starting and ending year. With these rows you can easily define different time spans for the trend statistics calculation of each time series. The starting and ending years are also shown in the cells **'Trend Statistics'!B6:C30**, and in **'Figure'!C11.**
- **The number of values** of each time series which are selected to trend calculation are shown in **row 9**. These values are also shown in the cells **'Trend Statistics'!D6:D30** and in **'Figure'!C12.** If the number of values for a time series is equal to or less than 9, the Mann-Kendall test is performed using the S statistics and the confidence interval for the Sen's slope estimate is not determined. If this number is at least 10, the Mann-Kendall test is performed using the Z statistic (normal approximation) and the 95% and 99% confidence intervals for the Sen's slope estimates are calculated.
- Cell **B8** shows **the number of the time series** from which the statistics will be calculated.

There is no input data checking in the trend-macro. If you get strange results or even errors, please check the input data you have entered. It is important that the values are entered in the appropriate cells. Some of the cells that are not allowed to be changed are protected.

The calculation of the trend statistics is started by clicking the **'Calculate Trend Statistics'** button in the **Annual data** worksheet. The Status bar near the bottom of the screen shows when the calculation process is ready. The summary table of the results will appear to the **Trend Statistics** worksheet (Figure 2) and the **Figure** worksheet (Figure 3) will be activated with the first time series.

3.2 Summary table of results

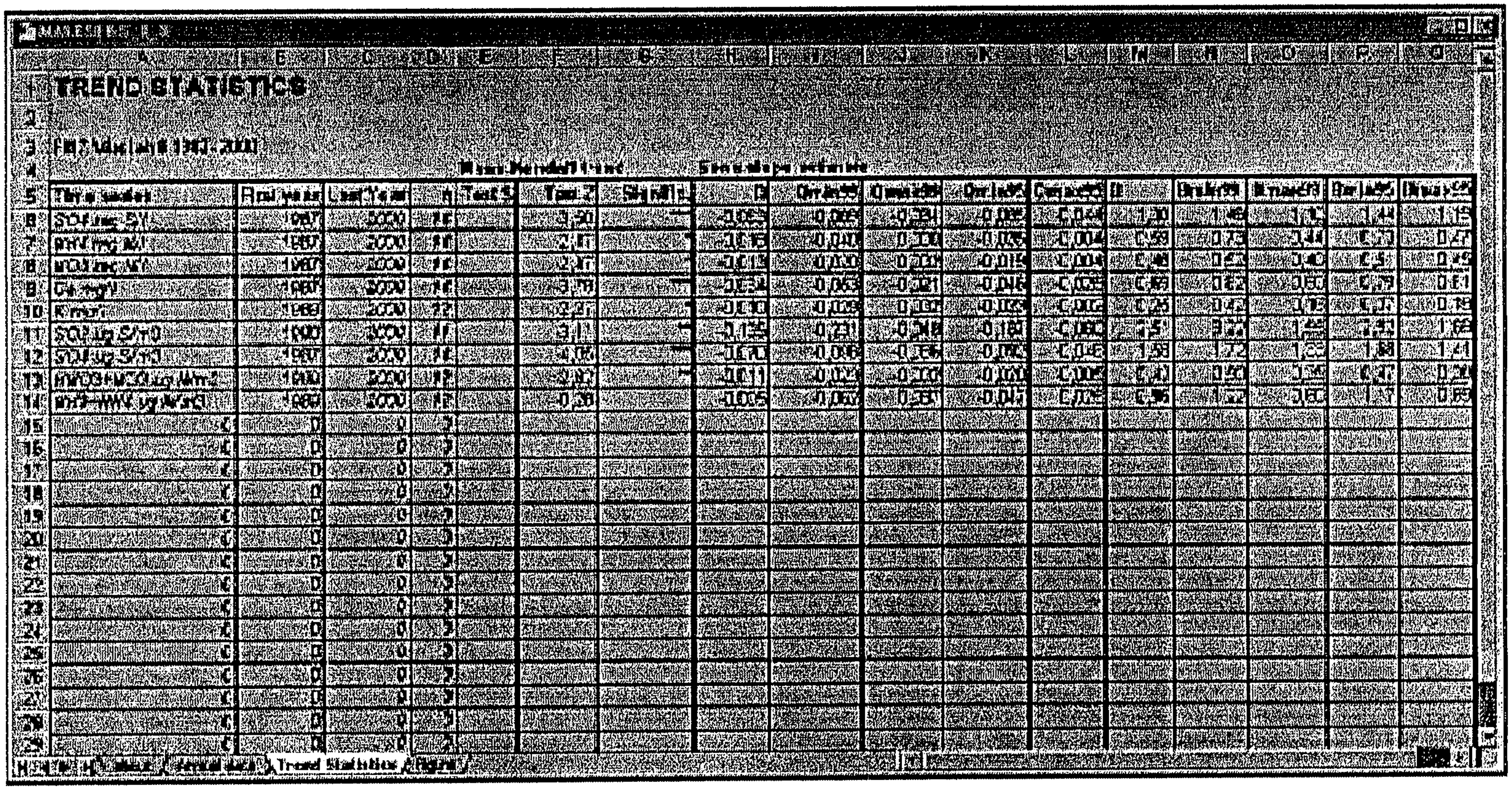
During the statistical calculations the summary table of the results in the **Trend Statistics** worksheet is updated. Results are given for each time series in rows starting from **row 6** (see Figure 2).

The values of the cell **A3** and of the area **A6:D30** are derived directly from the **Annual data** worksheet. The trend calculation procedure writes the results of the calculation to the area **E6:Q30** when you press the **"Calculate Trend Statistics"** button.

The columns in this worksheet have the following meanings:

- **Time series** (column **A**): the names of the time series are derived from the **Annual data** worksheet (from row **13**)
- **First year** (column **B**): starting year of each time series (from the **Annual data** worksheet)
- **Last year** (column **C**): ending year of each time series (from the **Annual data** worksheet)
- **n** (column **D**): the number of annual values in the calculation excluding missing values (from the **Annual data** worksheet).
- **Test S** (column **E**): If n is 9 or less, the test statistic *S* is displayed. The absolute value of *S* is compared to the probabilities of the Mann-Kendall nonparametric test for trend (Table A18 given in Gilbert 1987) to define if there is a monotonic trend or not at the level α of significance. A positive (negative) value of *S* indicates an upward (downward) trend. In n is larger than 9, this cell is empty.
- **Test Z** (column **F**): If n is at least 10, the test statistic Z is displayed. The absolute value of Z is compared to the standard normal cumulative distribution to define if there is a trend or not at the selected level α of significance. A positive (negative) value of Z indicates an upward (downward) trend. If n is 9 or less, this cell is empty.

Signific. (column **G**): the smallest significance level α with which the test shows that the null hypothesis of no trend should be rejected. If n is 9 or less, the test is based to



TREND STATISTICS

Figure 2. The **Trend Statistics** worksheet of MAKESENS shows the results of the calculation.

the S statistic and if n is at least 10, the test is based to the Z statistic (normal approximation). For the four tested significance levels the following symbols are used in the template:

***	if trend at $\alpha = 0.001$ level of significance
**	if trend at $\alpha = 0.01$ level of significance
*	if trend at $\alpha = 0.05$ level of significance
+	if trend at $\alpha = 0.1$ level of significance

If the cell is blank, the significance level is greater than 0.1.

- **Sen's slope estimate Q** (column H): the Sen's estimator for the true slope of linear trend i.e. change per unit time period (in this case a year)
- **Qmin99** (column I): the lower limit of the 99 % confidence interval of Q ($\alpha= 0.1$)
- **Qmax99** (column J): the upper limit of the 99 % confidence interval of Q ($\alpha= 0.1$)
- **Qmin95** (column K): the lower limit of the 95 % confidence interval of Q ($\alpha= 0.05$)
- **Qmax95** (column L): the upper limit of the 95 % confidence interval of Q ($\alpha= 0.05$)
- **B** (column M): estimate of the constant B in equation (6) f(year)=Q*(year-firstYear)+B for a linear trend
- **Bmin99** (column N): estimate of the constant Bmin99 in equation (6) f(year)=Qmin99*(year-firstYear)+Bmin99 for 99% confidence level of linear trend
- **Bmax99** (column O): estimate of the constant Bmax99 in equation (6) f(year)=Qmax99*(year-firstYear)+Bmax99 for 99% confidence level of linear trend:
- **Bmin95** (column P): estimate of the constant Bmin95 in equation (6) f(year)=Qmin95*(year-firstYear)+Bmin95 for 95% confidence level of a linear trend:
- **Bmax95** (column Q): estimate of the constant Bmax95 in equation (6) f(year)=Qmax95*(year-firstYear)+Bmax95 for 95% confidence level of a linear trend

When calculating the constants B in MAKESENS the time is used in the form $t = year - firstYear$, where *firstYear* is the first year of all data in the **Annual data** worksheet.

The confidence intervals are valid only if n is at least 10 and there are not many ties (equal values). If n is less that 10, the constants Q and B for the confidence intervals are not shown in MAKESENS.

3.3 Visual viewing of data and results

After the statistics calculation the results can be viewed both numerically and visually on the **Figure** worksheet (see Figure 3). The results are shown one time series at a time. You can switch from one time series to another by pressing the button **Next Time Series** and **Previous Time Series.** The title in cell **A4** is derived from the cell **'Annual data'!A3.**

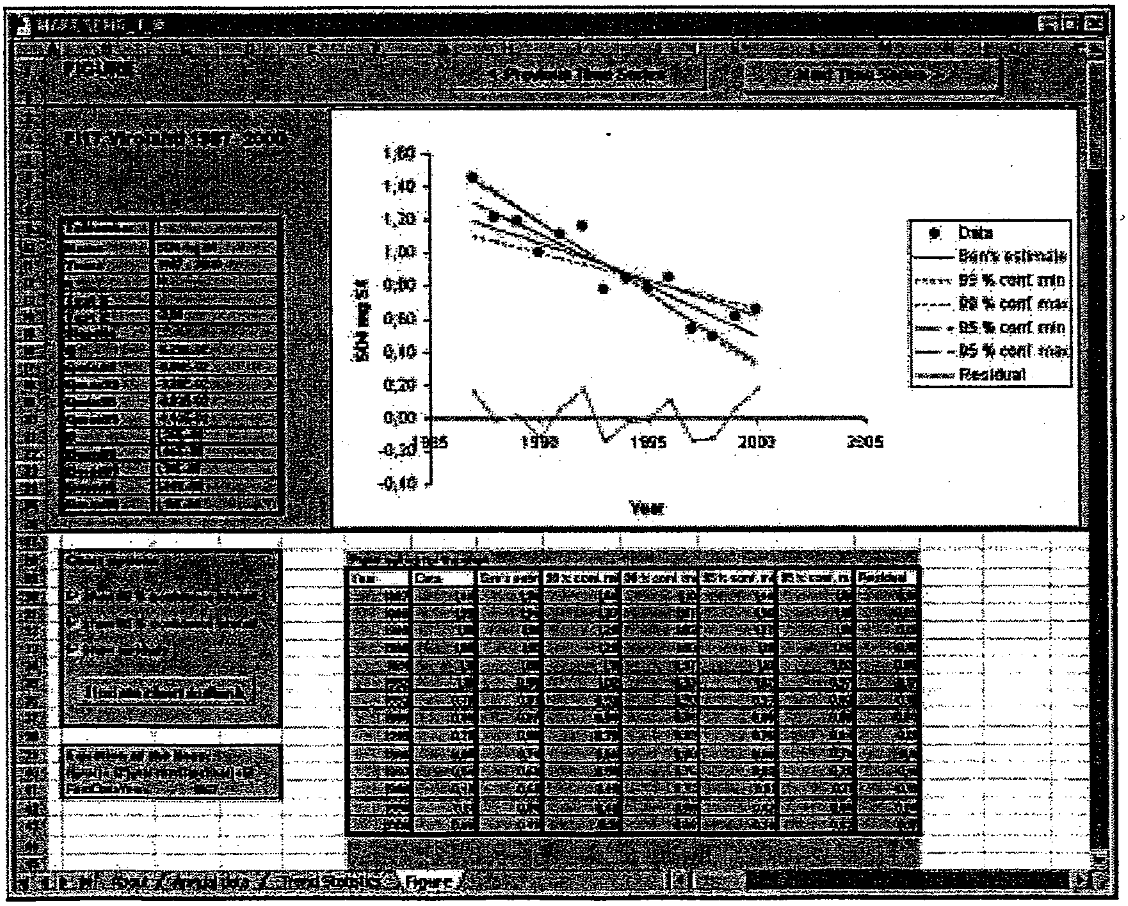


Figure 3. The **Figure** worksheet of MAKESENS.

The numerical results of the statistical calculation of one time series are shown in the area **B9:C25**. **'TsNumber'** is the ordinal number of the time series in the tables of the **Annual data** and **Trend Statistics** worksheets. The other values are derived from table **'Trend Statistics'!A5:Q30.** The first and the last year are combined to the same cell **C11**. All these values are updated when the button **Next Time Series** or **Previous Time Series** is pressed.

The table of point values for the chart is shown in columns **F:M,** from row 29 downwards. The years in column **F** and the data values in column **G** are derived from the **Annual data** worksheet. Column **H** contains the point values of the line for the Sen's estimator for a linear trend calculated with the equation f(year) = Q*(year-firstYear) + B. In columns **I:L** are the corresponding point values of the lines of 99% and 95% confidence intervals for the Sen's estimator. The calculated residuals (data minus trend) are shown in column **M.** All these values are updated when the **Next Time Series** or **Previous Time Series** button is pressed. The titles of the columns may be changed. The titles in the legend box of this chart are derived from these values.

In the chart the original data points of the time series, the Sen's estimator for a linear trend, the lines for 99% and 95% confidence intervals and the residuals (data minus trend) are shown.

In the **Chart options B28:D37** box you can quickly select whether the confidence intervals or residuals will be shown in the chart. The outlook of the chart can then be updated by pressing the **Update chart outlook** button. The macro recreates the chart and all the earlier chart settings are lost. The properties of the chart can also be modified directly with standard Excel tools but these modifications will be lost when the **Update chart outlook** button is pressed. The buttons **Next Time Series** or **Previous Time Series**, on the other hand, preserve all chart settings except the title of the value axis which will always be the name of the time series.

4 Examples

The graphs produced with MAKESENS serve as a visual help for the interpretation of the results given on the **Trend Statistics** worksheet. As an example the trend statistics of some time series from the Finnish EMEP station Virolahti (FI17) are shown in Figures 4 – 6 and briefly discussed here.

In Figure 4 there are two examples of annual time series: atmospheric SO_4^{2-} concentration and SO_4^{2-} concentration in precipitation which nicely fulfill the premises of the statistical methods used; The time series consist of annual averages with monotonously decreasing trends. The residuals seem to be from a random distribution indicating that a linear model may be applied. The statistical calculations give a high level of significance with narrow angles between the confidence lines.

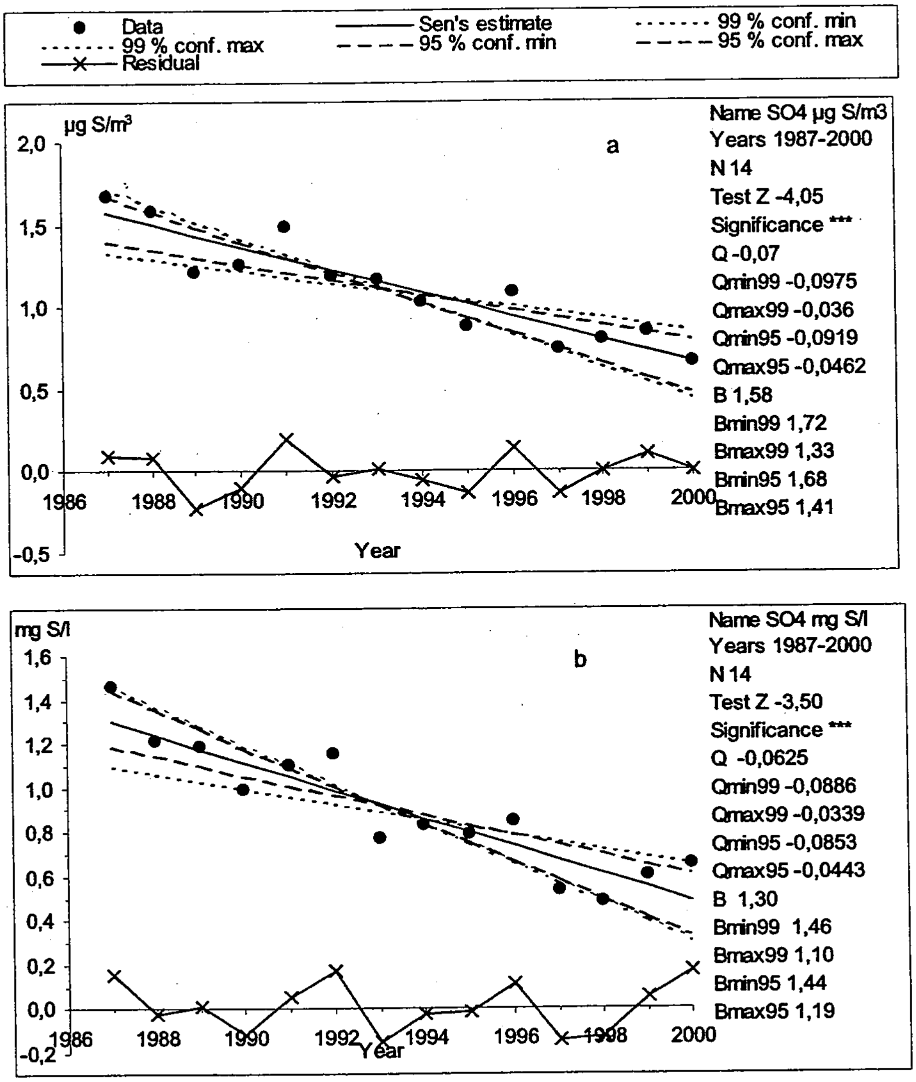


Figure 4. Annual time series and trend statistics of atmospheric SO_4^{2-} concentrations (a) and SO_4^{2-} concentrations in precipitation (b) at Virolahti FI17.

The case of NH_4^+ concentration in precipitation is a bit more problematic (Figure 5). The Mann-Kendall test indicates a decreasing trend at the 0.05 significance level but the Sen's slope gives non-positive slope even at the 1% confidence interval. Thus the decreasing trend seems to be more probable with the Sen's method than with the Mann-Kendall. The reason to this difference may be that the presumptions of the Sen's method are not totally fulfilled. The Sen's method uses a linear model for the trend but here the slope seems to diminish at the end which also can be seen from the residuals which are not random. However the trend seems to be monotonic and thus the Mann-Kendall test is suitable. This time series contains also two tied groups which may reduce the accuracy of these methods with few data values as in this case.

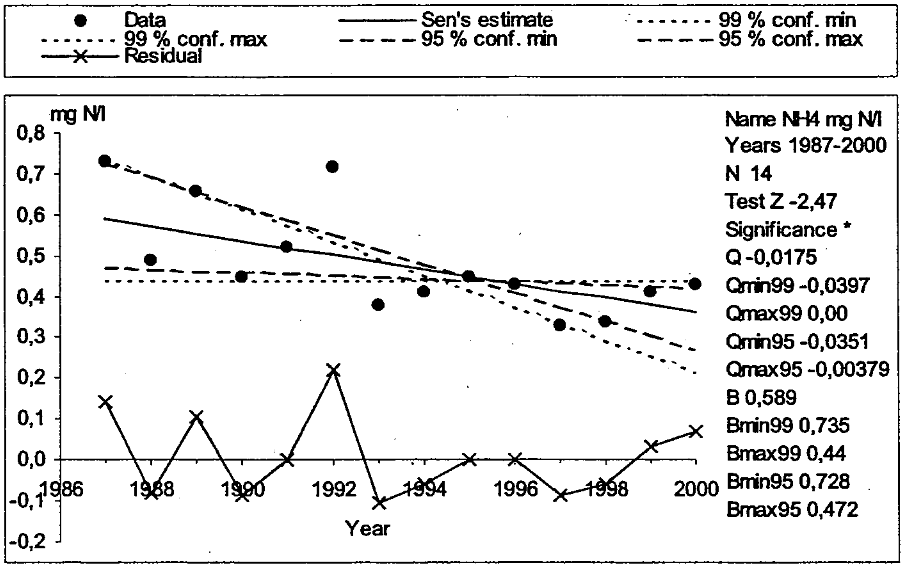


Figure 5. Annual time series and trend statistics of NH_4^+ in precipitation at Virolahti FI17.

The case of atmospheric NH_3+NH_4^+ concentration (Figure 6) is an example of time series to which neither of the used methods are statistically suitable. The trend is clearly first decreasing and then increasing and thus the trend is neither linear nor monotonic. This conclusion can also be made on the grounds of the residuals. However the statistical methods could be used separately to the decreasing and increasing parts of the time series but then the small number of data reduces the statistical significance of the results.

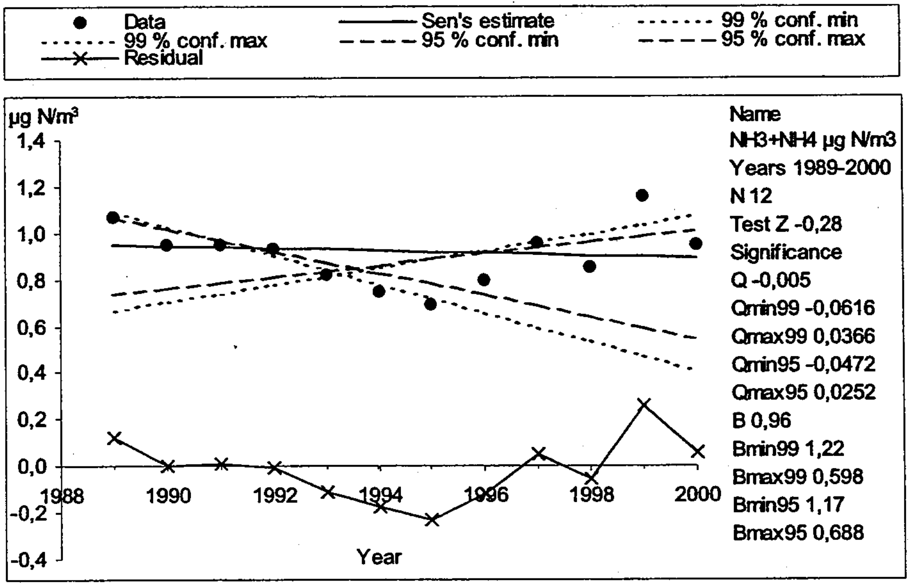


Figure 6. Annual time series and trend statistics of atmospheric NH_3 + NH_4^+ concentrations at Virolahti FI17.

5 Summary

An Excel template – MAKESENS – is developed for the calculation of the annual trend statistics. The procedure is based on the nonparametric Mann-Kendall test for the trend and the nonparametric Sen's method for the magnitude of the trend. The theory of calculation, the user's manual and the macro code are presented. As an example the annual trends of precipitation concentrations and atmospheric concentrations of some compounds measured at the Finnish air quality monitoring station Virolahti are calculated and briefly discussed.

Examination of the time series is very important before performing and interpreting the statistical calculations with MAKESENS. The Mann-Kendall method may be used in cases where the possible trend can be assumed to be monotonic. In the Sen's method it is assumed that the trend is linear and the residuals are from the same distribution with zero mean. The time series should fulfill these presumptions in order to produce correct statistical results with MAKESENS.

In the Mann-Kendall test missing values are allowed and the data need not conform to any particular distribution. The Sen's method is not greatly affected by gross data errors or outliers, and also it can be computed when data are missing.

Acknowledgements

The authors thank the Nordic Council of Ministers for the financial support to this work.

6 References

Gilbert, R.O., 1987. Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold , New York.

Sirois, Allan, 1998. A Brief and Biased Overview of Time Series Analysis or How to Find that Evasive Trend. In WMO report No. 133: WMO/EMEP workshop on Advanced Statistical methods and their Application to Air Quality Data sets (Helsinki, 14-18 September 1998).

TFMM 2000. Minutes of the First Meeting of the Task Force (23 - 25 October 2000, Vienna, Austria). http://www.ubavie.gv.at/tfmm/pages/meet.htm

7 Appendix 1. The macro code of MAKESENS

```
'   Copyright 2002 Finnish Meteorological Institute
'   Timo Salmi & Anu Määttä & Toni Amnell
'   MAKESENS Version 1.0

'COMMON SETTINGS
Option Base 1   'Default indexing of arrays starts from 1
'Code for missing data in arrays:
Const MissingValue As Double = -999999#
'Maximum number of data in one time series:
Const MaxData As Integer = 100
'Codes for different significance levels:

'Minimum count of data to use normal approximation
' in Mann-Kendall test. Below this value the S statistics
' is used:
Const MinMannKendNorm As Integer = 10
'Minimum count of data to calculate confidence interval
'in Sen's method
Const MinSenConf As Integer = 10

Const S001 As String = "***"    'alpha = 0.001
Const S01 As String = "**"      'alpha = 0.01
Const S05 As String = "*"       'alpha = 0.05
Const S1 As String = "+"        'alpha = 0.1

'Arrays of critical values of Mann-Kendall statistic S
' for significance levels 0.001, 0.01, 0.05 and 0.1
' of two-sided test when n is between 4 and 10.
' The arrays will be filled by the subroutine fillS
Dim S_001(4 To 10) As Integer
Dim S_01(4 To 10) As Integer
Dim S_05(4 To 10) As Integer
Dim S_1(4 To 10) As Integer

Private Sub CB_CalculateStatistics_Click()
' The main program of calculation
' - Retrieves the data values from the sheet "Annual data" with
'   the subroutine GetData
' - Calculates the statistics with the subroutines MannKendall
'   and Sen and with the function calcB and saves the results into
'   the sheet "Trend statistics"
' - Finally calls the workbook level routines makeCollection and
'   drawFigure preparing the sheet Figure

Dim nofCol As Integer 'Number of columns i.e. time series
Dim colno As Integer  'Column number of a time series
Dim firstYear As Integer 'first year of a time series
Dim baseYear As Integer  'first year of all time series
Dim nYears As Integer    'number of years in a time series
```

```
Dim n As Integer         'true data values in a time series
                         'i.e. missing values are not considered
Dim x(MaxData) As Double 'Array for data values of a time series
Dim s As Integer         'Mann-Kendall test statistic for n=4..10
Dim Z As Double          'Mann-Kendall test statistic for n>10
Dim signif As String     'significance of trend
'Sen's slope estimator Q and its 99% and 95% confidence levels:
Dim Q As Double, Qmin99 As Double, Qmax99 As Double
Dim Qmin95 As Double, Qmax95 As Double
'Constants B for equation of lines of Sen's slope and conf. intervals:
Dim B As Double, Bmin99 As Double, Bmax99 As Double
Dim Bmin95 As Double, Bmax95 As Double


' The result cells are emptied before the calculation starts
Worksheets("Trend Statistics").Range("E6:Q30") = ""

nofCol = Worksheets("Annual data").Cells(8, 2).value
baseYear = Worksheets("Annual data").Cells(14, 1).value
Call fillS    'initializes arrays of  Mann-Kendall probabilities

'Calculation of trend statistics for each time series at a time
For colno = 2 To nofCol + 1
    If Not GetData(colno, baseYear, firstYear, nYears, n, x) Then
        Exit Sub
    End If
    If n >= 2 Then   'nothing can be computed, if n<2
    'First the existence of trend is tested using Mann-Kendall method.
        Call MannKendall(nYears, x, s, Z, signif)
        If n < MinMannKendNorm Then
            Worksheets("Trend Statistics").Cells(4 + colno, 5) = s
        Else
            Worksheets("Trend Statistics").Cells(4 + colno, 6) = Z
        End If
         Worksheets("Trend Statistics").Cells(4 + colno, 7) = signif
        'Evaluation of Sen's slope estimator and confidence intervals
        Call Sen(nYears, x, Q, Qmin99, Qmax99, Qmin95, Qmax95)
         Worksheets("Trend Statistics").Cells(4 + colno, 8) = Q
         B = calcB(nYears, x, firstYear, baseYear, Q)
         Worksheets("Trend Statistics").Cells(4 + colno, 13) = B

        If n >= MinSenConf Then
            Worksheets("Trend Statistics").Cells(4 + colno, 9) = Qmin99
            Worksheets("Trend Statistics").Cells(4 + colno, 10) = Qmax99
            Worksheets("Trend Statistics").Cells(4 + colno, 11) = Qmin95
            Worksheets("Trend Statistics").Cells(4 + colno, 12) = Qmax95
        'Coefficients B for equation of linear trend f(t)=Qt+B
            Bmin99 = calcB(nYears, x, firstYear, baseYear, Qmin99)
            Bmax99 = calcB(nYears, x, firstYear, baseYear, Qmax99)
            Bmin95 = calcB(nYears, x, firstYear, baseYear, Qmin95)
            Bmax95 = calcB(nYears, x, firstYear, baseYear, Qmax95)
            Worksheets("Trend Statistics").Cells(4 + colno, 14) = Bmin99
            Worksheets("Trend Statistics").Cells(4 + colno, 15) = Bmax99
            Worksheets("Trend Statistics").Cells(4 + colno, 16) = Bmin95
```

```
            Worksheets("Trend Statistics").Cells(4 + colno, 17) = Bmax95
        End If
    End If
Next colno

' Draw the figure of the first component
Sheets("Figure").Cells(9, 3).value = 1
Sheets("Figure").Cells(10, 3).value = Sheets("Annual data").Cells(13,
2).value
Application.Run "makeCollection"
Application.Run "DrawFigure"
End Sub 'CB_CalculateStatistics_Click

Private Function GetData(ByVal colno As Integer, ByVal baseYear As
Integer, firstYear As Integer, nYears As Integer, n As Integer, x() As
Double) As Boolean
' Retrieving of data of one time series into the array x()
' colno is the column of the worksheet "Annual data" where the
' values of the time series exist.
' The real number of annual values n in time series is calculated
' If the cell is empty it is understood as a missing value.

Dim rowno As Integer      'row of the data cell
Dim lastYear As Integer   'last year of the time series
Dim nVal As Integer       'counter for number of true data
Dim i As Integer          'counter for data loop
Dim Error As Integer
firstYear = Worksheets("Annual data").Cells(10, colno).value
lastYear = Worksheets("Annual data").Cells(11, colno).value
nYears = lastYear - firstYear + 1

nVal = 0
For i = 1 To nYears
    If firstYear < baseYear Then
        Error = MsgBox("For the time series """ + _
        Worksheets("Annual data").Cells(13, colno).value + _
        """ first year is too early!")
        GetData = False
        Exit Function
    End If
    rowno = 13 + i + firstYear - baseYear
    If IsEmpty(Worksheets("Annual data").Cells(rowno, colno)) Then
        x(i) = MissingValue
    Else
        nVal = nVal + 1
        x(i) = Worksheets("Annual data").Cells(rowno, colno)
    End If
Next i
n = nVal
GetData = True
End Function ' GetData

Private Sub MannKendall(ByVal nYears As Integer, x() As Double, s As
Integer, Z As Double, signif As String)
```

```
'Calculates the MannKendall test
'Calls the function tiedSum
'Uses the string constants S001, S01, S05 and S1

Dim absS As Integer       'value of absS
Dim varS As Double        'the variance of S
Dim absZ As Double          'value of abs(Z)
Dim k As Integer, j As Integer  'counters for slopes
Dim n As Long          'number of true values in x()

Z = MissingValue            ' returns MissingValue for Z
                           ' if they are not calculated
'Computing of the Mann-Kendall statistic S.
signif = ""
n = IIf(x(nYears) <> MissingValue, 1, 0)
s = 0
For k = 1 To nYears - 1
    If x(k) <> MissingValue Then
        n = n + 1
        For j = k + 1 To nYears
            If x(j) <> MissingValue Then
                s = s + Sgn(x(j) - x(k))
            End If
        Next j
    End If
Next k

If n < 4 Then
'If n is less than 4, the method can not be used at all
    Exit Sub
ElseIf n < MinMannKendNorm Then
'If n is between 4 and 10, S is compared directly to Mann-Kendall
statistics for S
    absS = Abs(s)
    signif = Switch(absS >= S_001(n), S001, absS >= S_01(n), S01, absS >=
S_05(n), S05, absS >= S_1(n), S1, True, "")
Else 'n>=MinMannKendNorm
'If n is at least 10, the normal distribution is used
'Firstly the variance VAR(S) is calculated
'The correction term for ties is calculated by the function tiedSum
    varS = (n * (n - 1) * (2 * n + 5) - tiedSum(nYears, x)) / 18#
'Calculation  of test statistic Z using S and its variance VAR(S)
    Z = Switch(s > 0, (s - 1) / Sqr(varS), s < 0, (s + 1) / Sqr(varS), s
= 0, 0#)
'The absolute value of Z is compared to critical value Z[1-alpha/2]
'which is obtained from the standard normal table. The presence and
'significance of the trend is evaluated by testing four different
'levels of significance: '0.001, 0.01, 0.05 and 0.1
    absZ = Abs(Z)
    signif = Switch(absZ > 3.292, S001, absZ > 2.576, S01, absZ > 1.96,
S05, absZ > 1.645, S1, True, "")
End If

End Sub 'MannKendall
```

```
Private Sub Sen(ByVal nYears As Integer, x() As Double, Q As Double,
Qmin99 As Double, Qmax99 As Double, Qmin95 As Double, Qmax95 As Double)
'Calculates Sen's slope estimator Q and its 99% (Qmax99,Qmin99)
' and 95 % (Qmax95, Qmin95)confidence levels
' Calls the function tiedSum and the subroutine
CalulateConfidenceInterval

Dim nofQ As Integer      'number of value pairs
Dim Qarray(MaxData * (MaxData - 1) / 2) As Double 'Array for the slopes
of value pairs
Dim k As Integer, j As Integer 'counters for loops
Dim n As Long            'number of true values in x()
Dim Calpha As Double      'C-alpha for calculation of conf.intervals of Q

'Computing of slopes of individual value pairs into Qarray
nofQ = 0   'used as counter for Qarray
n = IIf(x(nYears) = MissingValue, 0, 1)
For k = 1 To nYears - 1
    If x(k) <> MissingValue Then
        n = n + 1
        For j = k + 1 To nYears
            If x(j) <> MissingValue Then
                nofQ = nofQ + 1
                Qarray(nofQ) = (x(j) - x(k)) / (j - k)
            End If
        Next j
    End If
Next k

'The median of individual slopes in Qarray  is the Sen's
'slope estimator. The median is calculated by the function "median".
Q = median(nofQ, Qarray)

If n >= MinSenConf Then
'The confidence intervals are calculated only if n is at least 10.
'Computing of variance VAR(S) of Mann-Kendall statistics S.
'The correction term for ties is calculated by the function tiedSum
    varS = (n * (n - 1) * (2 * n + 5) - tiedSum(nYears, x)) / 18#

'The 100(1-alpha)% two-sided confidence intervals for the
'Sen's slope are computed with two values of alpha: 0.01 and 0.05
'which means 99% and 95% confidence intervals. The values of
'Z[1-alpha/2] are obtained from the standard normal table.
'Case alpha=0.01: Z[1-alpha/2]=Z[0.995]=2.576
    Calpha = 2.576 * Sqr(varS)
    Call CalculateConfidenceInterval(Calpha, nofQ, Qarray, Qmin99,
Qmax99)

'Case alpha=0.05: Z[1-alpha/2]=1.96
    Calpha = 1.96 * Sqr(varS)
    Call CalculateConfidenceInterval(Calpha, nofQ, Qarray, Qmin95,
Qmax95)
Else
```

```
    Qmin99 = MissingValue
    Qmax99 = MissingValue
    Qmin95 = MissingValue
    Qmax95 = MissingValue
End If
End Sub 'Sen

Private Function tiedSum(n As Integer, x() As Double) As Integer
'Calculates sum related to tied groups(= two or more equal values)
'   for the variance of Mann-Kendall statistics S
'n = number of values in the array x including missing values
'Function tiedSum is called by subroutines Sen and MannKendallNorm

Dim m As Integer          ' number of tied groups
Dim tval() As Double      ' data values of tied groups
ReDim tval(n)
Dim t() As Integer, nt As Integer ' number of data in tied groups
ReDim t(n)
Dim p, i As Integer      'indexes for the loops
Dim newValue As Boolean
Dim tSum As Integer

'Calculation of the number of tied groups m and the number of data
' in tied groups t()
m = 0
For i = 1 To n - 1
    If x(i) <> MissingValue Then
        newValue = True
        If m > 0 Then
            For p = 1 To m
               If x(i) = tval(p) Then
                    newValue = False 'this value is alredy managed
                    Exit For
               End If
            Next p
        End If

        If newValue Then
            nt = 1  'number of equal values x(i)
            For p = i + 1 To n
                If x(p) = x(i) Then
                    nt = nt + 1
                End If
            Next p

            If nt > 1 Then ' new group only if nt>1
                m = m + 1
                t(m) = nt
                tval(m) = x(i)
            End If
        End If
    End If
Next i
```

```
'Calculating the sum related to tied groups for variance
tSum = 0
If m > 0 Then
    For p = 1 To m
        tSum = tSum + t(p) * (t(p) - 1) * (2 * t(p) + 5)
    Next p
End If
tiedSum = tSum
End Function 'tiedSum

Sub CalculateConfidenceInterval(ByVal Calpha As Double, ByVal nofQ As
Integer, Qarray() As Double, lowerLimit As Double, upperLimit As Double)
'Computes confidence interval for Sen's slope estimate.
'Input parameters:  Calpha = Z[1-alpha/2],
'                   nofQ - number of slopes of all data pairs
'                   Qarray - array of slopes of all data pairs
'Subroutine returns the lowerLimit and upperLimit.
'Calls the subroutine SortArray
'Is called by the subroutine Sen
    Dim M1 As Double         'M1:th largest ordered slope
    Dim M2 As Double         'M2:th largest ordered slope
    Dim M1int As Integer     'integer part of M1 (>0)
    Dim M2int As Integer     'integer part of M2+1 (>0)
    Dim QarraySort() As Double
    ReDim QarraySort(nofQ)

    'The array Qarray is sorted to the array QarraySort
    Call SortArray(nofQ, Qarray, QarraySort)
    M1 = (nofQ - Calpha) / 2
    M2 = (nofQ + Calpha) / 2

    If M1 > 1 Then
    'to be sure that index does not point outside QarraySort
        M1int = Int(M1) 'find the integer part of M1
        'Interpolation of the lower limit
        lowerLimit = QarraySort(M1int) + (M1 - M1int) * (QarraySort(M1int
+ 1) - QarraySort(M1int))
    Else
        lowerLimit = QarraySort(1)
    End If

    If M2 < nofQ - 1 Then
    'to be sure that index does not point outside QarraySort
        M2int = Int(M2 + 1) 'because the indexing of QarraySort begins
from zero
        'Interpolation of the upper limit
        upperLimit = QarraySort(M2int) + (M2 + 1 - M2int) *
(QarraySort(M2int + 1) - QarraySort(M2int))
    Else
        upperLimit = QarraySort(nofQ)
    End If
End Sub 'CalculateConfidenceInterval
```

```
Public Function calcB(nYears As Integer, x() As Double, firstYear As
Integer, baseYear As Integer, Q As Double) As Double
' calculates the constant B for the equation of linear trend f(t)=Q*t+b.
' The zero point of time axis is the "baseYear"
' Calls the function median
Dim n As Integer    'the number of true values in time series
Dim year As Integer 'the true year of the data value
Dim i As Integer    'index for loop
Dim val() As Double 'array of differences
ReDim val(nYears)

n = 0
For i = 1 To nYears
    year = firstYear + i - 1
    If x(i) <> MissingValue Then
        n = n + 1
        val(n) = x(i) - Q * (year - baseYear)
    End If
Next i

' the estimate for B is median of the calculated differences
calcB = median(n, val)
End Function ' calcB

Private Function median(nofV As Integer, values() As Double) As Double
' calculates median of values in the array values(), indexed from 1 to
nofV
' calls the subroutine sortArray
' is called by the fuction calcB and by the subroutine Sen
    Dim i As Integer
    Dim sortedValues() As Double
    ReDim sortedValues(nofV)

    Call SortArray(nofV, values, sortedValues)
    If nofV Mod 2 = 0 Then     'nofv is even
        i = Int(nofV / 2)
        median = (sortedValues(i + 1) + sortedValues(i)) / 2
    Else                                   'nOfvalues is odd
        median = sortedValues((nofV + 1) / 2)
    End If
End Function 'median

Sub SortArray(ByVal nofV As Integer, values() As Double, sortedValues()
As Double)
'This subroutine ranks the values of an array from smallest to largest.
'The sorting method is SELECTION SORT
'The ranked values are stored into the other array called sortedValues.
'Input parameters:  nofV - number of values in the array values
'                   values - values to be ranked, indexed from 1 to nofV
'Subroutine returns the sorted array at sortedValues.
'Is called by the function median and by the subroutine
'CalculateConfidence interval

Dim ind As Integer, i As Integer, j As Integer
```

```
Dim minV As Double, maxV As Double
Dim carray() As Double   'the data is first copied to this array
ReDim carray(nofV)
Dim ignoreV As Double    'value that is ignored in carray when sorting

For i = 1 To nofV       'Copy the original array to carray
    carray(i) = values(i)
Next i

'Find the smallest and largest value
ind = 1
minV = carray(1)  'initialize the smallest value
maxV = carray(1)  'initialize the largest value
For i = 2 To nofV
    If carray(i) < minV Then
        minV = carray(i)
        ind = i
    End If
    If carray(i) > maxV Then
        maxV = carray(i)
    End If
Next i

sortedValues(1) = minV 'the smallest data value
ignoreV = minV - 10    'smaller value than the smallest data value
carray(ind) = ignoreV  'this value is later ignored in sorting

'now sort the values
For j = 2 To nofV
    minV = maxV
    For i = 1 To nofV
        'find the minimum from the rest of the array
        If carray(i) <= minV And carray(i) > ignoreV Then
            minV = carray(i)
            ind = i
        End If
    Next i
    sortedValues(j) = minV
    carray(ind) = ignoreV  'from now on this element is ignored
Next j
End Sub 'SortArray

Private Sub fillS()
'Fills the arrays S_nnn of probabilities for two-tailed
' Mann-Kendall test
'The index of tables is the number of data if n=4...10
'Each array entry is an absolute value of the Mann-Kendall
' statistic S, with which the probability that there is no trend
' is less than the probability level p related to the array:
' S_001: p=0.001, S_01: p=0.01, S_05: p=0.05 and S_1: p=0.1.
' Source of values: Gilbert, 1987, Table A18
'Value 9999 indicates that the probability level can not be
' reached with given number of data
```

```
Dim n As Integer
For n = 4 To 10
    S_001(n) = 9999
    S_01(n) = 9999
    S_05(n) = 9999
    S_1(n) = 9999
Next n
S_001(7) = 21
S_001(8) = 26
S_001(9) = 30
S_001(10) = 35
S_01(6) = 15
S_01(7) = 19
S_01(8) = 22
S_01(9) = 26
S_01(10) = 29
S_05(5) = 10
S_05(6) = 11
S_05(7) = 15
S_05(8) = 18
S_05(9) = 20
S_05(10) = 23
S_1(4) = 6
S_1(5) = 8
S_1(6) = 11
S_1(7) = 13
S_1(8) = 16
S_1(9) = 18
S_1(10) = 21

End Sub
```

ATTACHMENT B

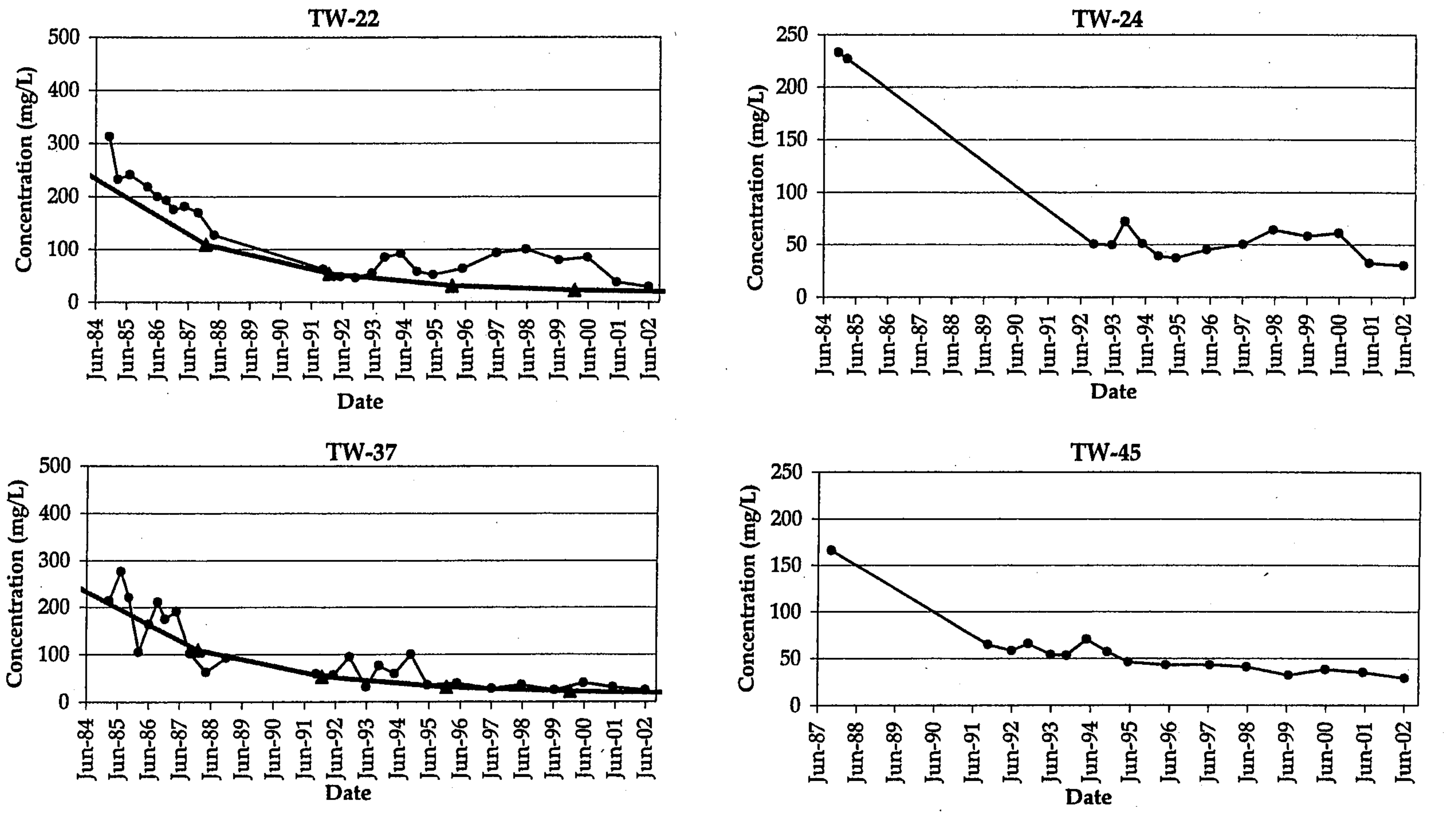
OUTPUT OF STATISTICAL ANALYSES—MAKESENS GRAPHS

(PLEASE SEE ATTACHED CD)

ATTACHMENT B

ATTACHMENT C

RI SOLUTE TRANSPORT MODEL OUTPUT



Legend

—●— Chloride Concentration (mg/L) —▲— Predicted

FIGURE C-01: CHLORIDE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates

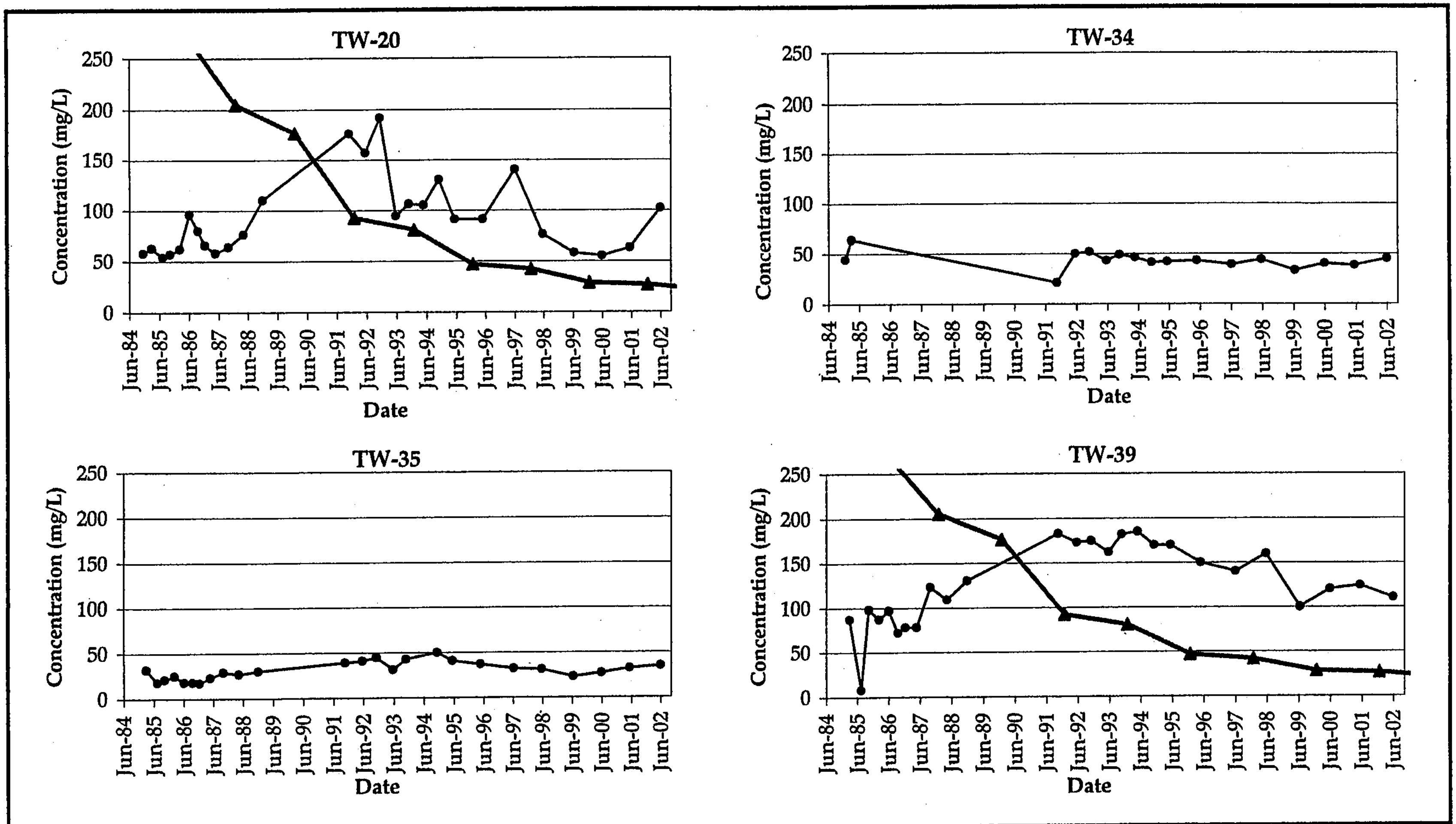
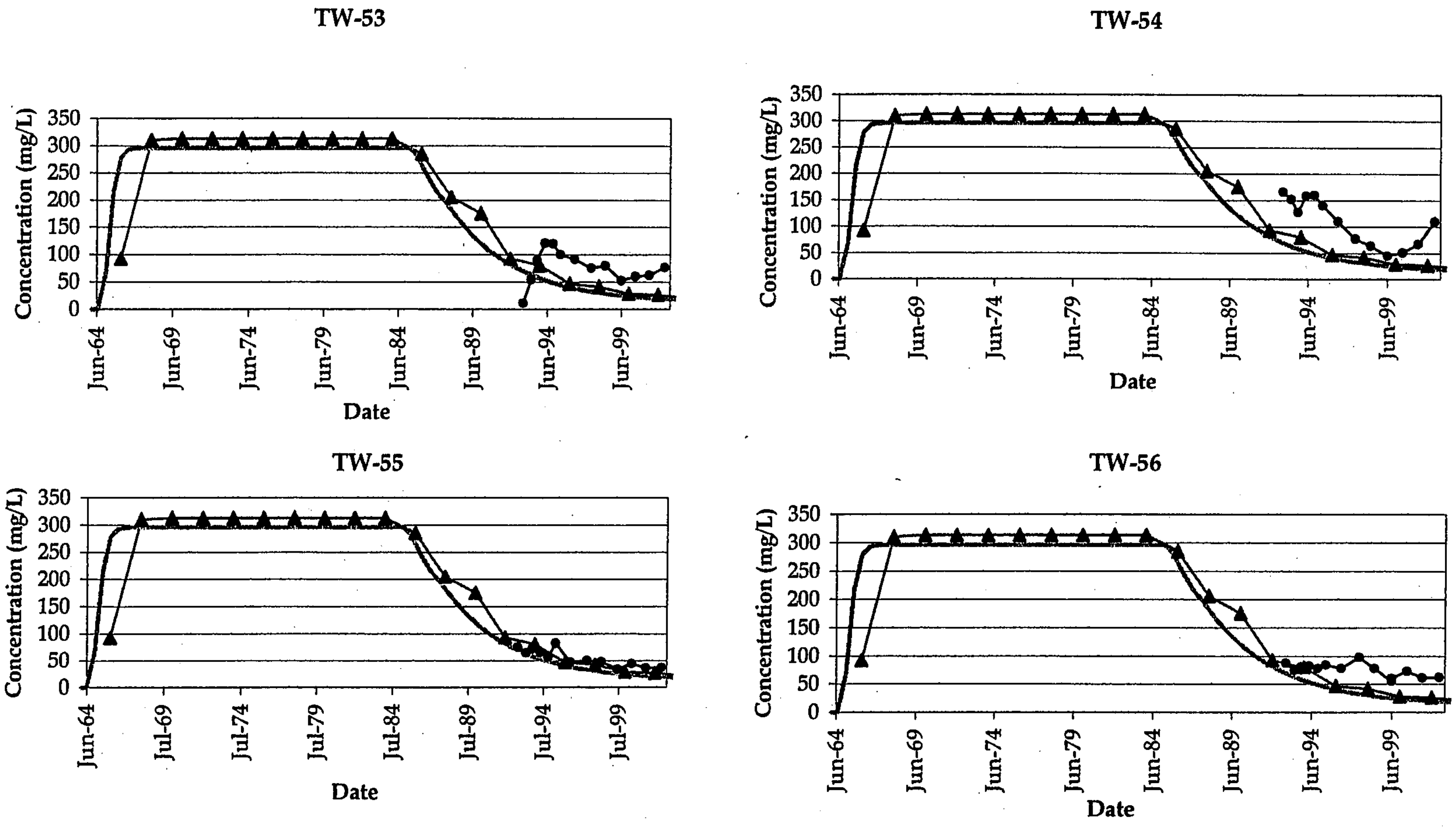


FIGURE C-2: CHLORIDE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



Legend

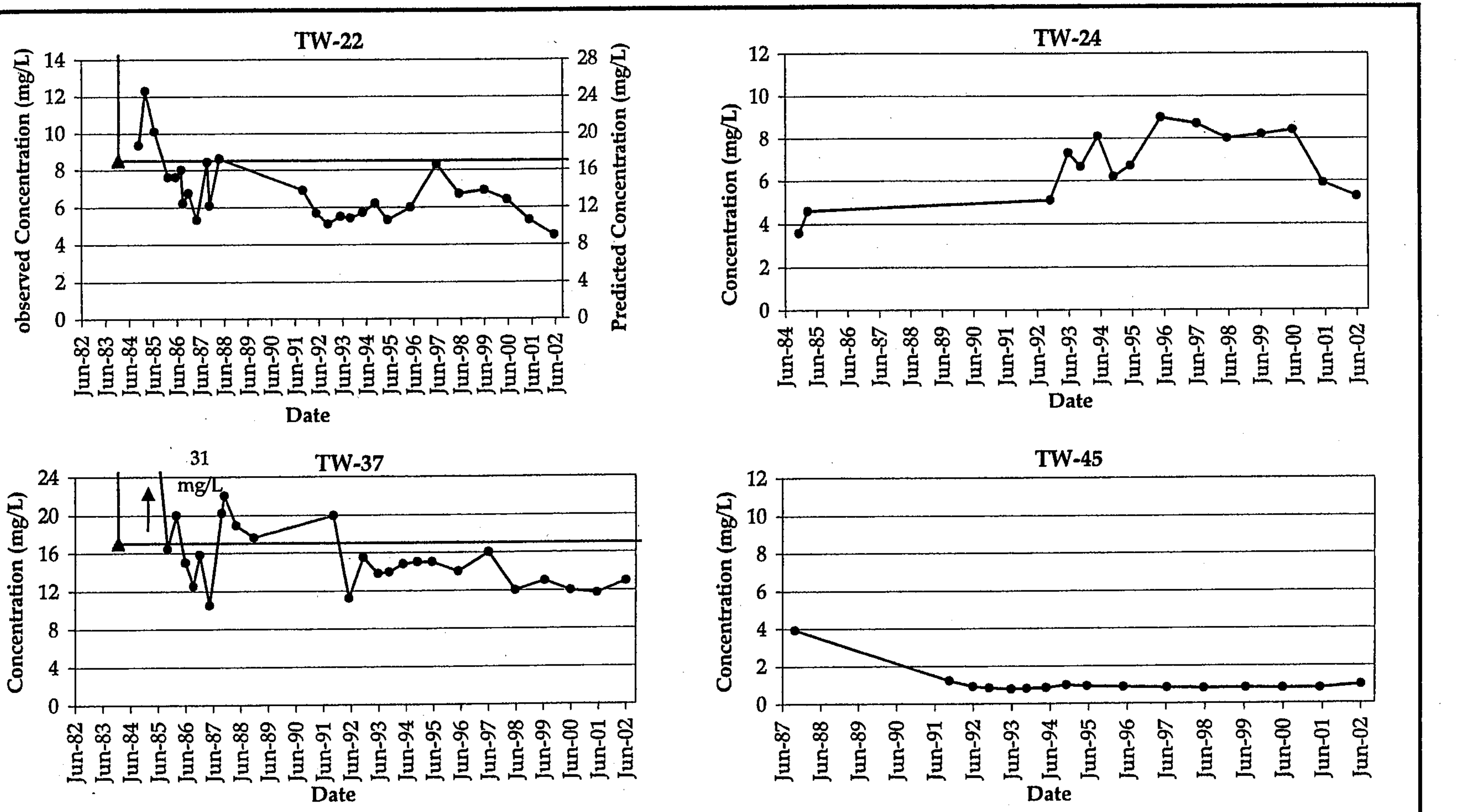
—●— Chloride Concentration (mg/L)
—▲— Predicted
—— GoldSim

FIGURE C-3: CHLORIDE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



Legend

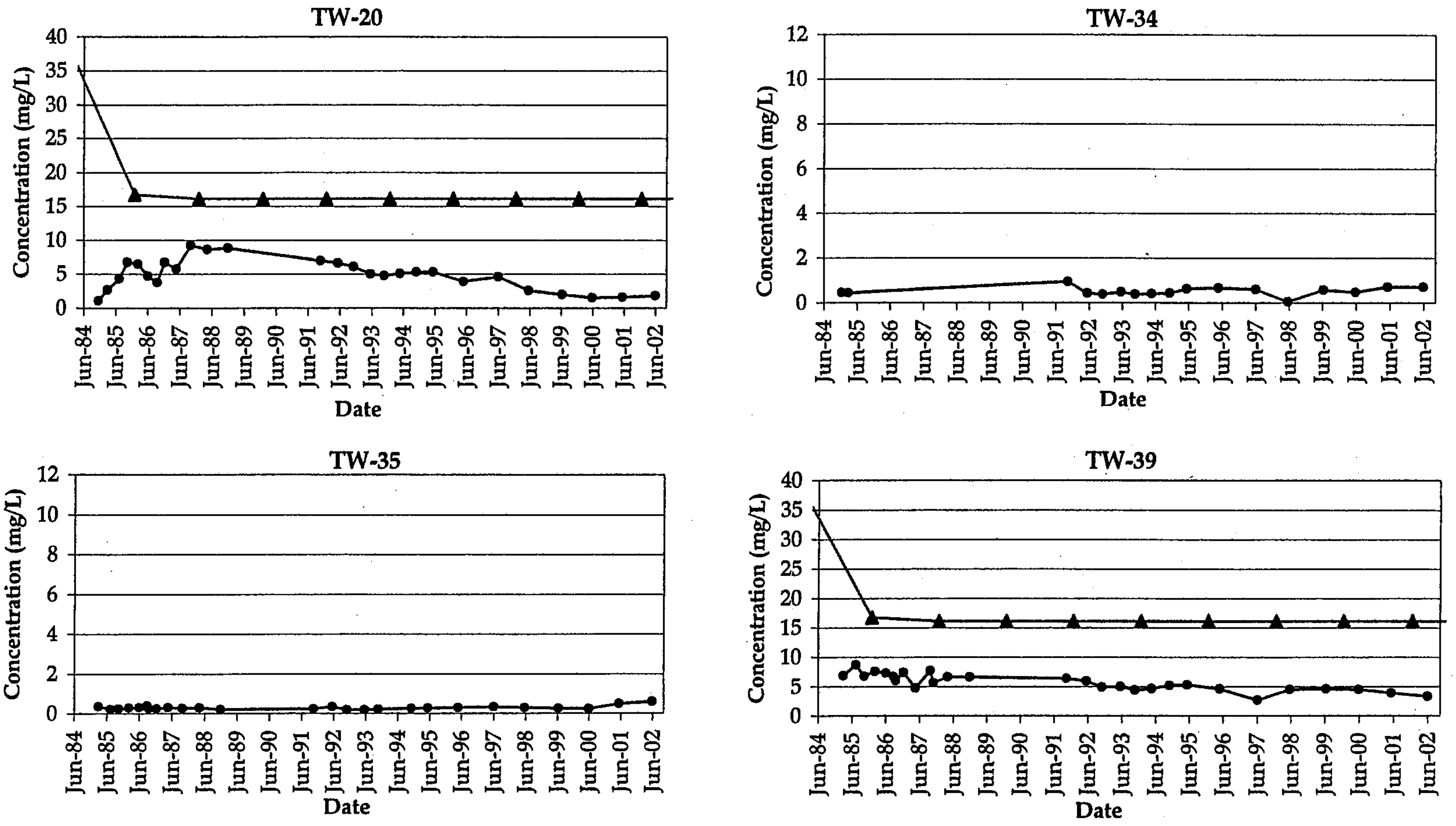
—●— Fluoride Concentration (mg/L)
—▲— Predicted Concentration

FIGURE C-4: FLUORIDE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



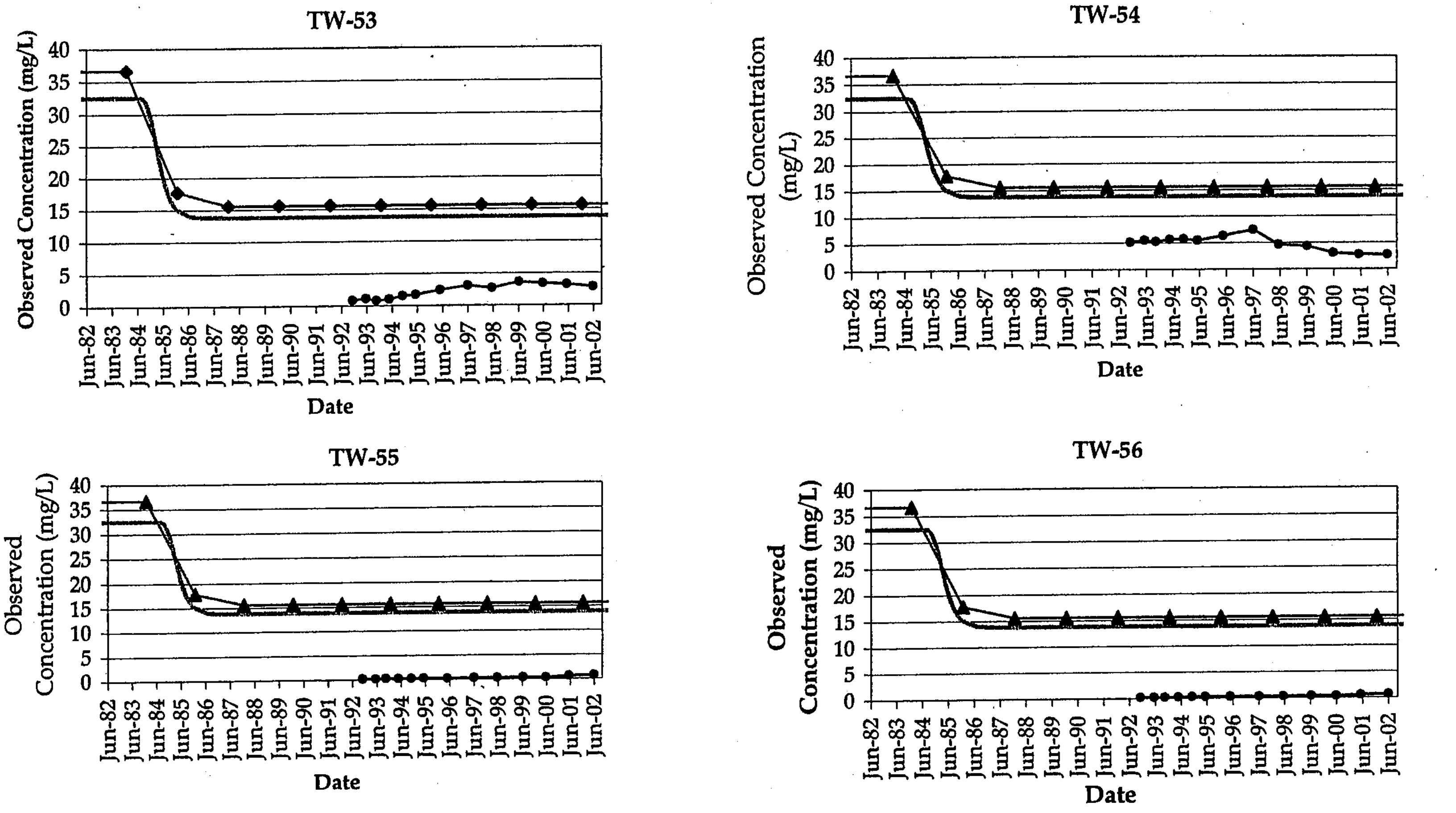
Legend

FIGURE C-5: FLUORIDE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

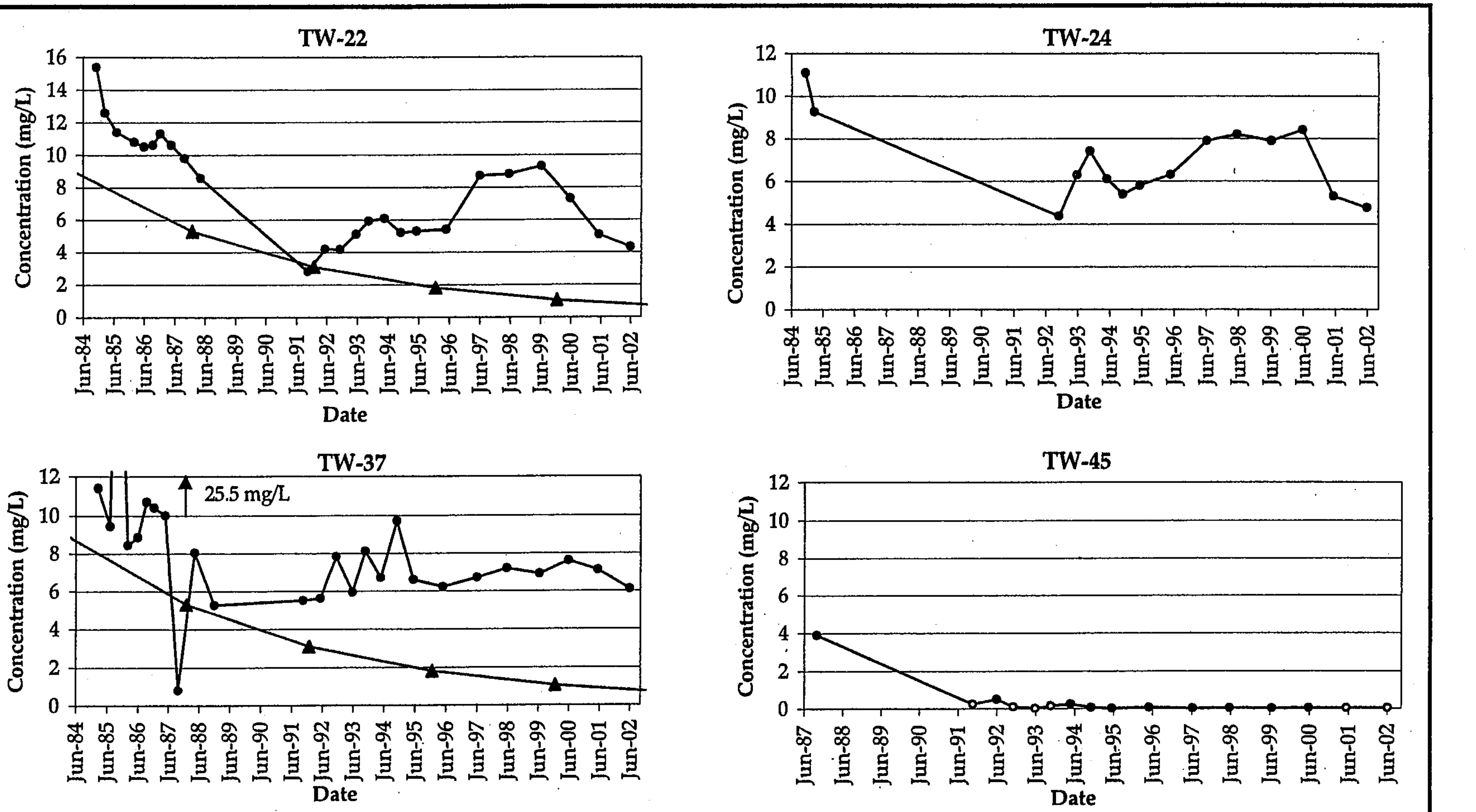
—●— Fluoride Concentration (mg/L)
—◆— Predicted Concentration (mg/L)
—— GoldSim

FIGURE C-6: FLUORIDE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

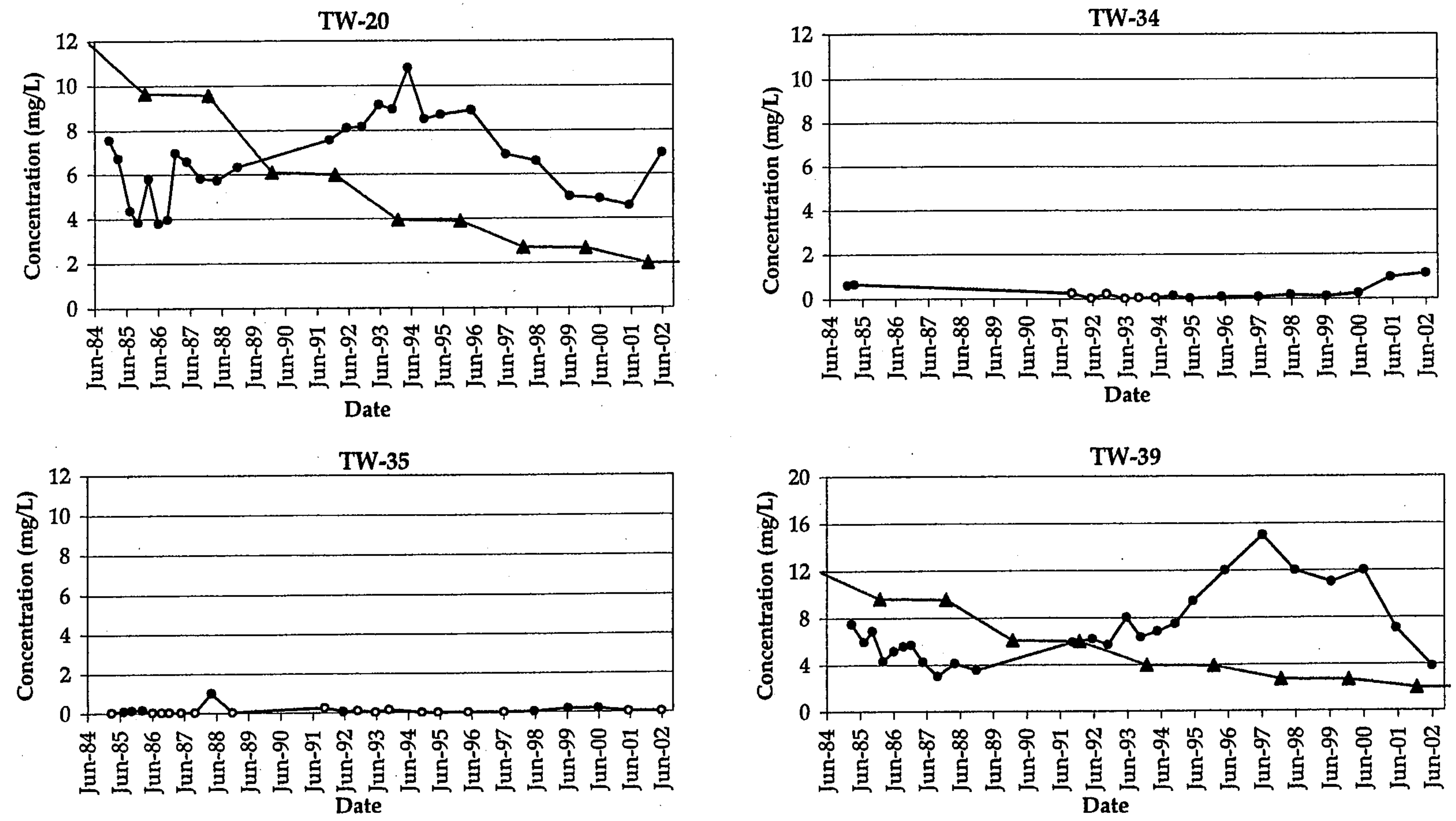
- ●— Nitrate as N Concentration (mg/L)
- ○ Non-Detects
- ▲— Predicted Concentrations

FIGURE C-7: NITRATE AS N IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

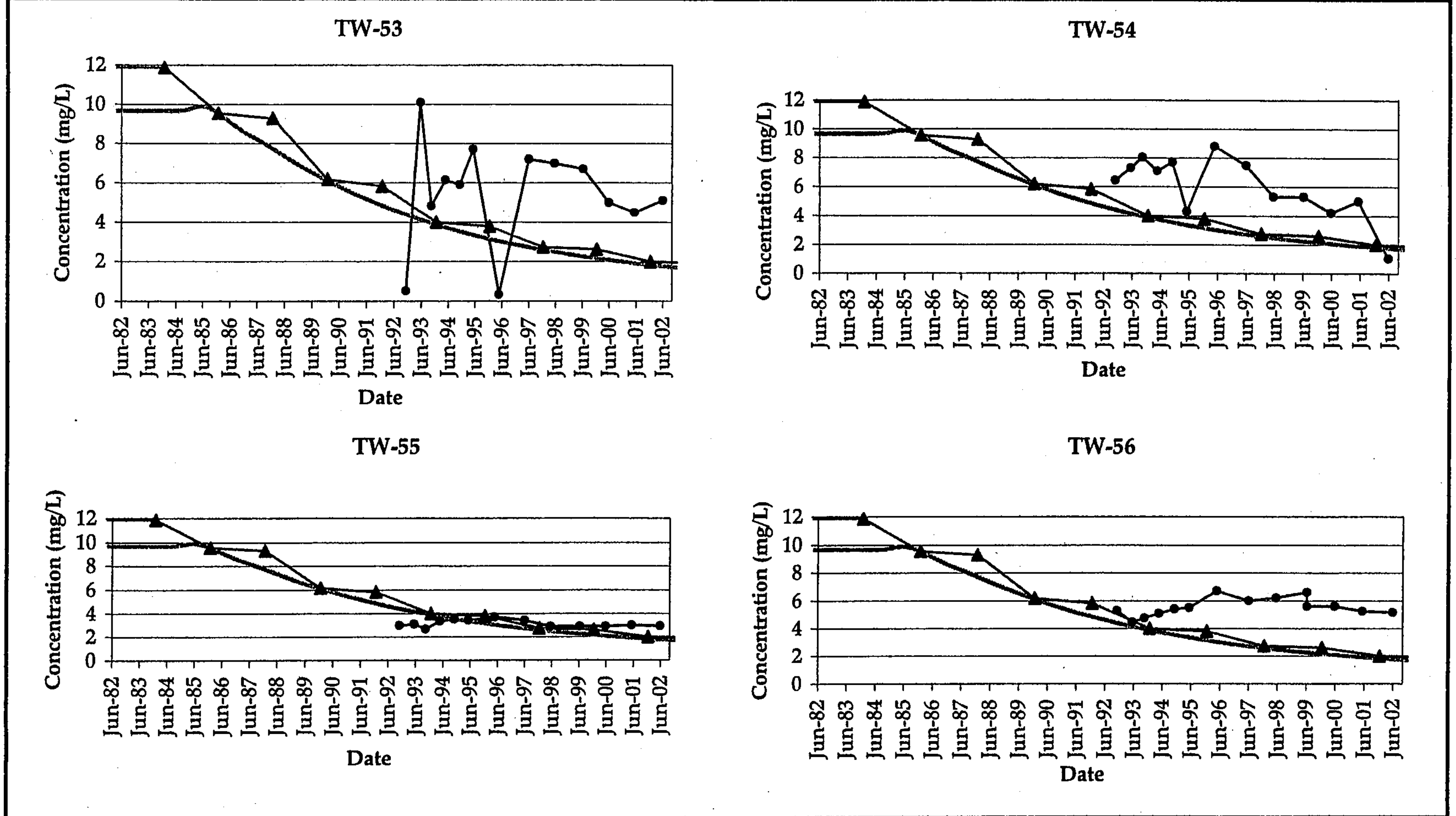
- —●— Nitrate as N Concentration (mg/L)
- ○ Non-Detects
- —▲— Predicted Concentration

FIGURE C-8: NITRATE AS N IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

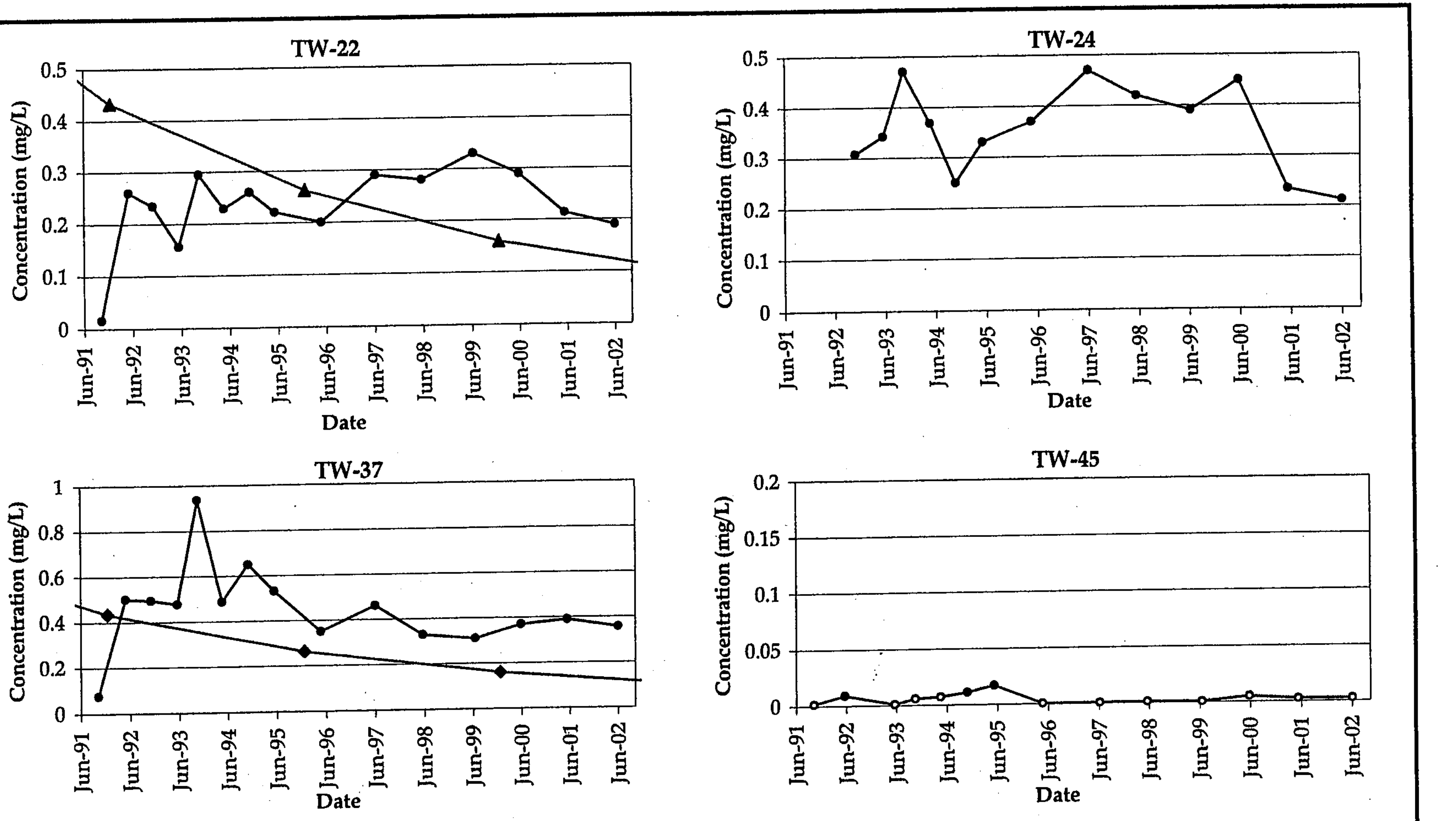
—●— Nitrate as N Concentration (mg/L)
—▲— Predicted Concentration
—— GoldSim

FIGURE C-9: NITRATE AS N IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

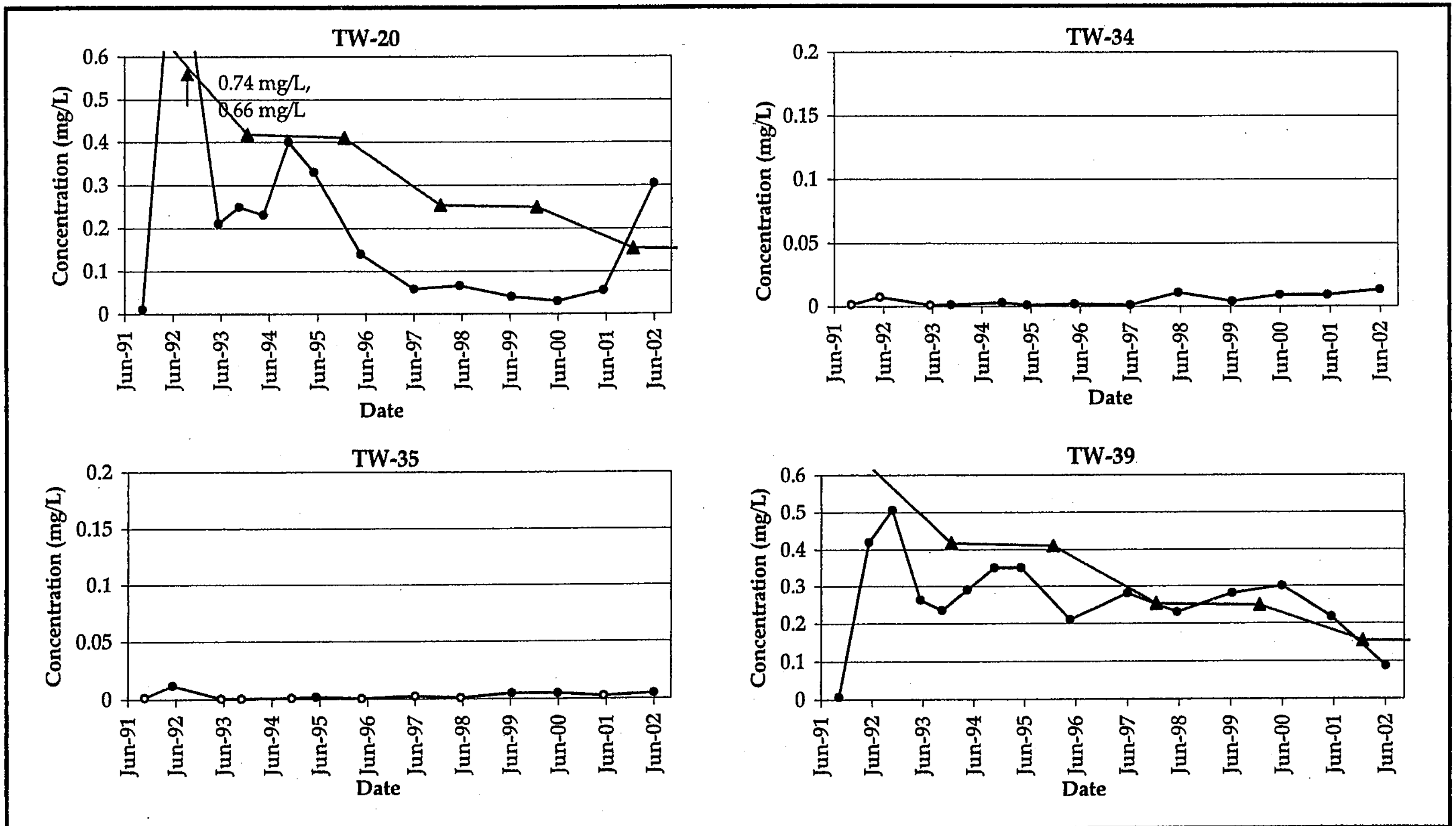
- ●— Selenium Concentration (mg/L)
- ○ Non-Detects
- ▲— Predicted Concentration

FIGURE C-10: SELENIUM IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



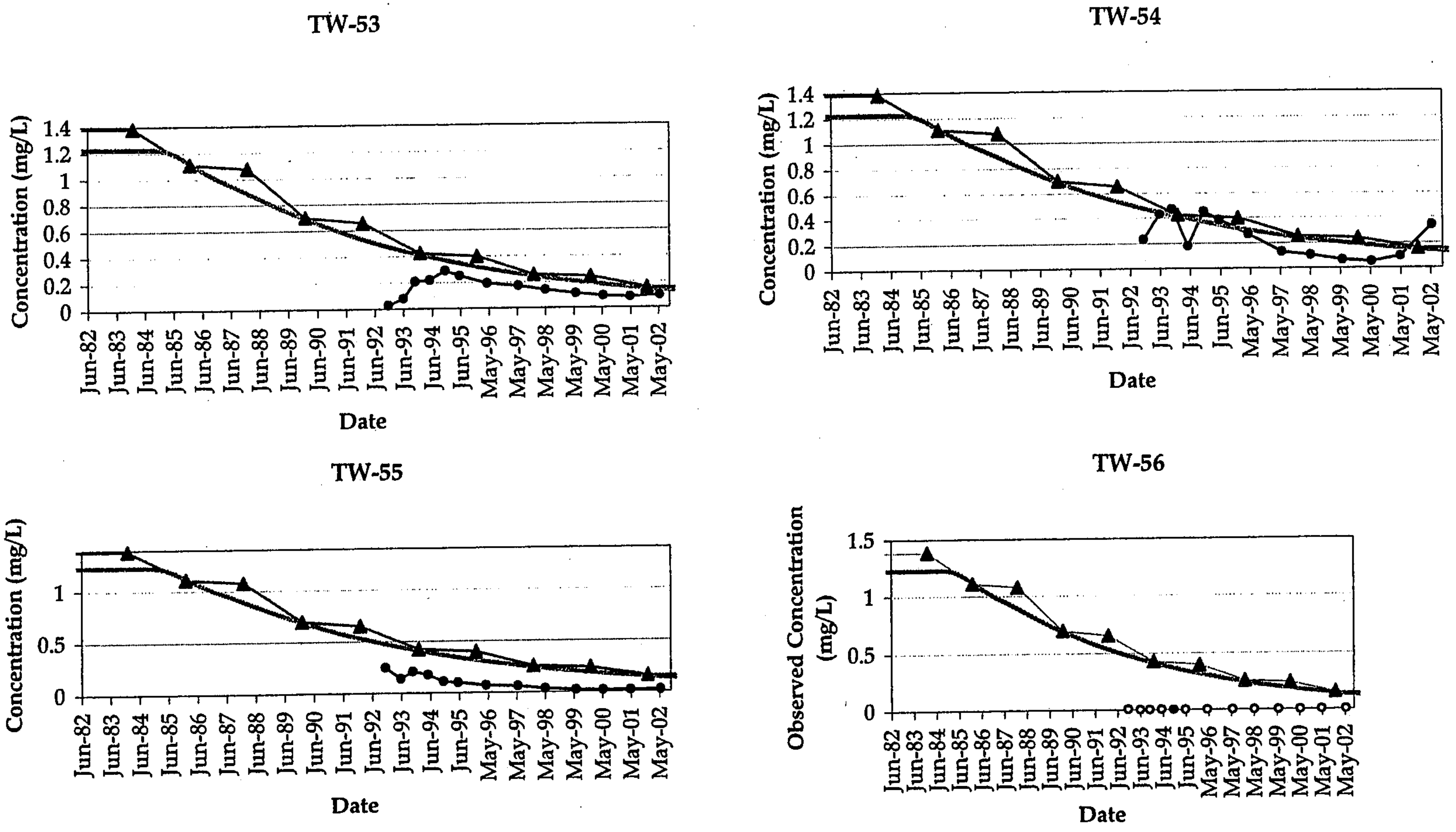
Legend

FIGURE C-11: SELENIUM IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

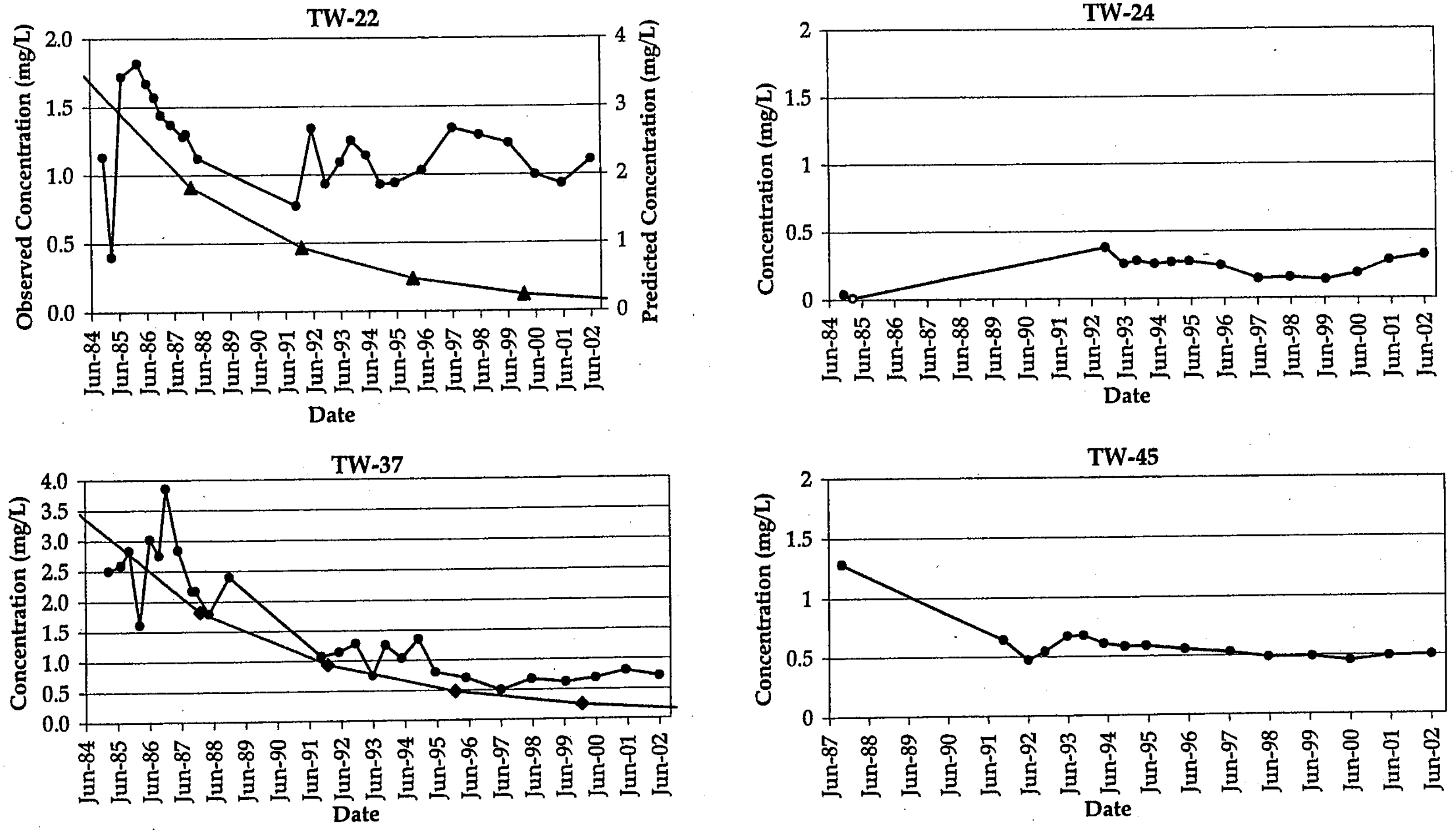
- ● Selenium Concentration (mg/L)
- ○ Non-Detects
- ▲ Predicted Concentration
- — GoldSim

FIGURE C-12: SELENIUM IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

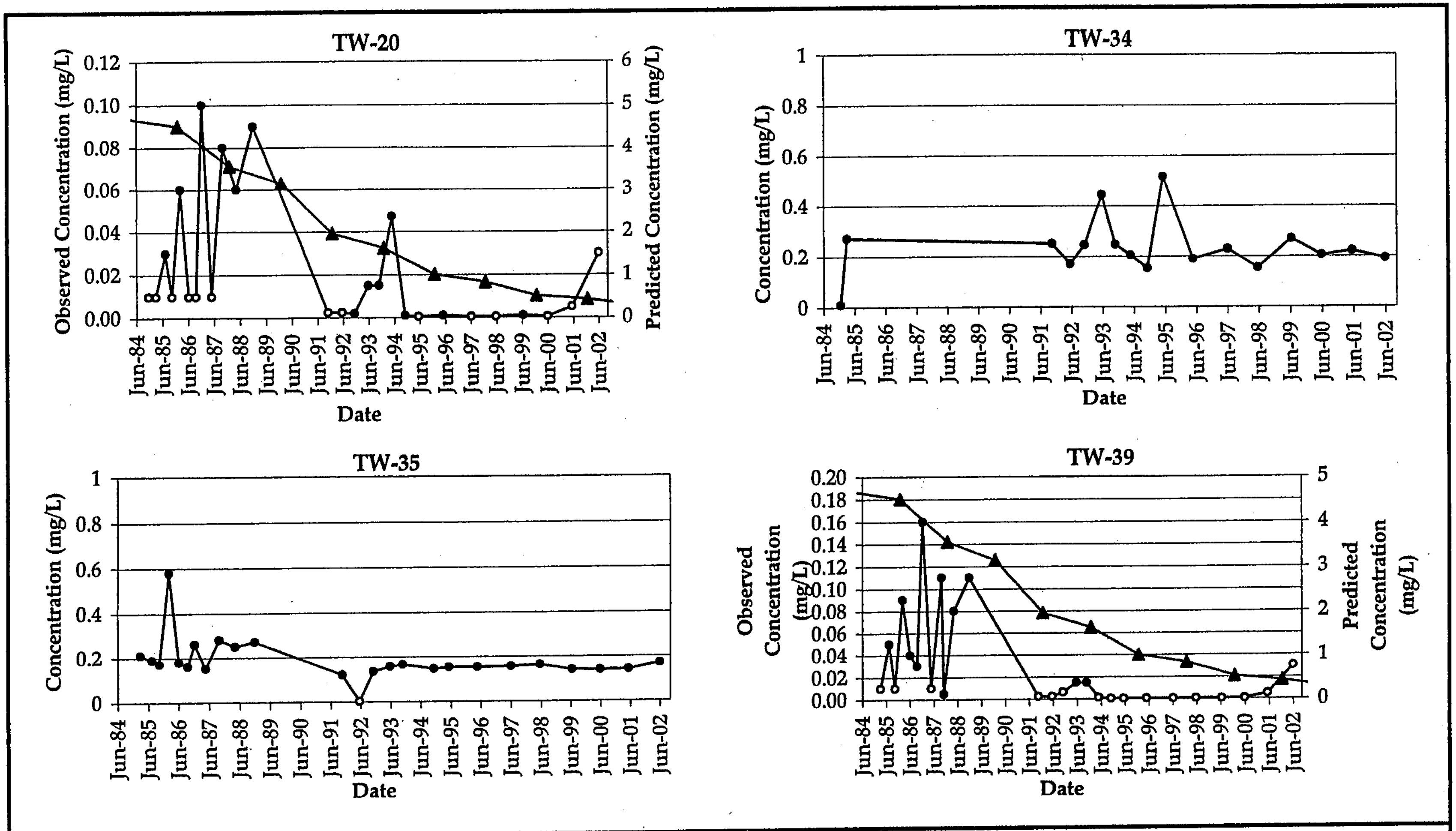
—●— Manganese Concentration (mg/L)
○ Non-Detects
—▲— Predicted Concentration

FIGURE C-13: MANGANESE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Manganese_AppD.xls

Golder Associates



Legend

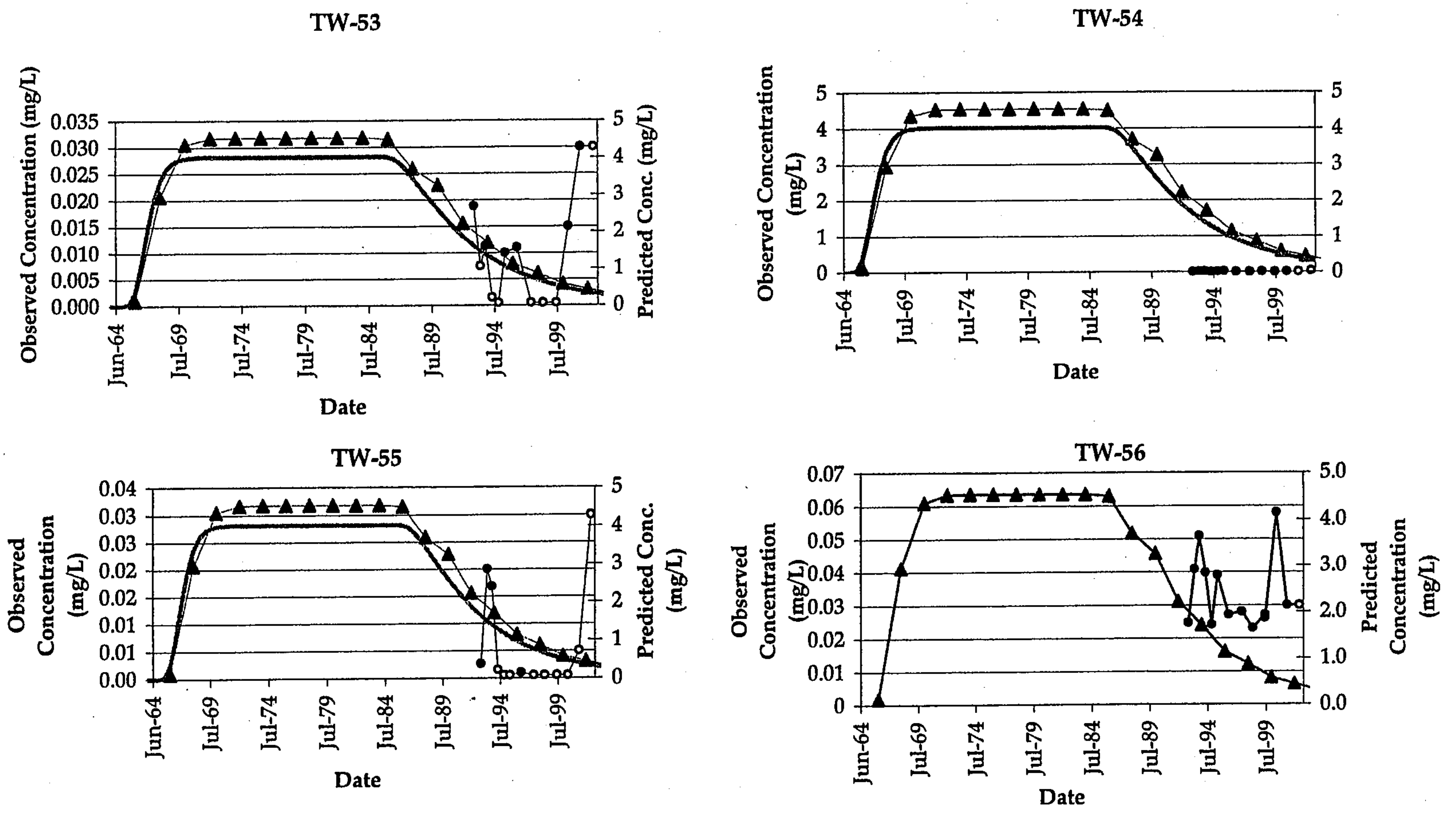
- ●— Manganese Concentration (mg/L)
- ○ Non-Detects
- ▲— Predicted Concentration

FIGURE C-14: MANGANESE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Manganese_AppD.xls

Golder Associates



Legend

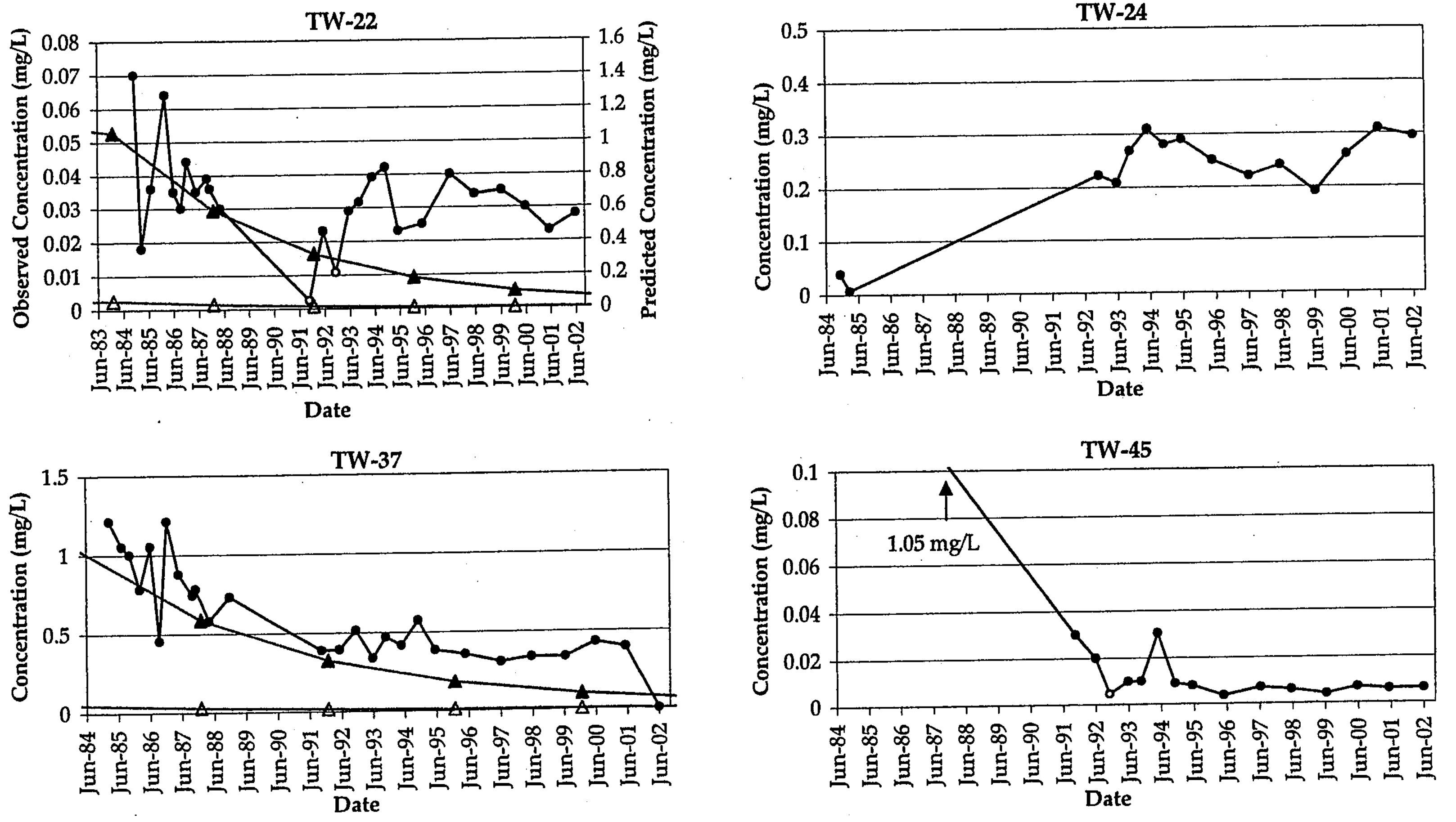
—●— Manganese Concentration (mg/L)
○ Non-Detects
—▲— Predicted Concentration
— GoldSim

FIGURE C-15: MANGANESE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Manganese_AppD.xls

Golder Associates



Legend

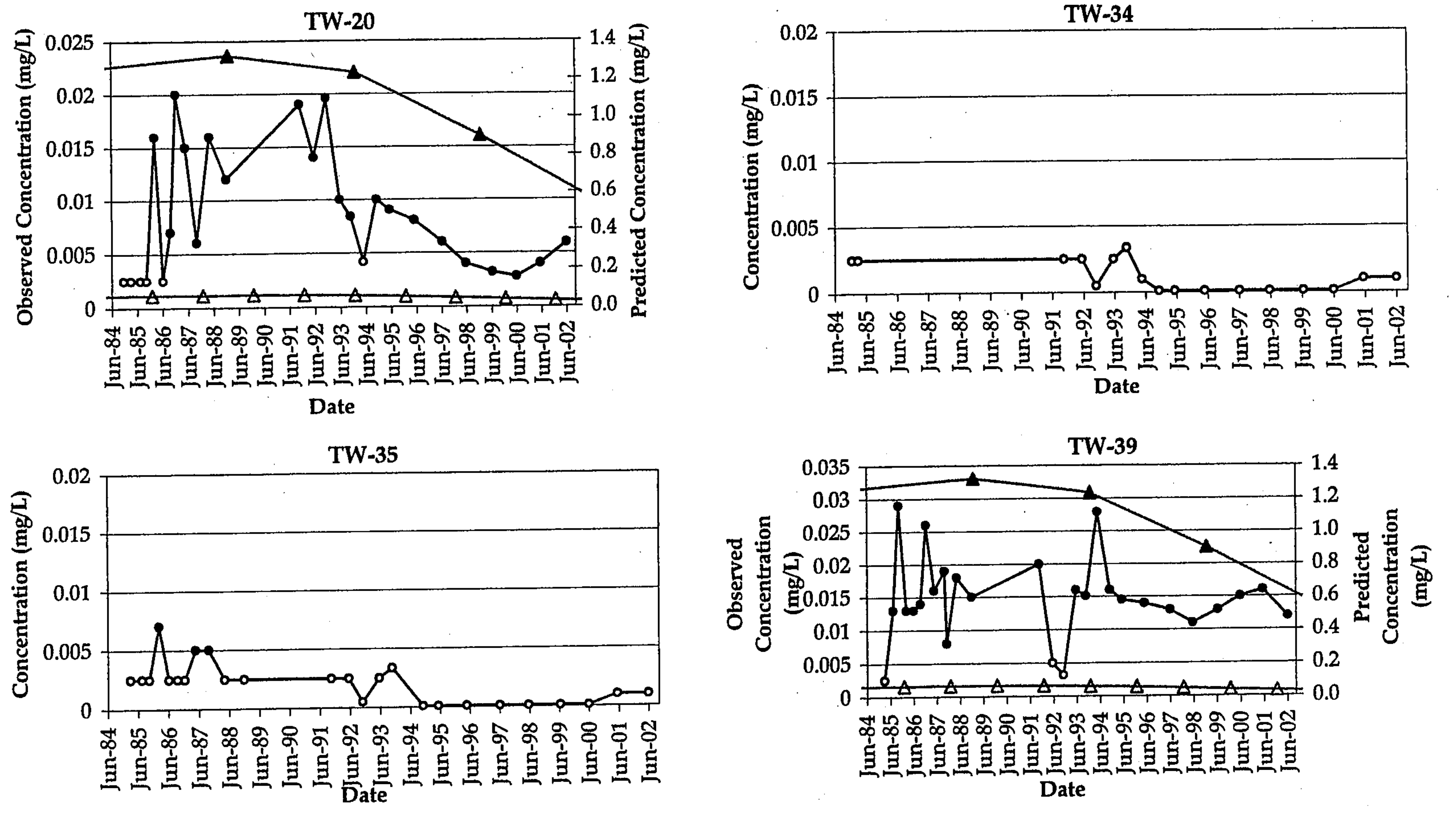
- —●— Cadmium Concentration (mg/L)
- ○ Non-Detects
- —▲— Predicted - No Solubility Control
- —△— Predicted - Solubility Control

FIGURE C-16: CADMIUM IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Legend

—●— Cadmium Concentration (mg/L)

○ Non-Detects

—▲— Predicted - No Solubility Control

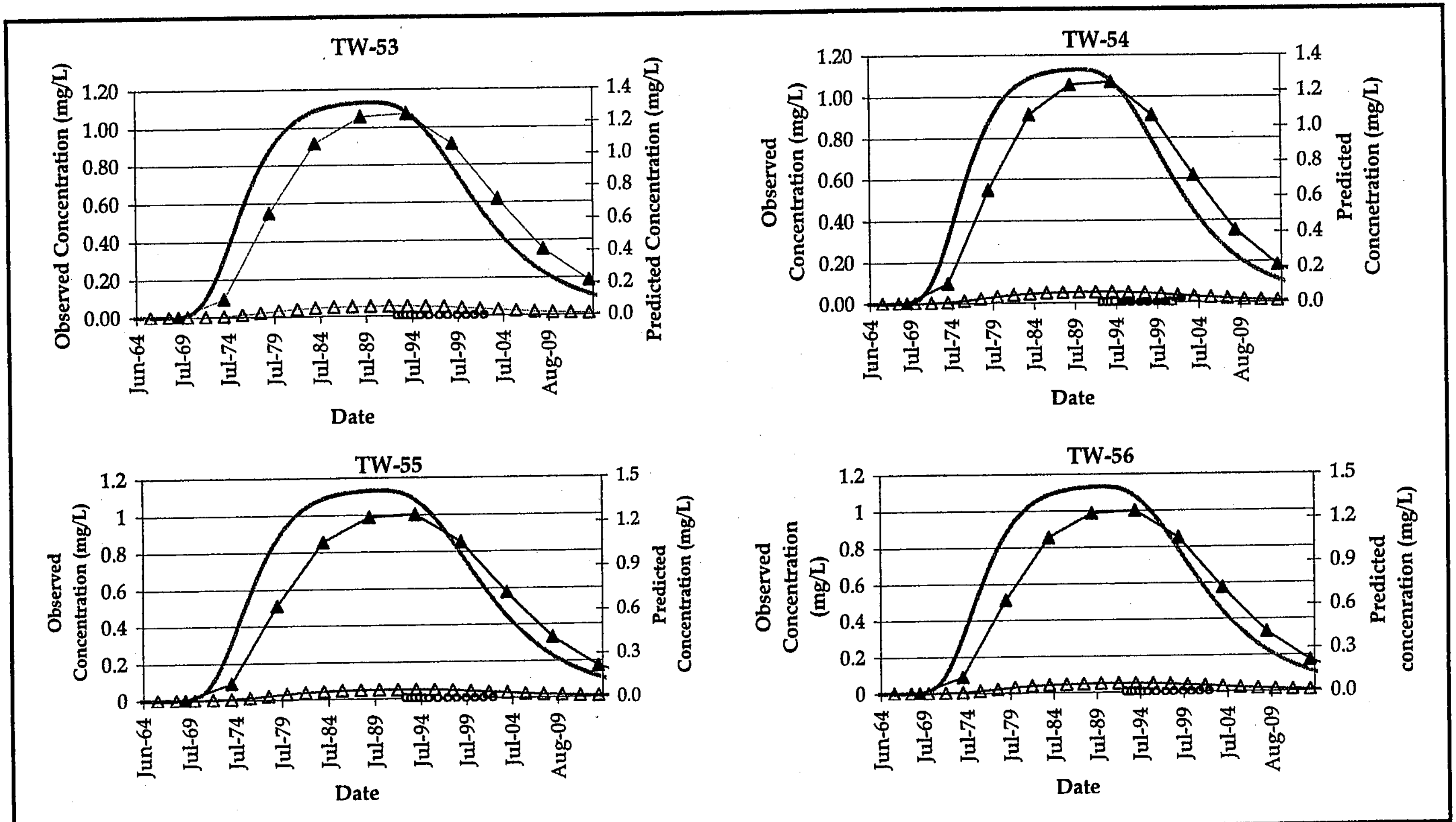
—△— Predicted - Solubility Control

FIGURE C-17: CADMIUM IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Legend
- ● Cadmium Concentration (mg/L)
- —o— Non-Detects
- ━━ Predicted-GoldSim
- —▲— Predicted - No Solubility Control
- —△— Predicted - Solubility Control

FIGURE C-18: CADMIUM IN SOUTHERN BOUNDARY WELLS

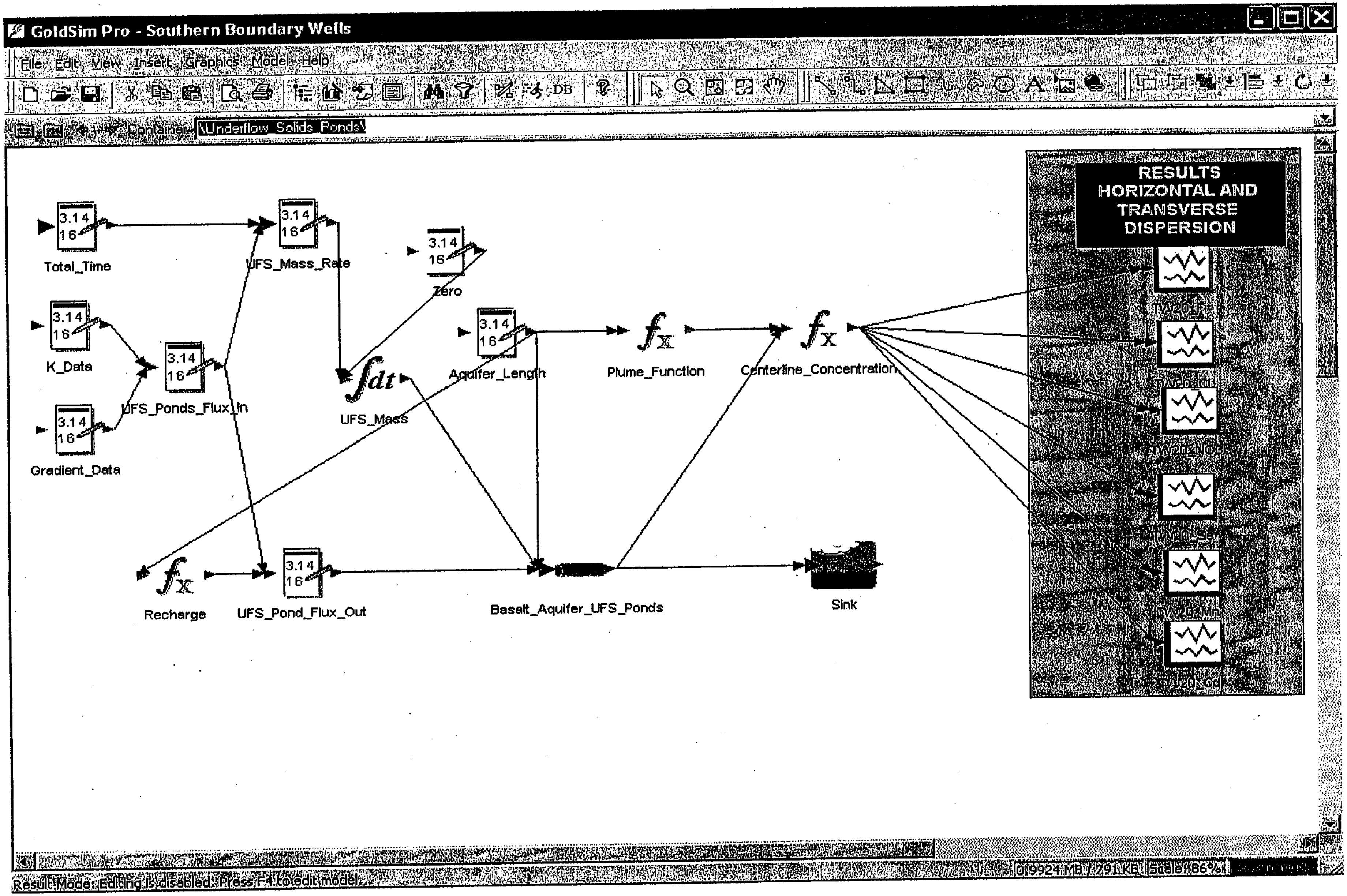
Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates

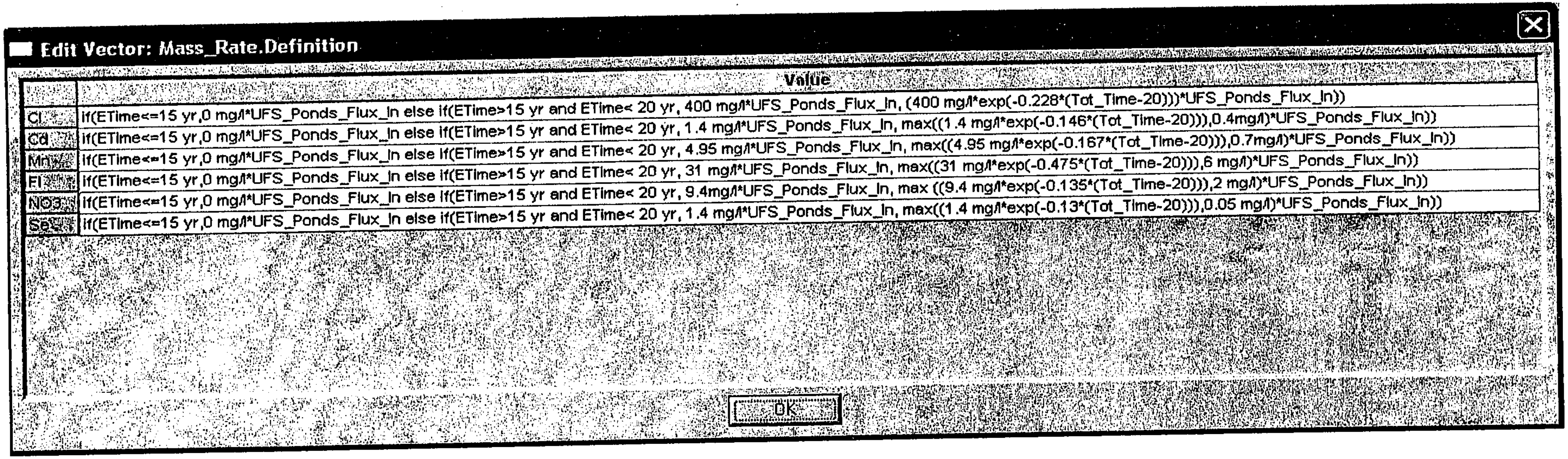
ATTACHMENT D

GOLDSIM SOLUTE TRANSPORT MODEL OUTPUT



Result Mode: Editing is disabled. Press F4 to edit model.

GoldSim Model Setup



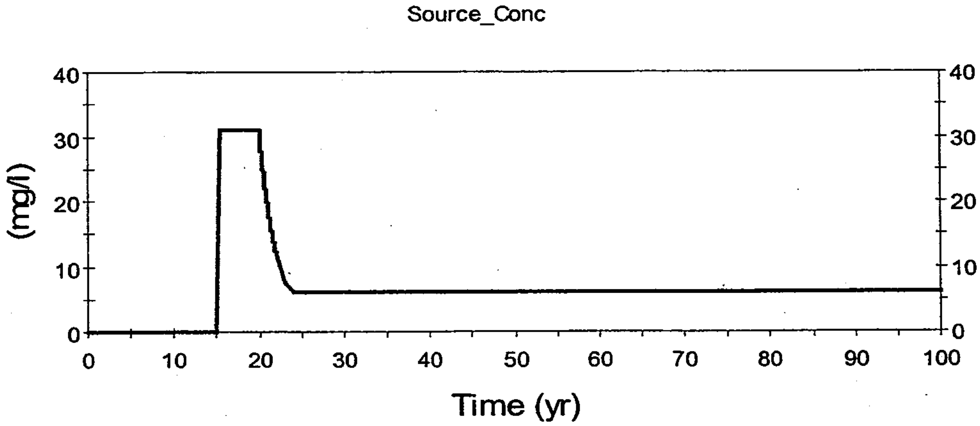
Edit Vector: Mass_Rate.Definition

	Value
Cl	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 400 mg/l*UFS_Ponds_Flux_In, (400 mg/l*exp(-0.228*(Tot_Time-20)))*UFS_Ponds_Flux_In))
Cd	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 1.4 mg/l*UFS_Ponds_Flux_In, max((1.4 mg/l*exp(-0.146*(Tot_Time-20))),0.4mg/l)*UFS_Ponds_Flux_In))
Mn	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 4.95 mg/l*UFS_Ponds_Flux_In, max((4.95 mg/l*exp(-0.167*(Tot_Time-20))),0.7mg/l)*UFS_Ponds_Flux_In))
Fl	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 31 mg/l*UFS_Ponds_Flux_In, max((31 mg/l*exp(-0.475*(Tot_Time-20))),6 mg/l)*UFS_Ponds_Flux_In))
NO3	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 9.4mg/l*UFS_Ponds_Flux_In, max ((9.4 mg/l*exp(-0.135*(Tot_Time-20))),2 mg/l)*UFS_Ponds_Flux_In))
Se	if(ETime<=15 yr,0 mg/l*UFS_Ponds_Flux_In else if(ETime>15 yr and ETime< 20 yr, 1.4 mg/l*UFS_Ponds_Flux_In, max((1.4 mg/l*exp(-0.13*(Tot_Time-20))),0.05 mg/l)*UFS_Ponds_Flux_In))

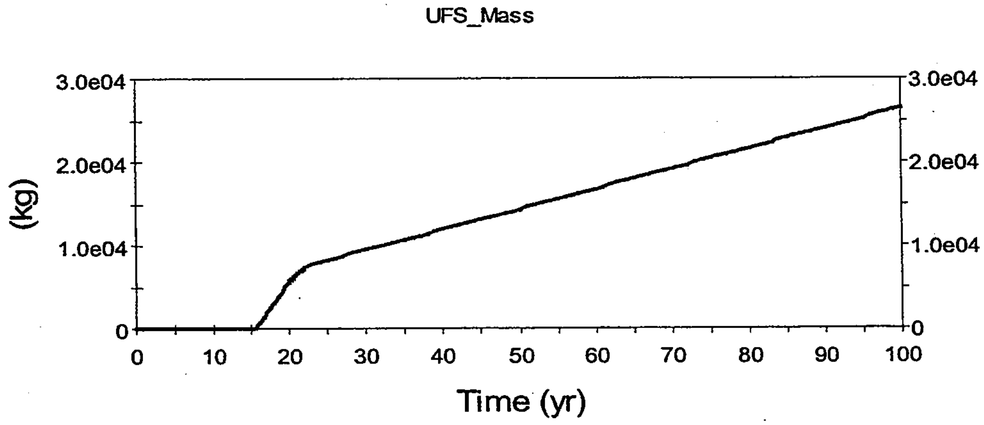
Time history of mass from old UFS Ponds

concentration input

Chloride



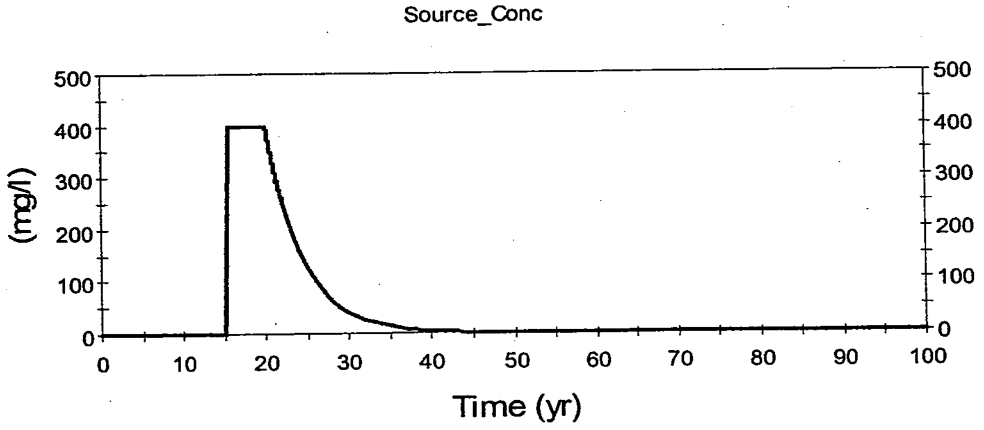
Fluoride concentrations-Old UFS Ponds



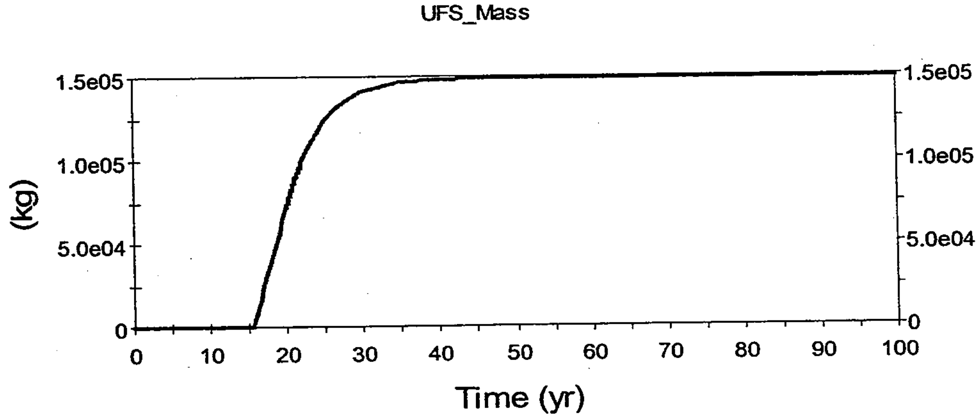
Fluoride mass from old UFS Ponds

F data

Chloride



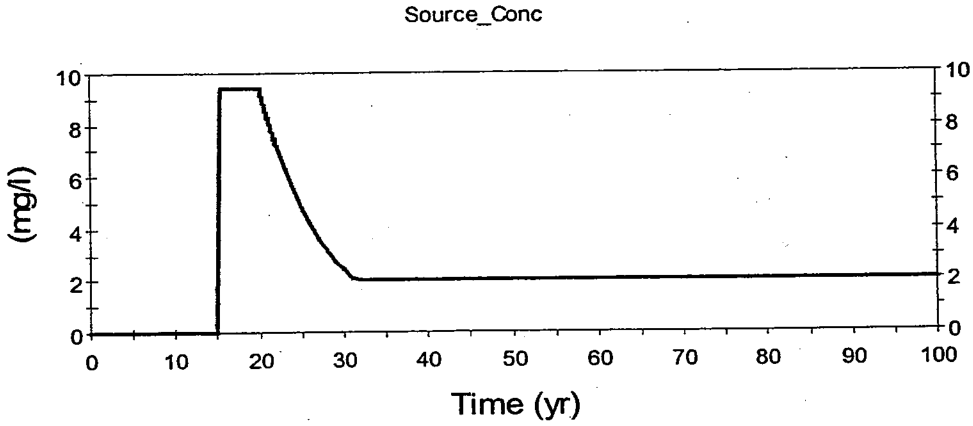
Chloride concentrations-Old UFS Ponds



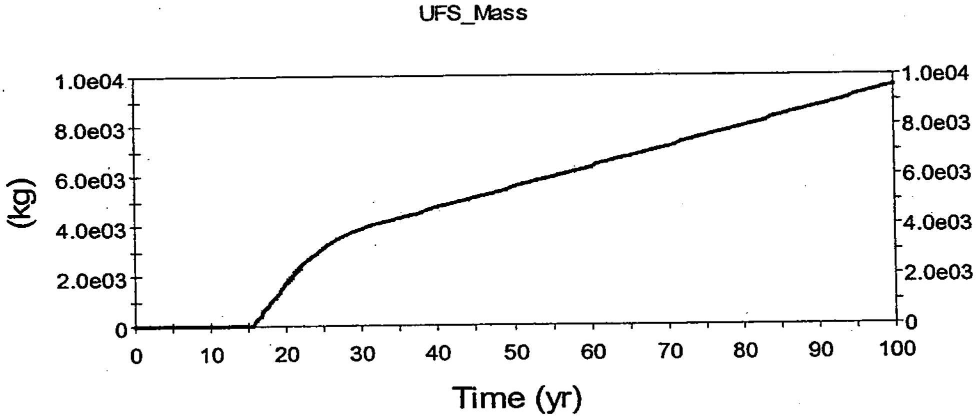
Chloride mass from old UFS Ponds

Cl data

Chloride



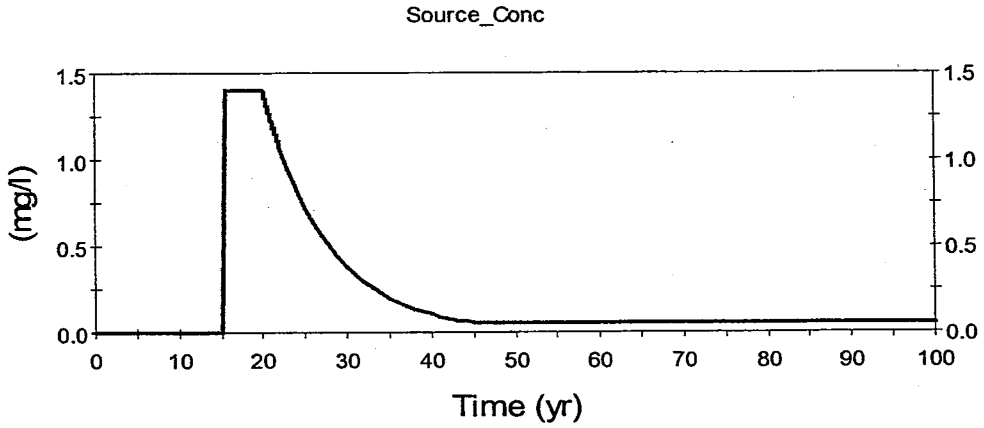
Nitrate concentrations-Old UFS Ponds



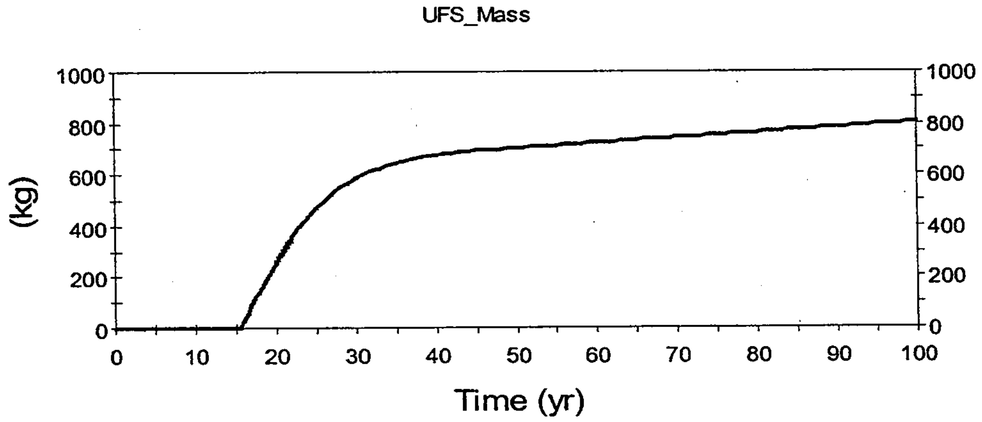
Nitrate mass from old UFS Ponds

NO3 data

Chloride



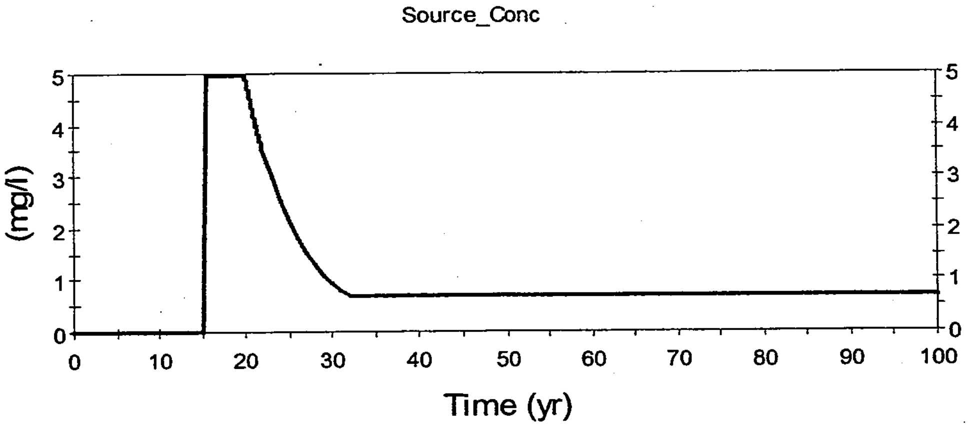
Selenium concentrations-Old UFS Ponds



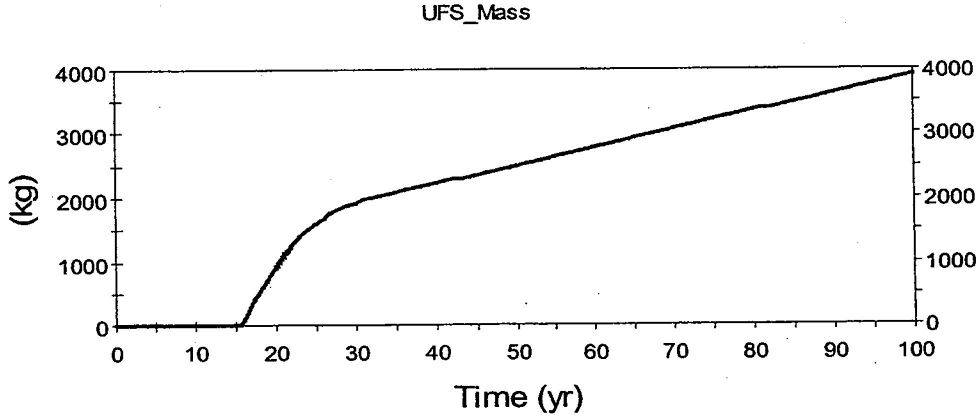
Selenium mass from old UFS Ponds

Se data

Chloride



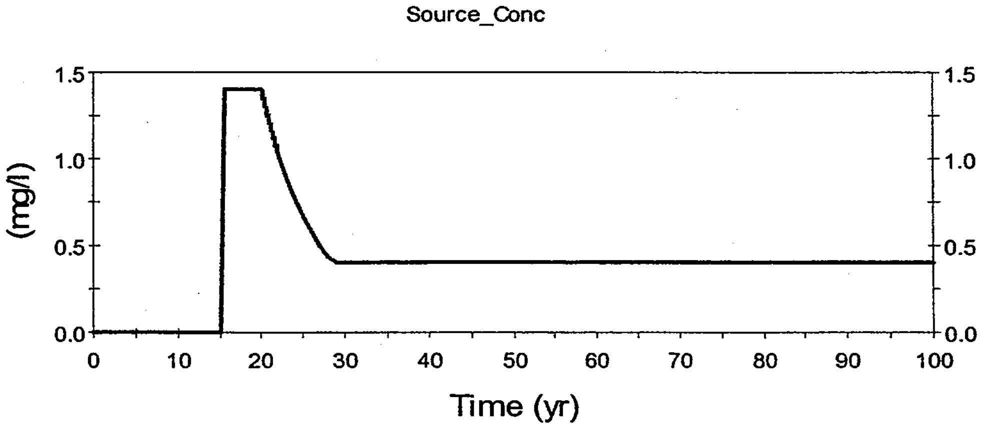
Manganese concentrations-Old UFS Ponds



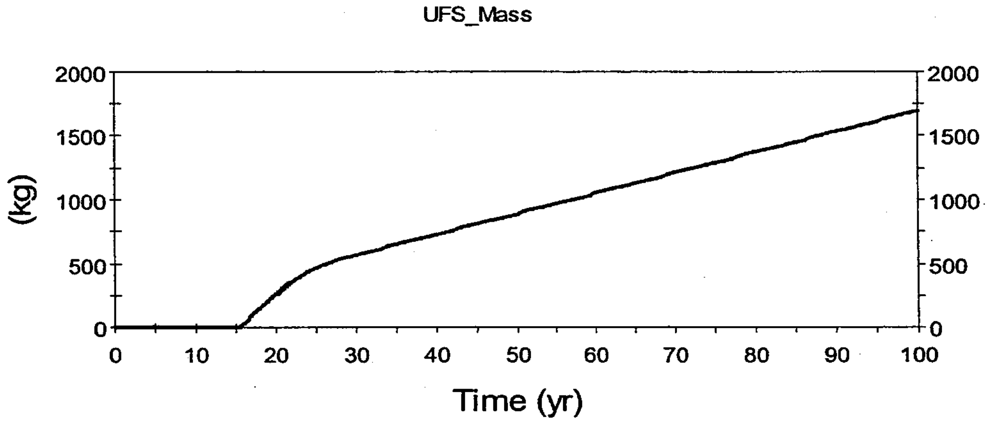
Manganese mass from old UFS Ponds

Mn data

Chloride

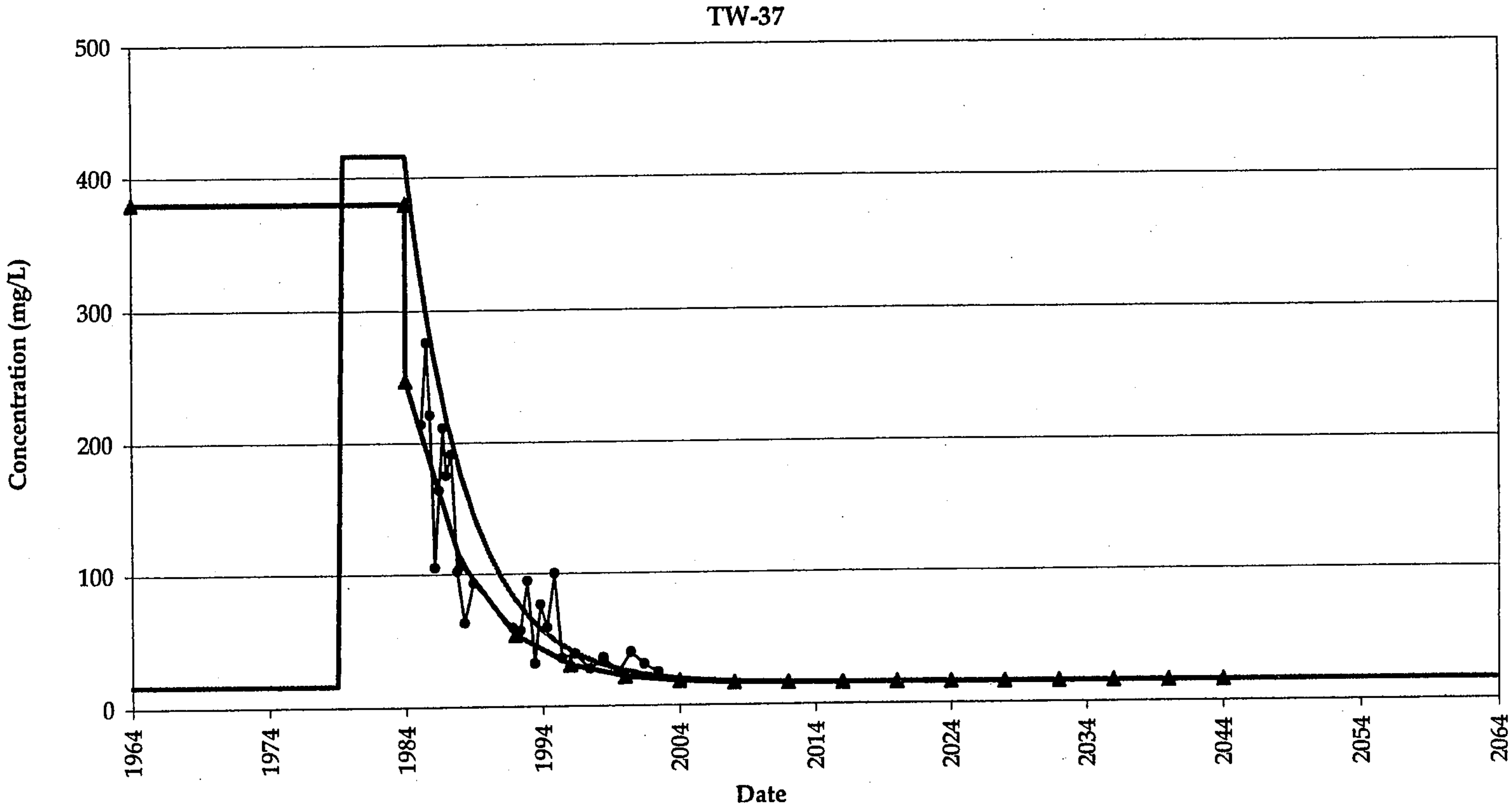


Cadmium concentrations-Old UFS Ponds



Cadmium mass from old UFS Ponds

Cd data



Note: Includes background concentration of 16 mg/L.

Legend

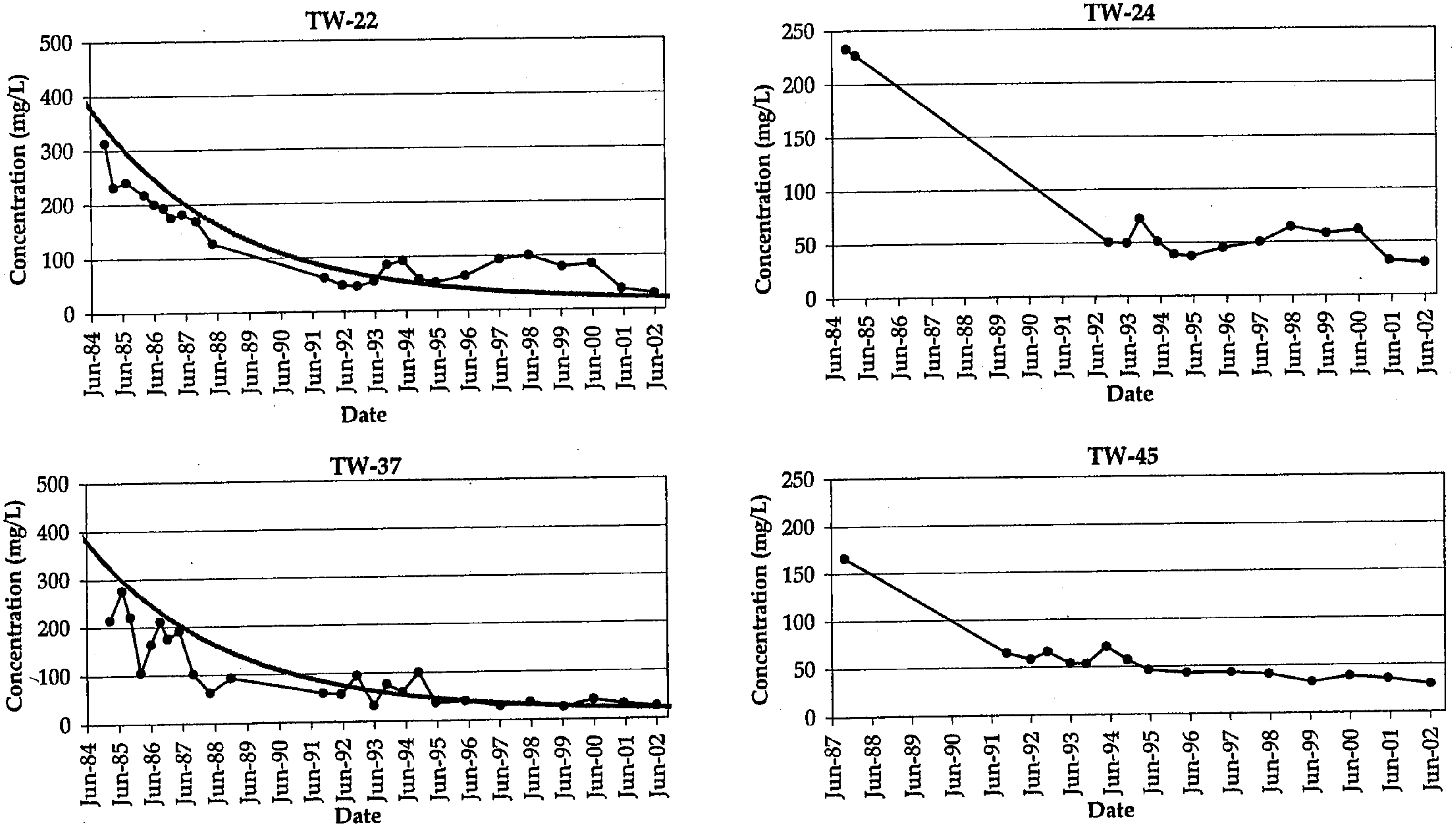
—●— Chloride Concentration (mg/L)

—— Predicted Source Concentration-No Solubility Control

—▲— Old Model Source Concentration-No Solubility Control

FIGURE D-1: CHLORIDE IN UNDERFLOW SOLIDS POND SOURCE AREA

Golder Associates



Legend

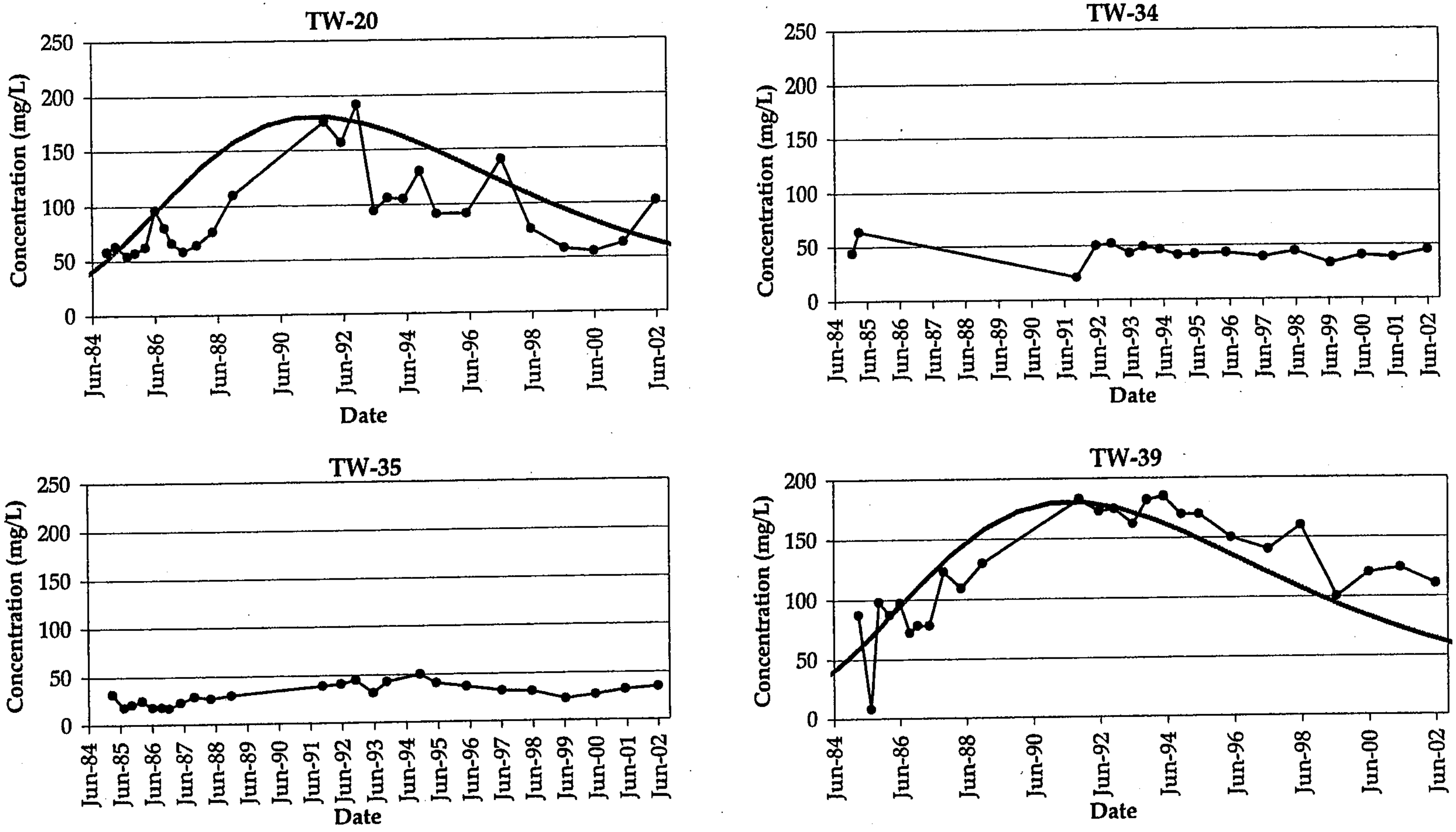
—●— Chloride Concentration (mg/L)
▬▬ Predicted Concentration

FIGURE D-2: CHLORIDE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



Legend

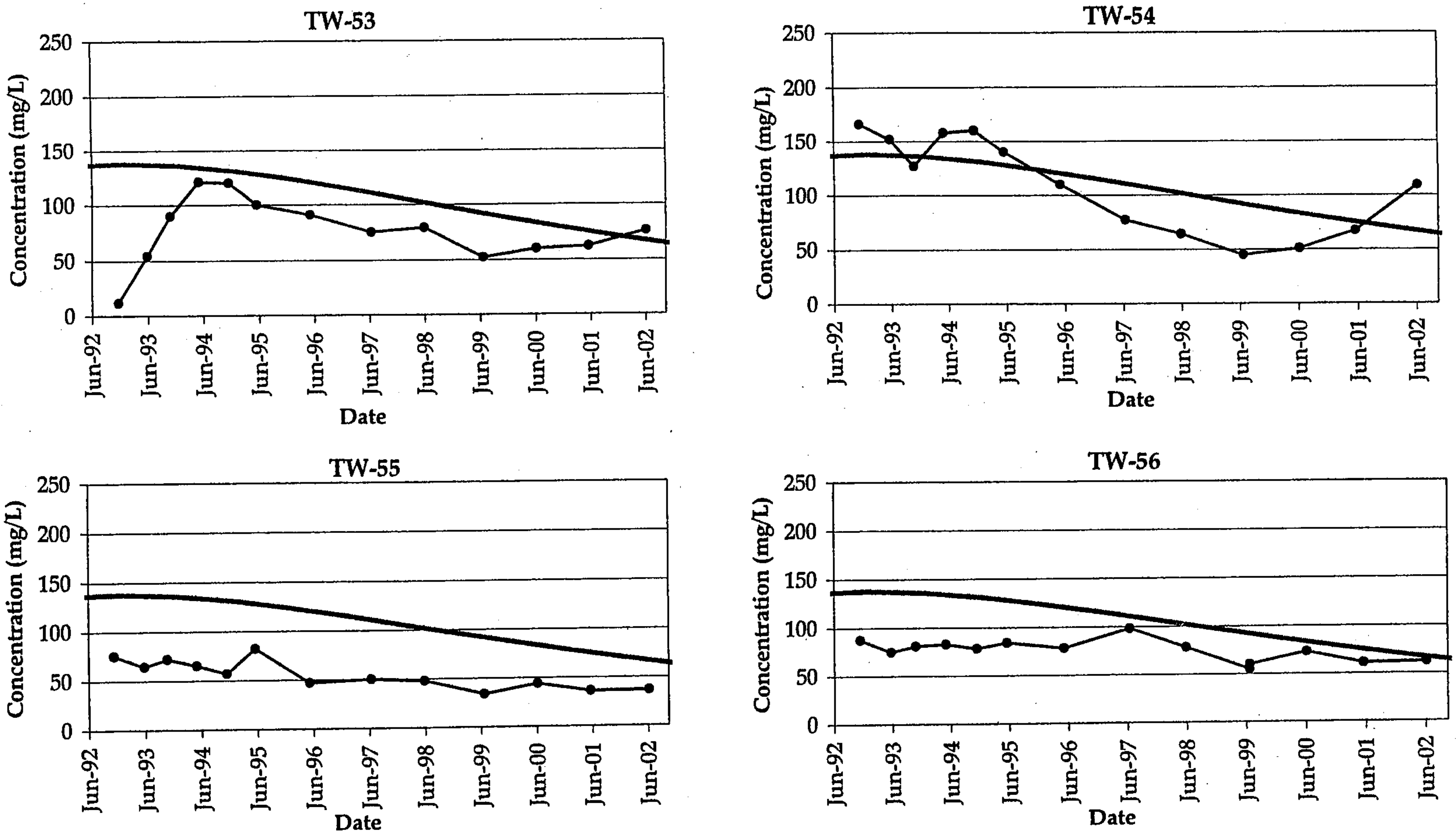
—●— Chloride Concentration (mg/L)
—— Predicted Concentration

FIGURE D-3: CHLORIDE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



Legend

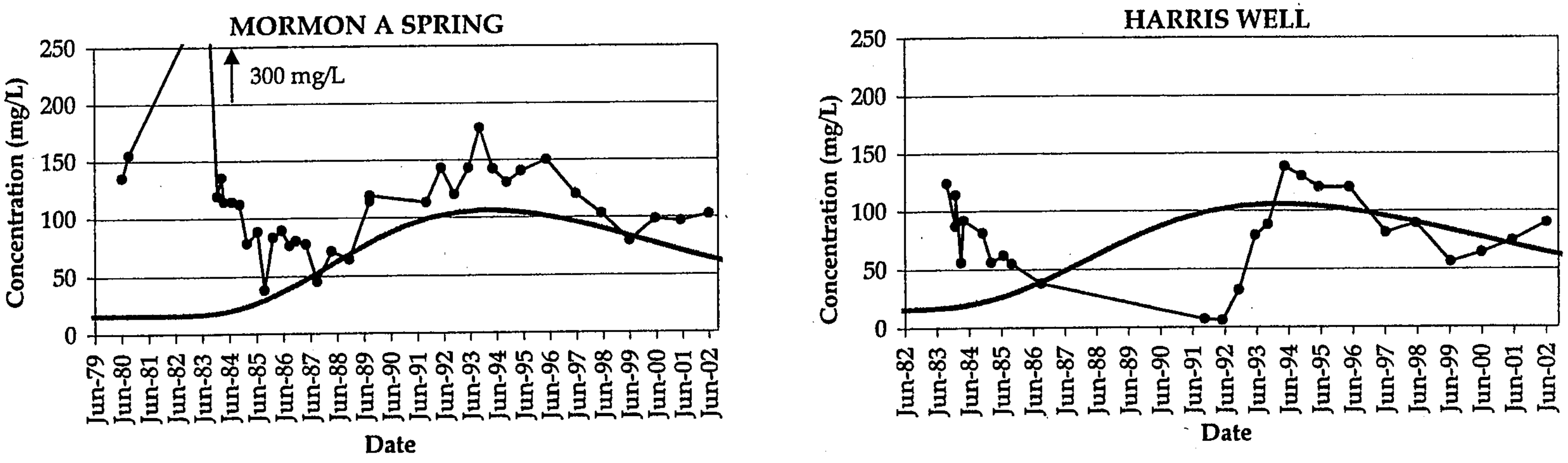
—●— Chloride Concentration (mg/L)
▬▬ Predicted Concentration

FIGURE D-4: CHLORIDE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



Legend

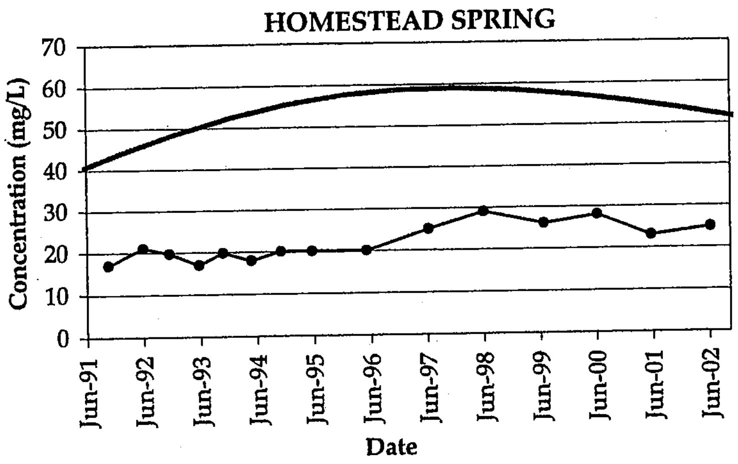
—●— Chloride Concentration (mg/L)
—— Predicted Concentration

FIGURE D-5: CHLORIDE IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates



HOMESTEAD SPRING

Legend

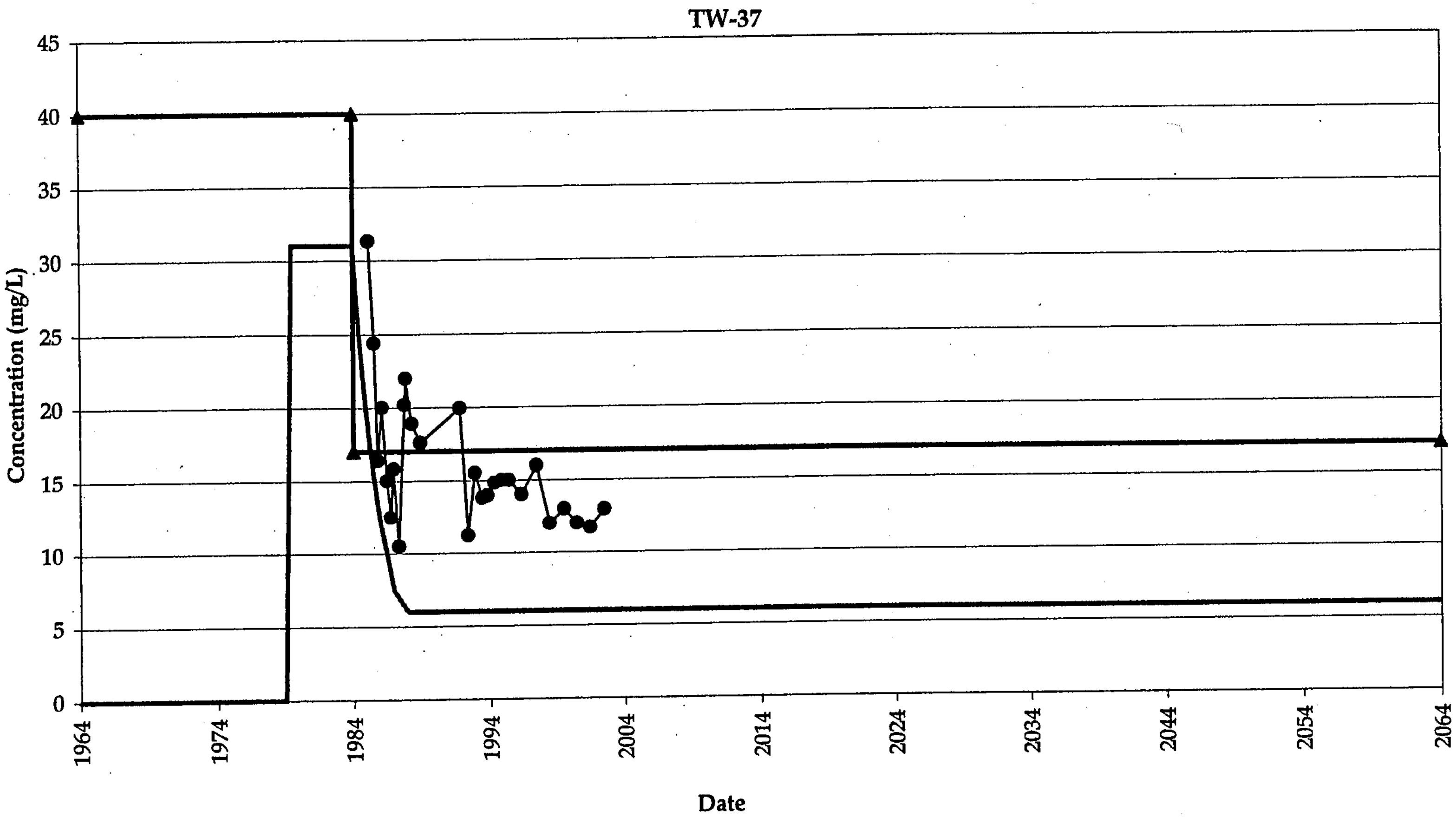
—●— Chloride Concentration (mg/L)
—— Predicted Concentration

FIGURE D-6: CHLORIDE IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Chloride_AppG.xls

Golder Associates

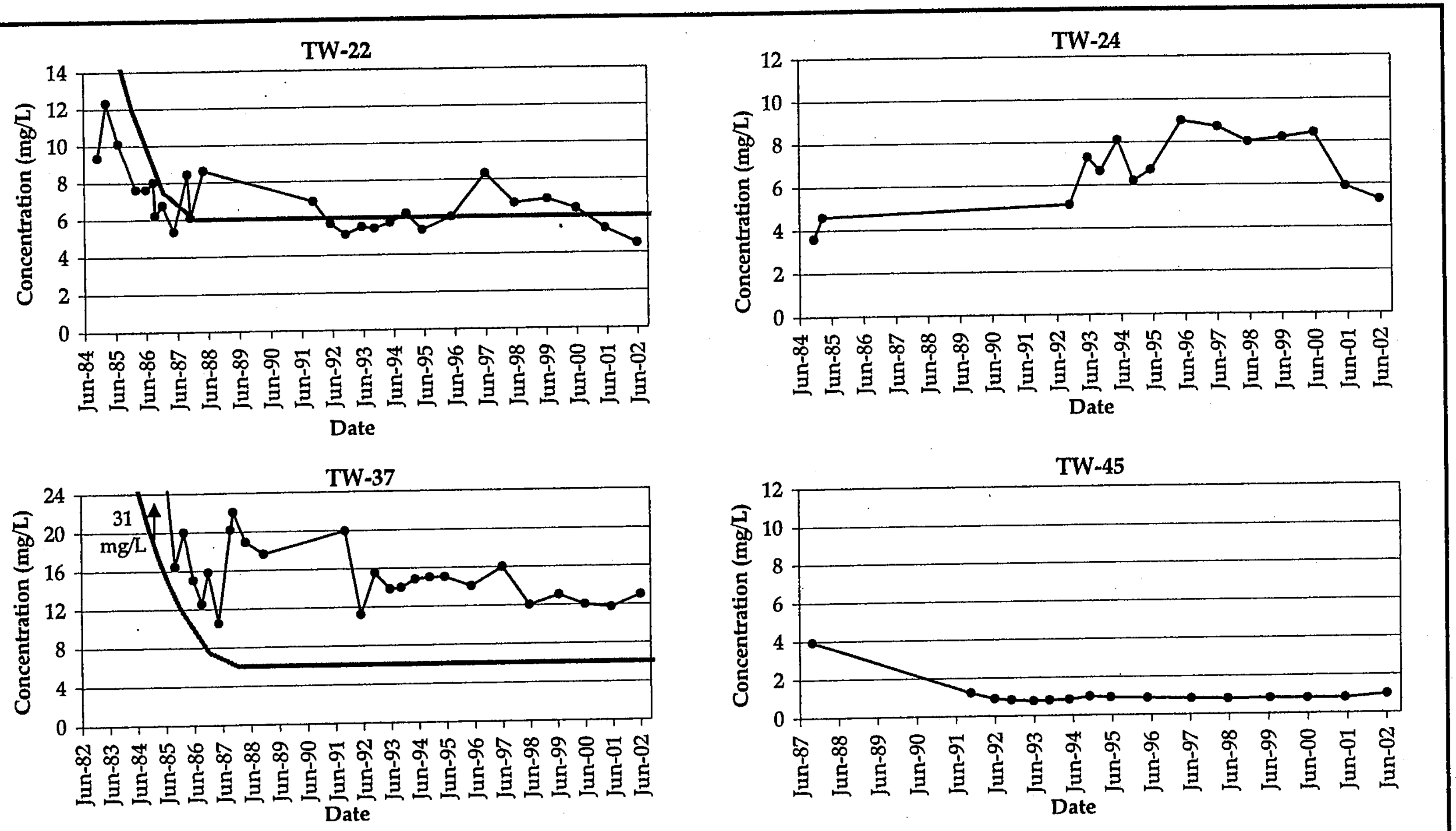


Constant source concentration of 6 mg/l after 1988 based on observed downstream concentrations.

Legend

FIGURE D-7: FLUORIDE IN UNDERFLOW SOLIDS POND SOURCE AREA

Golder Associates



Legend

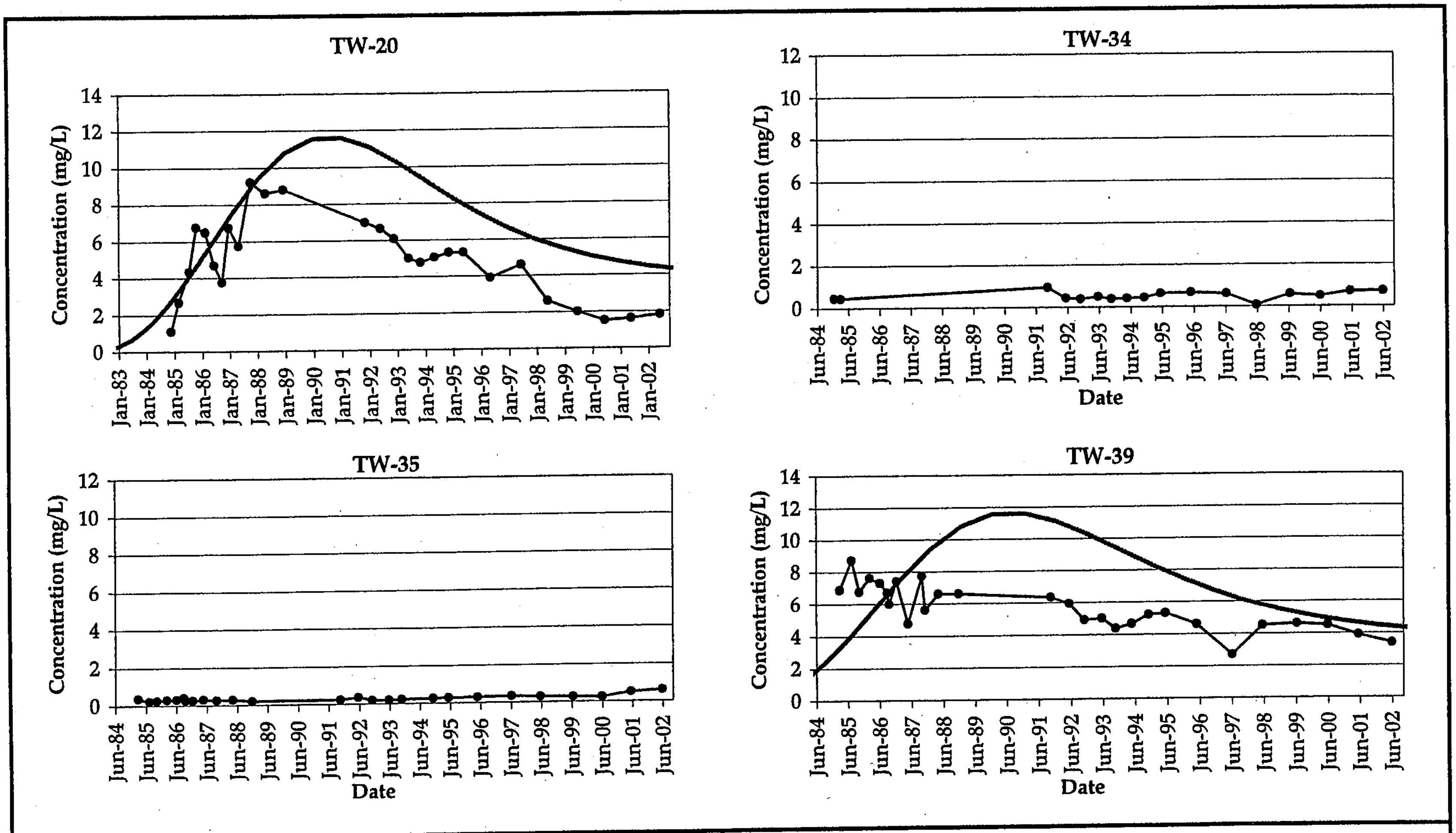
—●— Fluoride Concentration (mg/L)
—— Predicted Concentration

FIGURE D-8: FLUORIDE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

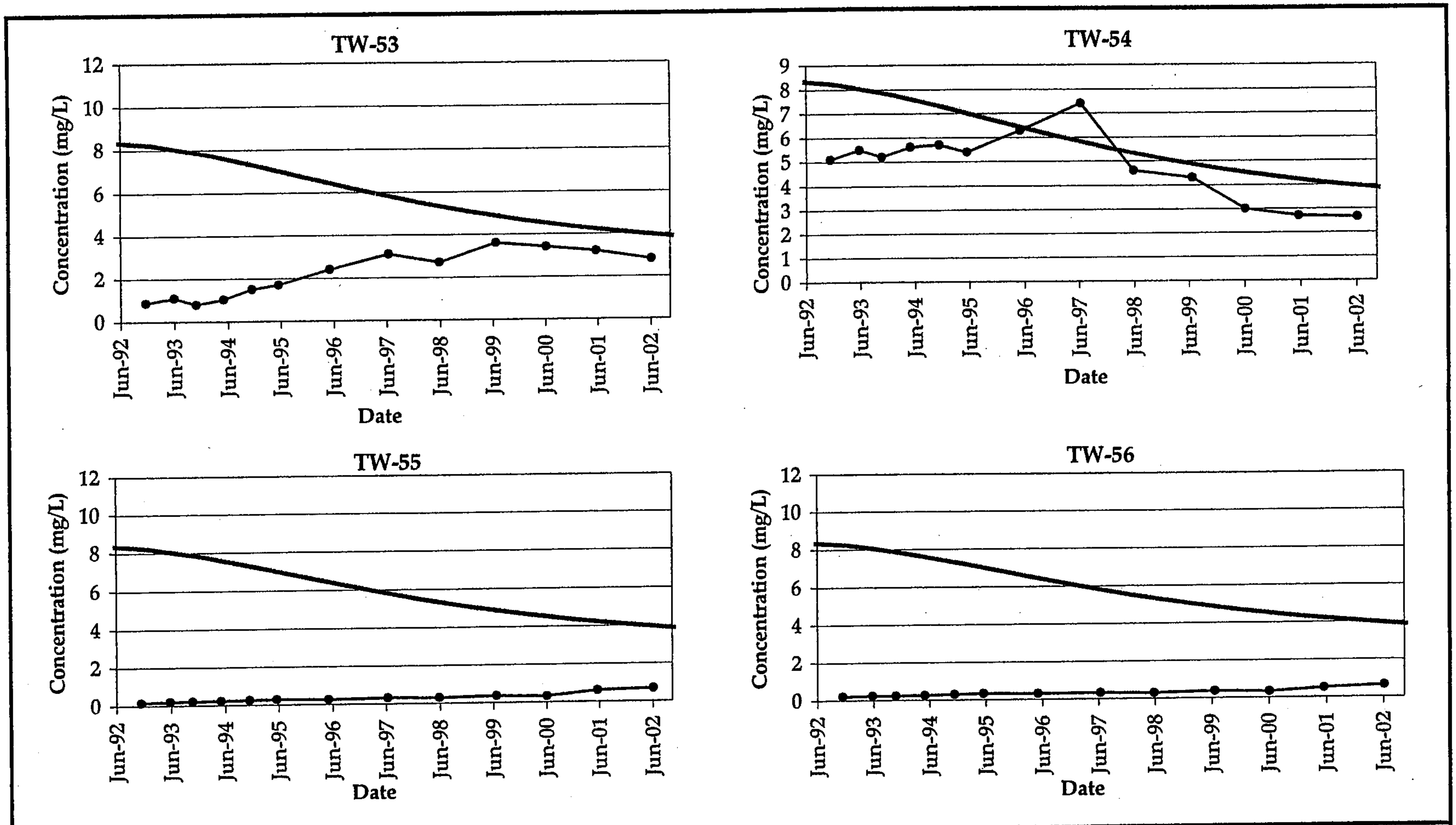
- —●— Fluoride Concentration (mg/L)
- —— Predicted Concentration

FIGURE D-9: FLUORIDE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

—●— Fluoride Concentration (mg/L)

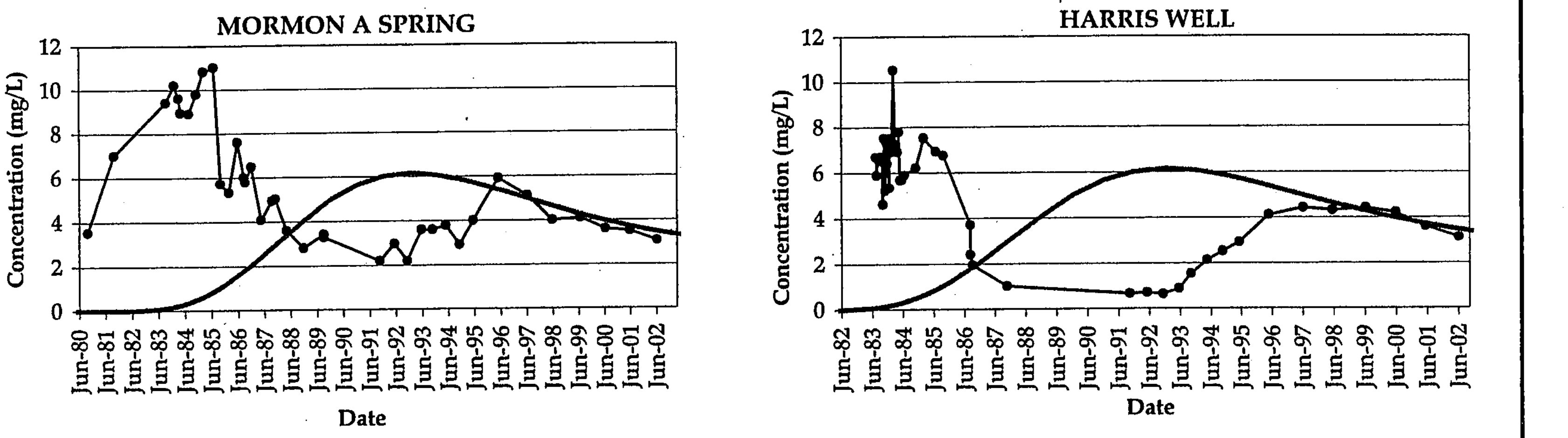
—— Predicted Concentration

FIGURE D-10: FLUORIDE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

—●— Fluoride Concentration (mg/L)

▬ Predicted Concentration

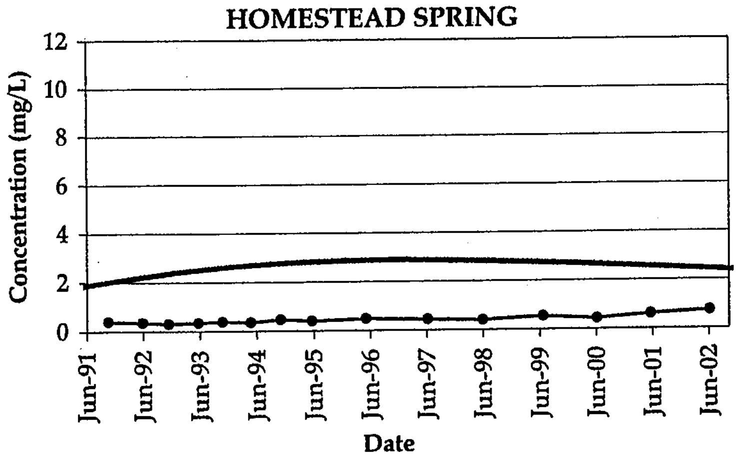
Remediation Goal (4 mg/L)

FIGURE D-11: FLUORIDE IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates



Legend

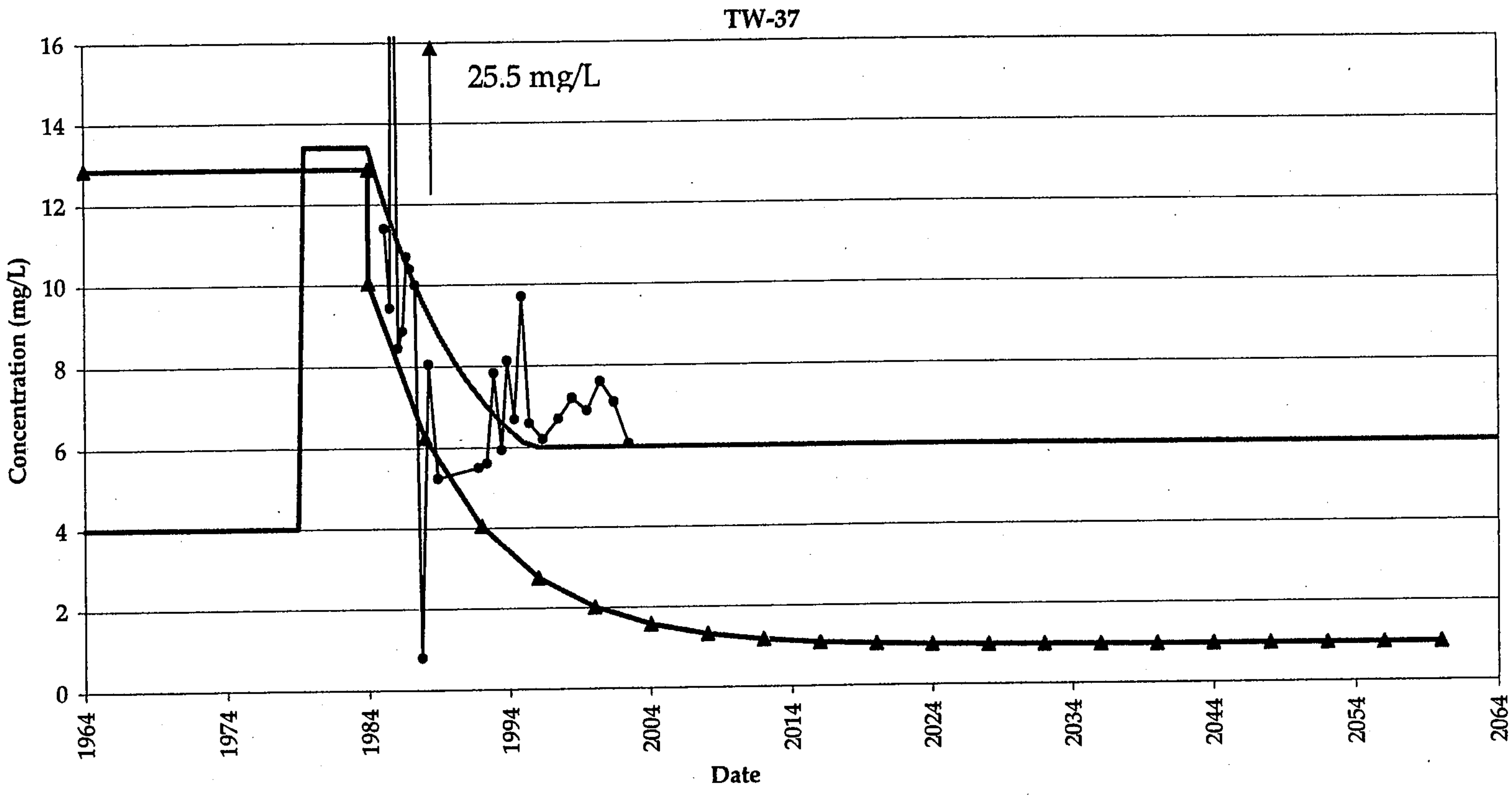
—●— Fluoride Concentration (mg/L)
—— Predicted Concentration(10,000 feet from UFS Ponds)

FIGURE D-12: FLUORIDE IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Fluoride_AppC.xls

Golder Associates

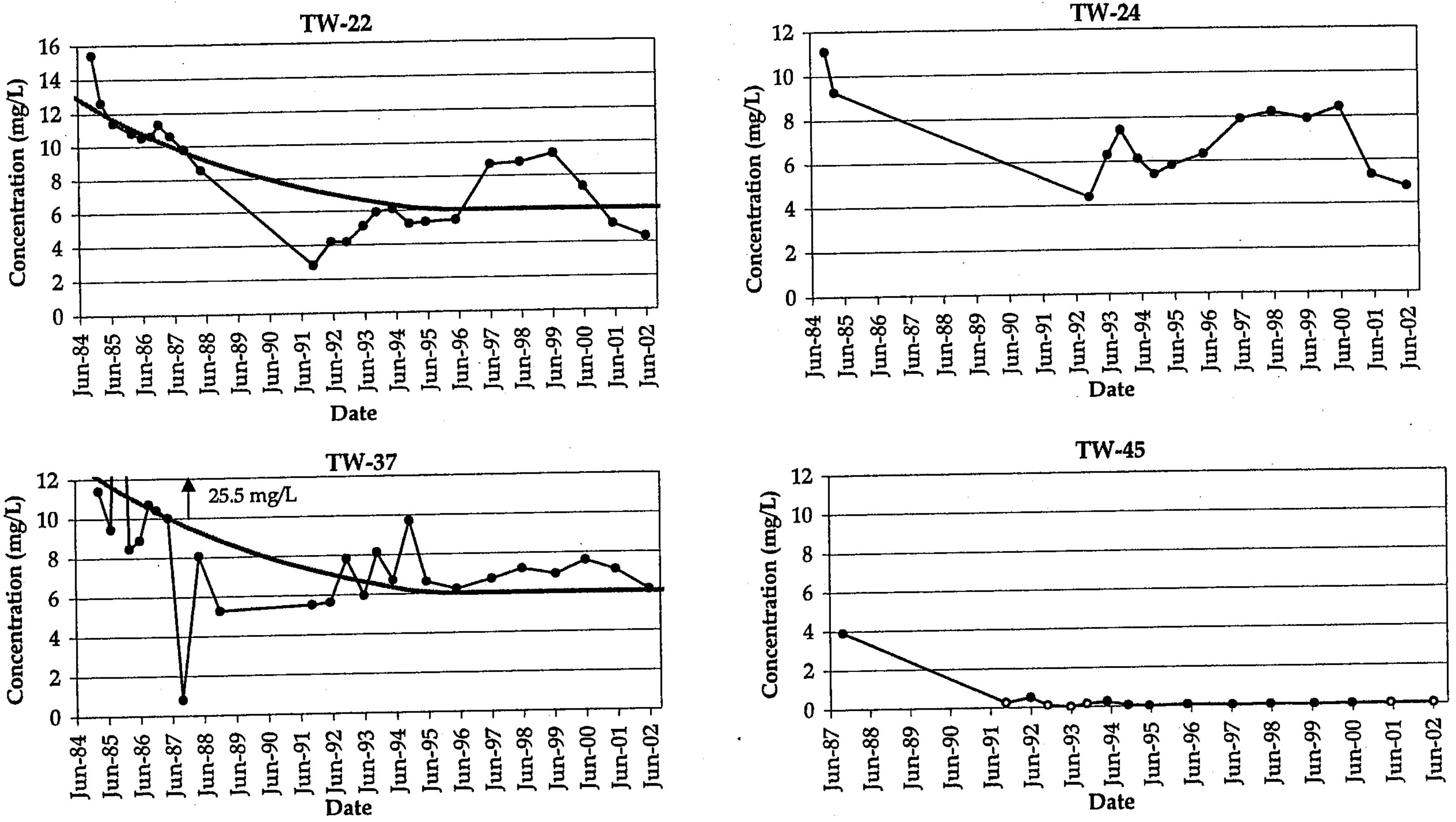


Note: Includes background concentration of 4 mg/L.

Legend

FIGURE D-13: NITRATE AS N IN UNDERFLOW SOLIDS POND SOURCE AREA

Golder Associates



TW-22

TW-24

TW-37

TW-45

Legend

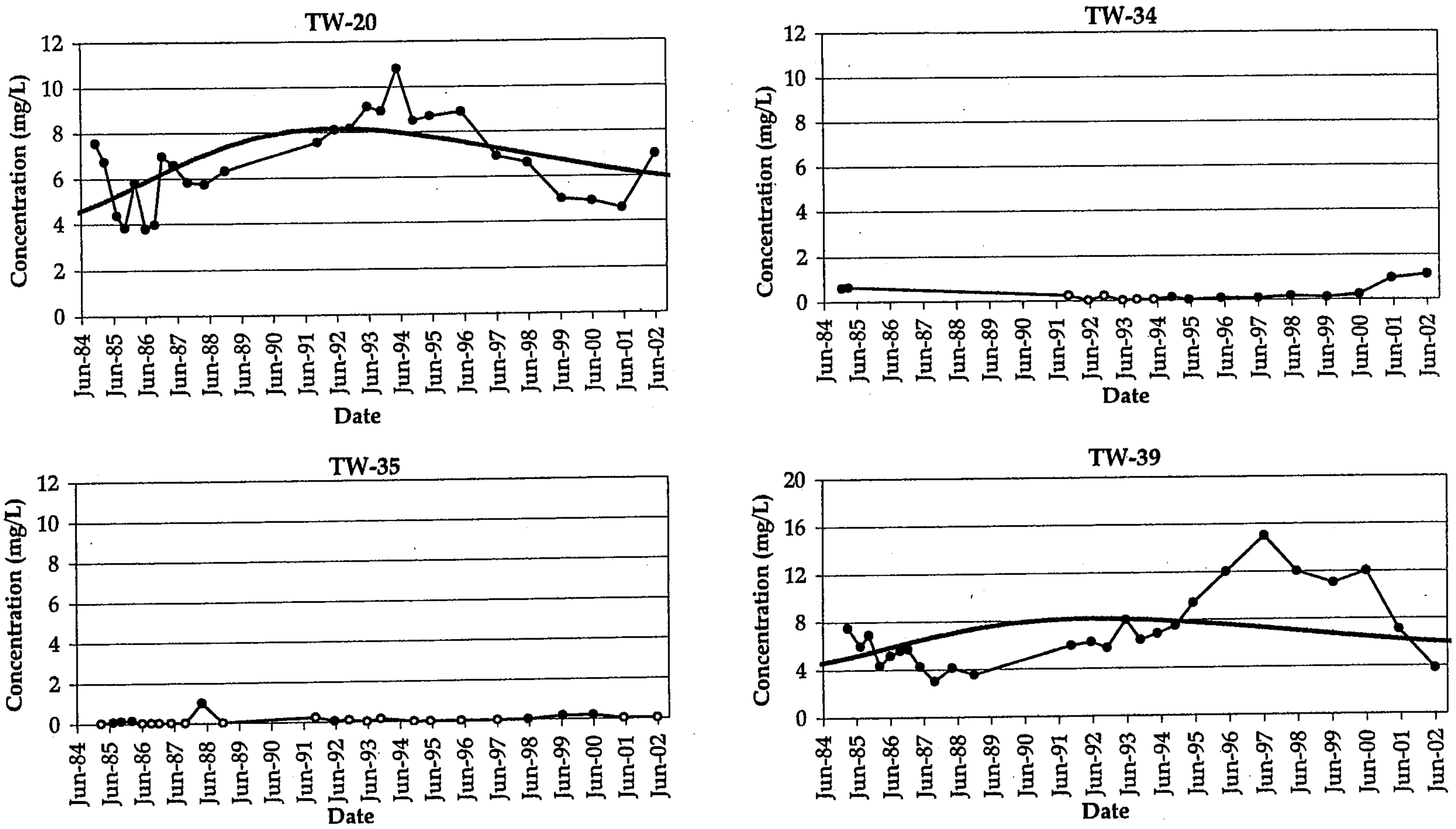
- ●— Nitrate as N Concentration (mg/L)
- ○ Non-Detects
- — Predicted Concentration

FIGURE D-14: NITRATE AS N IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

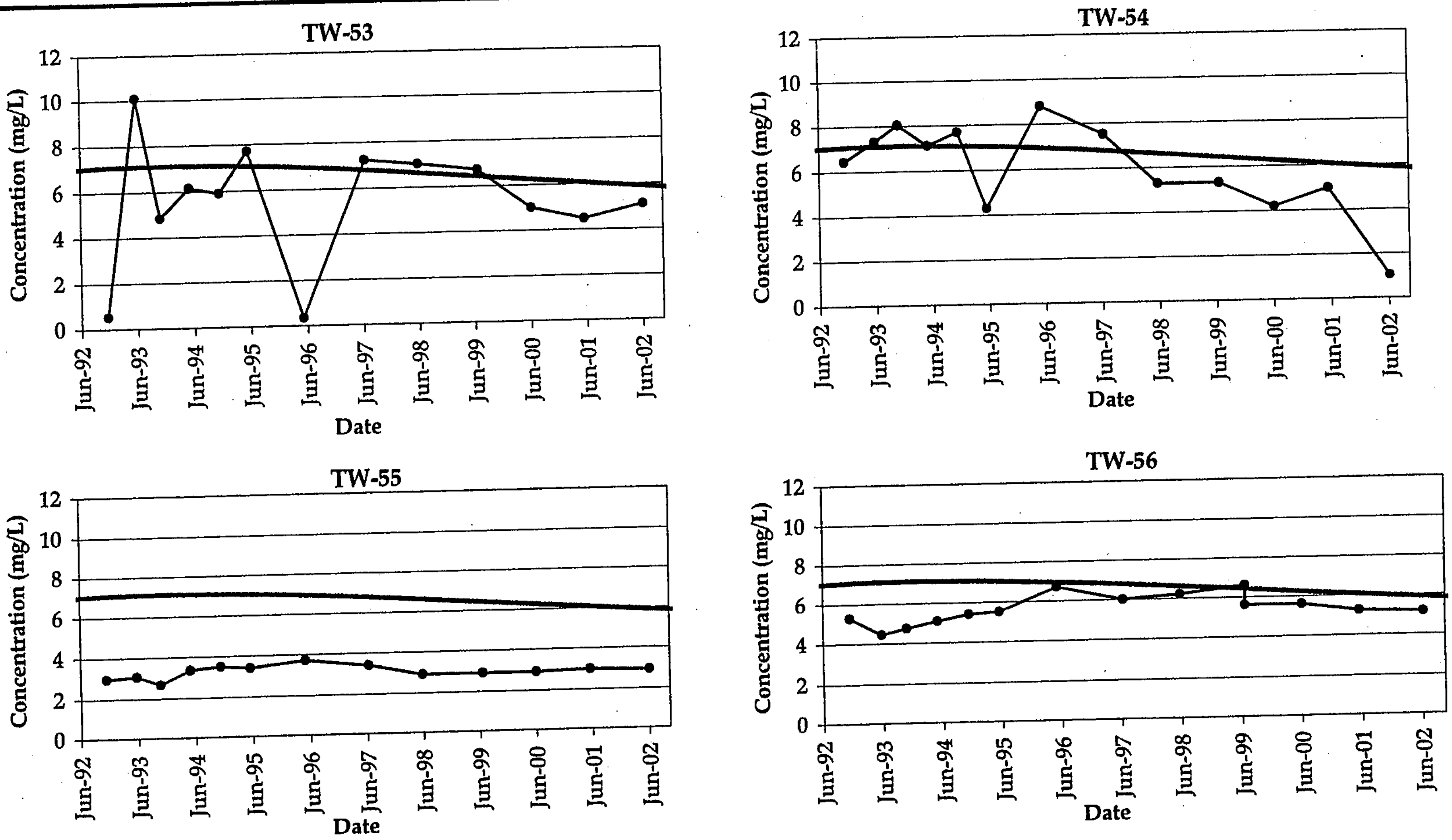
●— Nitrate as N Concentration (mg/L)
○ Non-Detects
▬ Predicted Concentration

FIGURE D-15: NITRATE AS N IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

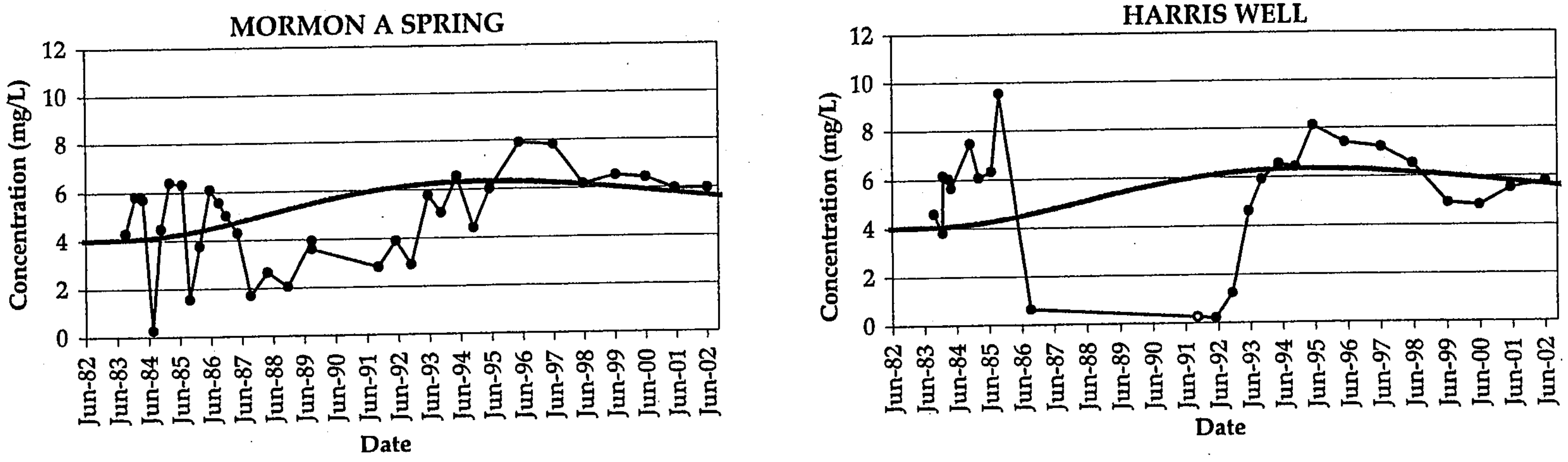
—●— Nitrate as N Concentration (mg/L)
▬ Predicted Concentration

FIGURE D-16: NITRATE AS N IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

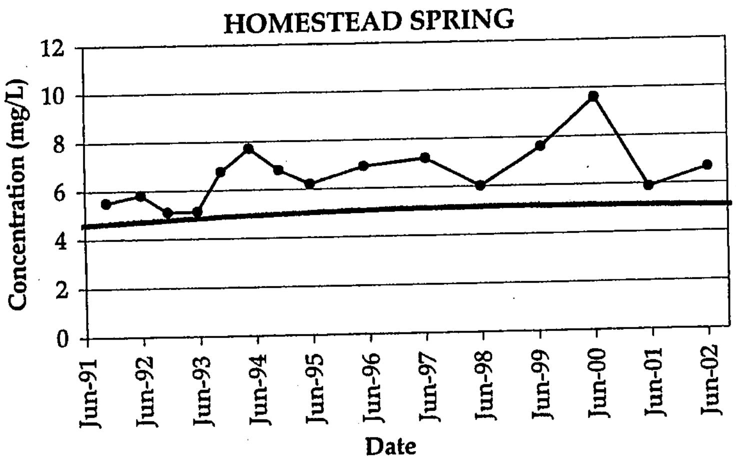
- ●— Nitrate as N Concentration (mg/L)
- ○ Non-Detects
- —— Predicted Concentration

FIGURE D-17: NITRATE AS N IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



Legend

—●— Nitrate as N Concentration (mg/L)

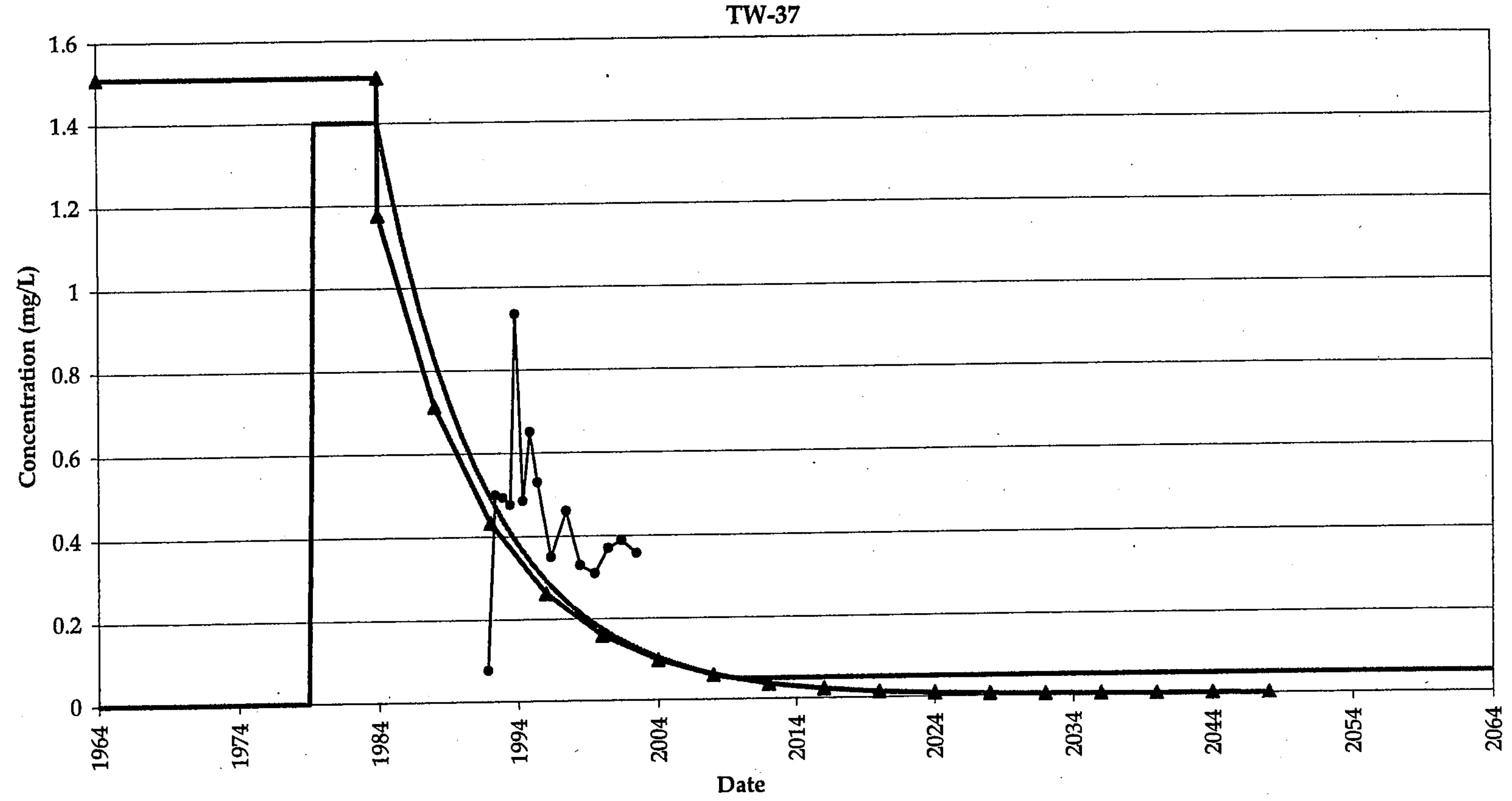
—— Predicted Concentration (10,000 feet from UFS Ponds)

FIGURE D-18: NITRATE AS N IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Nitrate_AppE.xls

Golder Associates



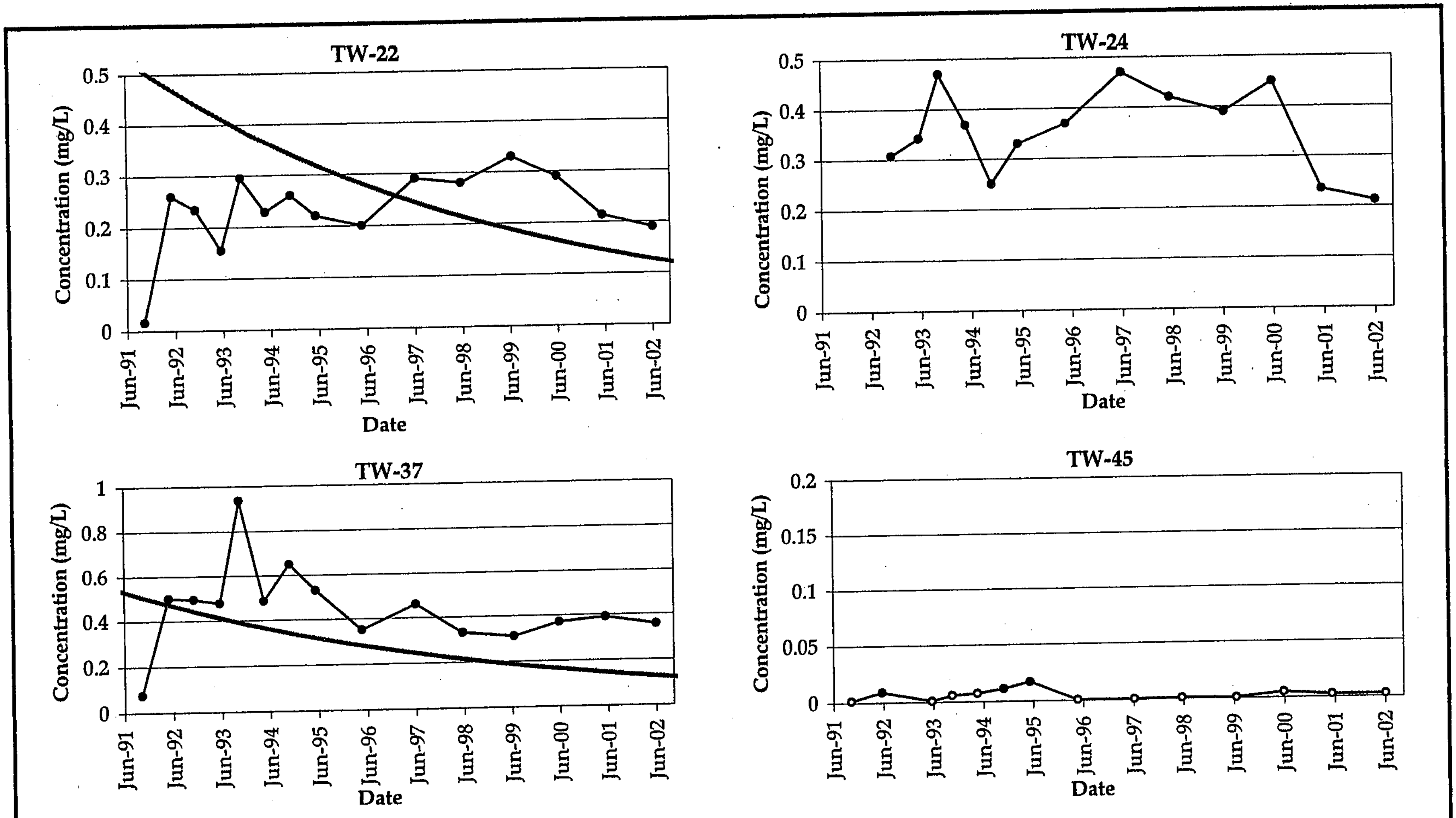
Constant source concentration of 0.7 mg/l after 1995 based on observed downstream concentrations.

Legend

- —●— Selenium Concentrations (mg/L)
- —— Predicted Source Concentrations
- —▲— Predicted Concentrations-Old Model

FIGURE D-19: SELENIUM IN UNDERFLOW SOLIDS POND SOURCE AREA

Golder Associates



Legend

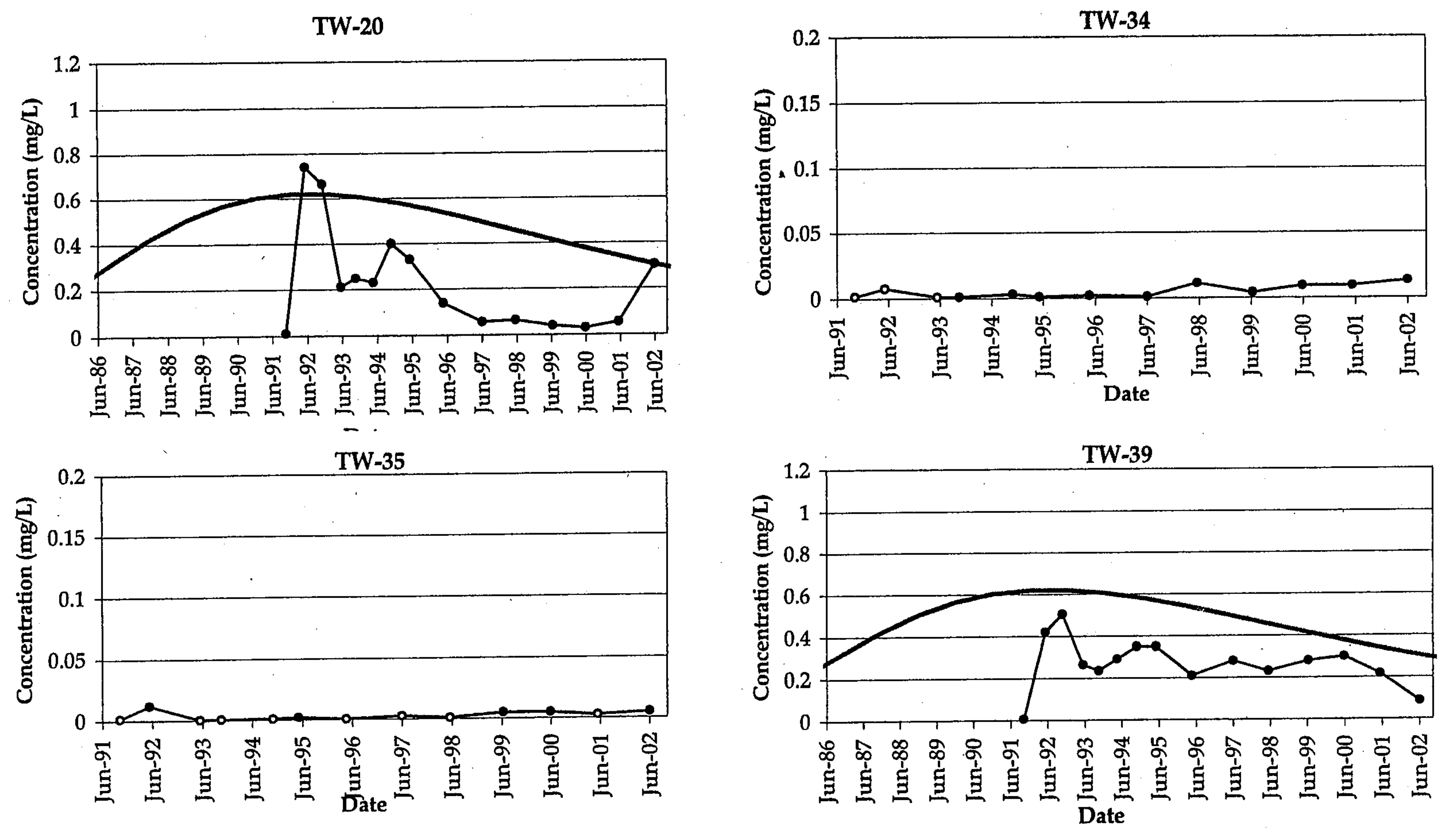
- ●— Selenium Concentration (mg/L)
- ○ Non-Detects
- — Predicted Concentration

FIGURE D-20: SELENIUM IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

—●— Selenium Concentration (mg/L)

○ Non-Detects

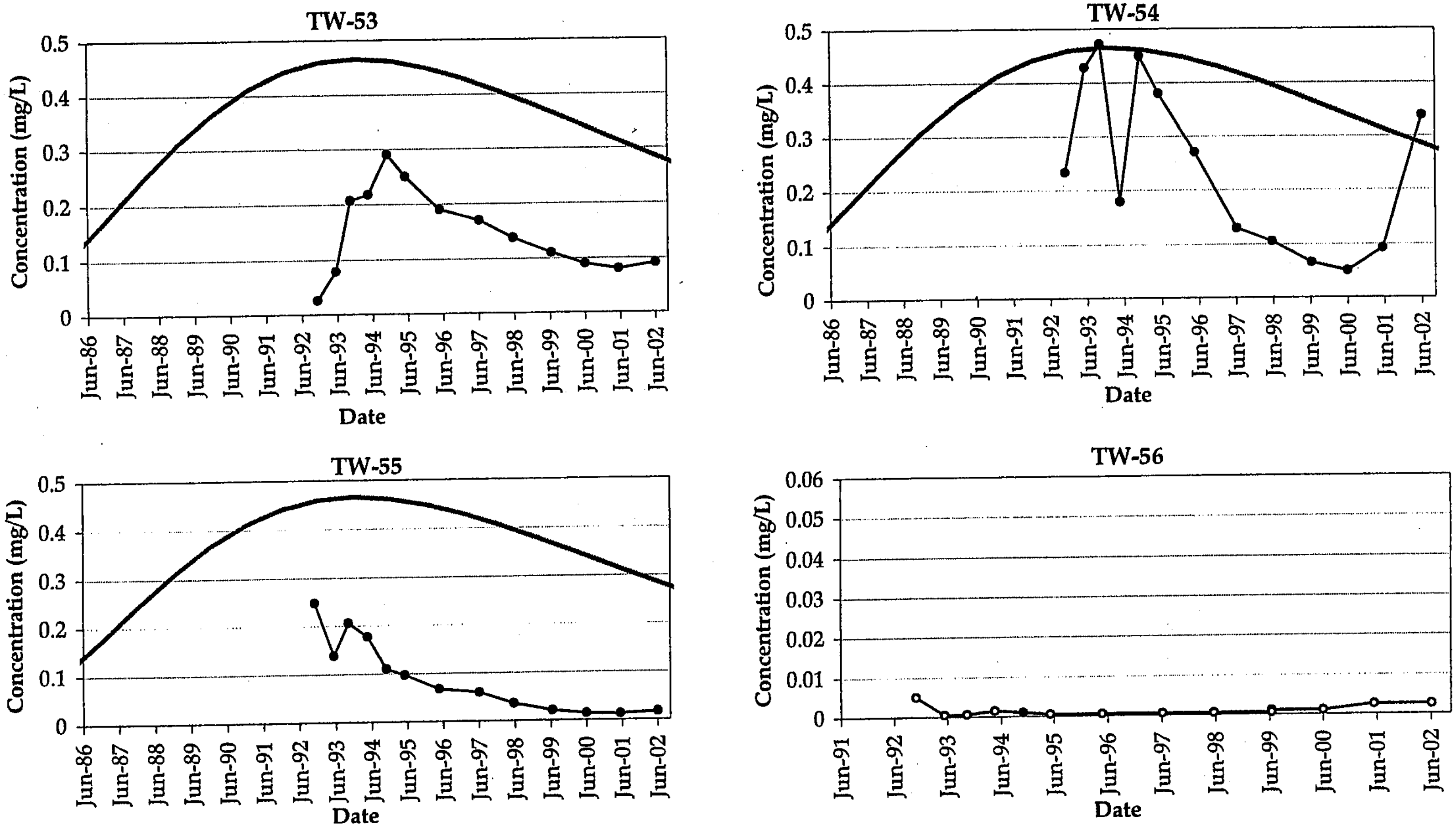
— Predicted Concentration

FIGURE D-21: SELENIUM IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

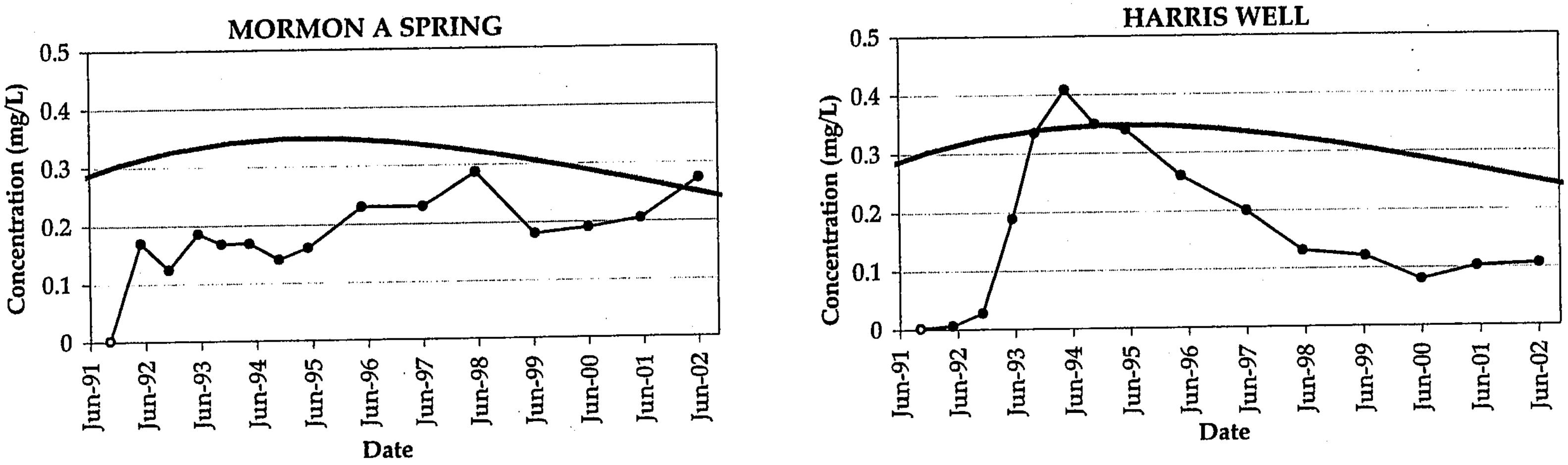
—●— Selenium Concentration (mg/L)
○ Non-Detects
—— Predicted Concentration

FIGURE D-22: SELENIUM IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

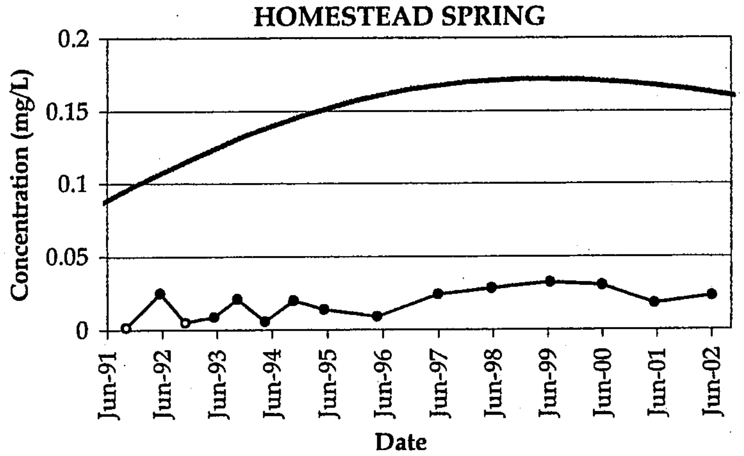
- —●— Selenium Concentration (mg/L)
- ○ Non-Detects
- —— Predicted Concentrations

FIGURE D-23: SELENIUM IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



Legend

—●— Selenium Concentration (mg/L)

○ Non-Detects

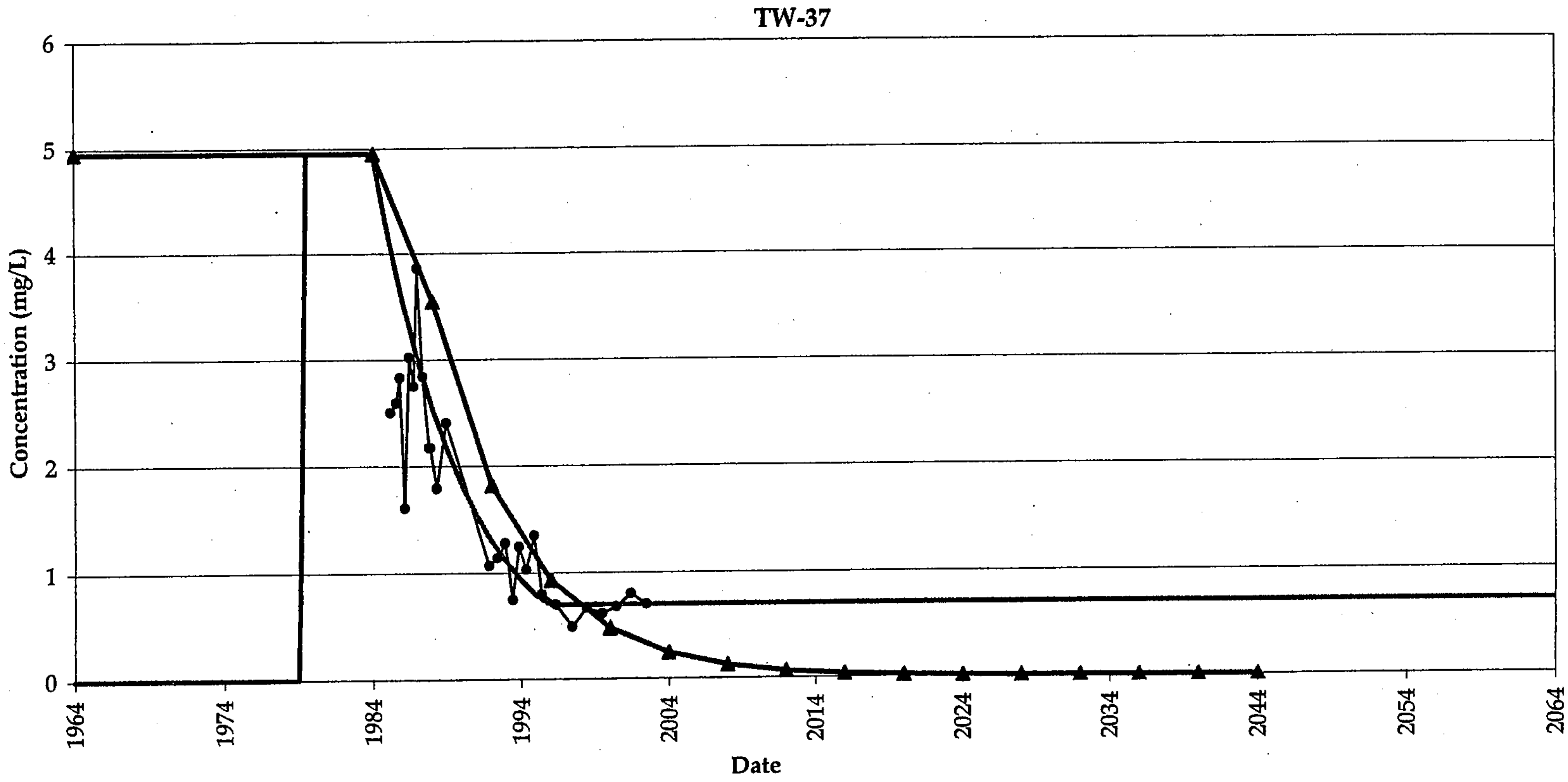
—— Predicted Concentration (10,000 feet from UFS

FIGURE D-24: SELENIUM IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Selenium_AppF.xls

Golder Associates



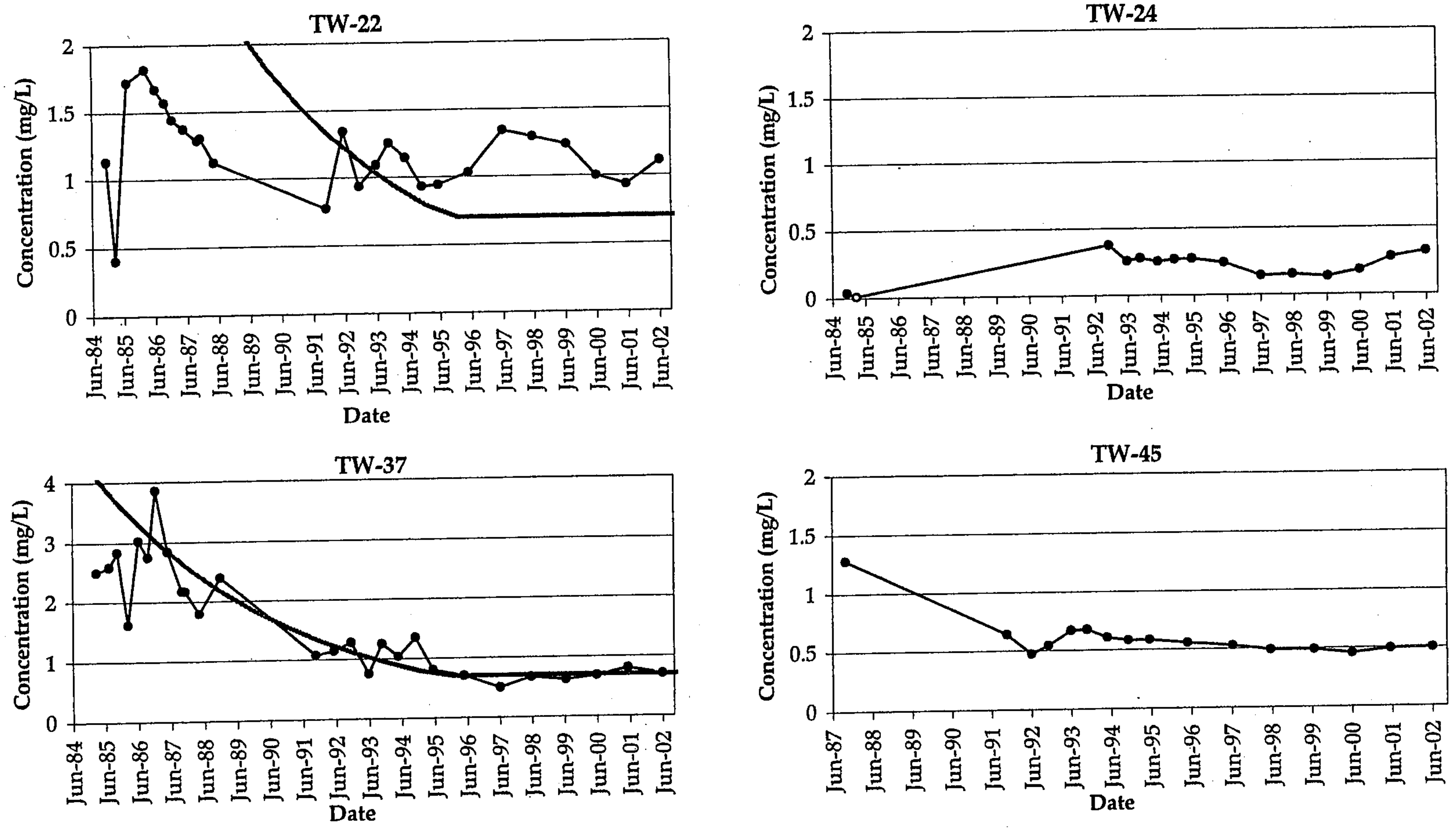
Constant source concentration of 0.7 mg/l after 1995 based on observed concentrations.

Legend

- Manganese Concentrations (mg/L)
- Predicted Source Concentration
- Predicted Concentration-RI Model

FIGURE D-25: MANGANESE IN UNDERFLOW SOLIDS POND SOURCE AREA

Golder Associates



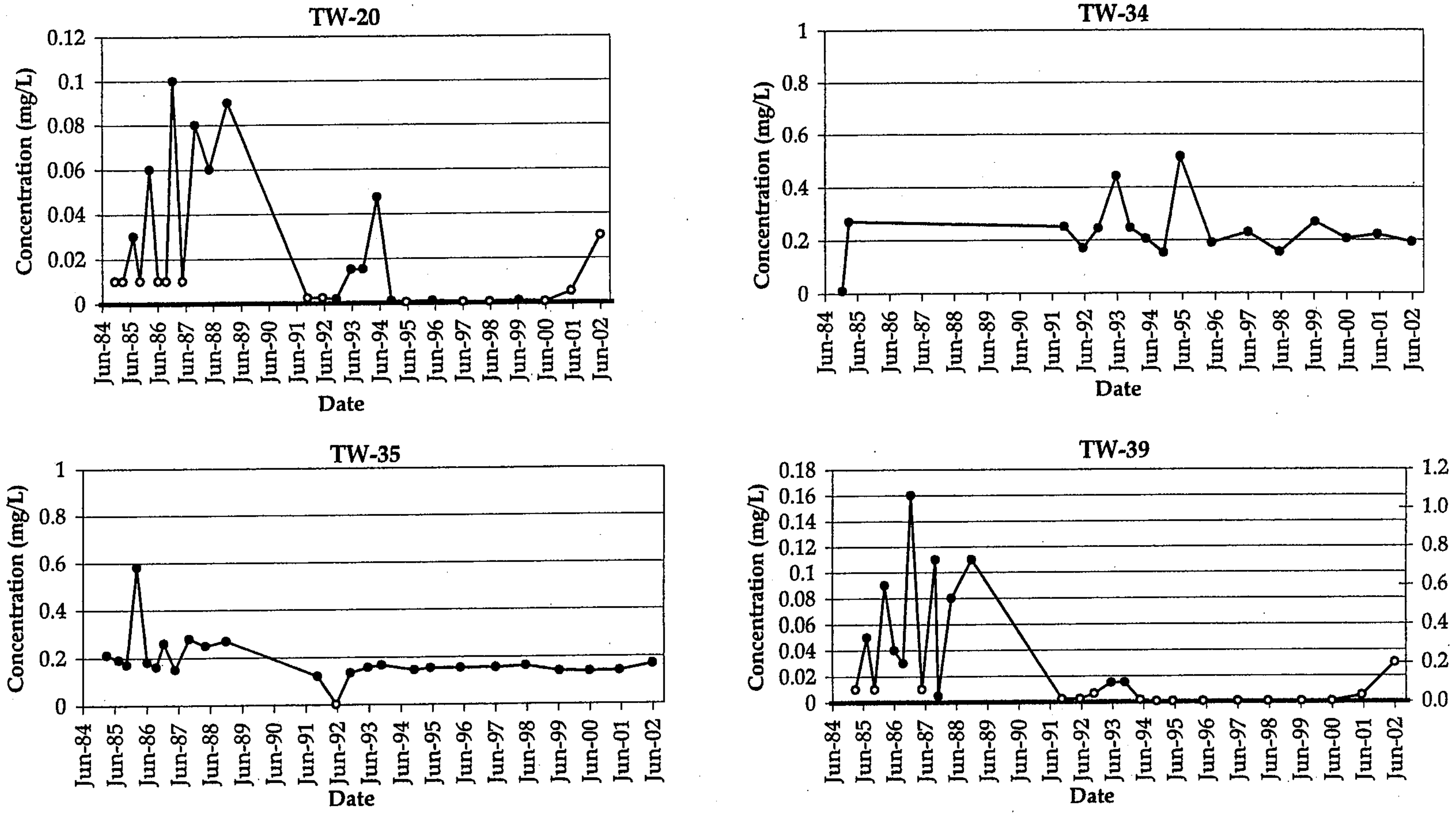
Legend

●— Manganese Concentration (mg/L)
○ Non-Detects
— Predicted Concentration

FIGURE D-26: MANGANESE IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID
913-1101.605, 11/22/02,
Manganese_AppD.xls

Golder Associates



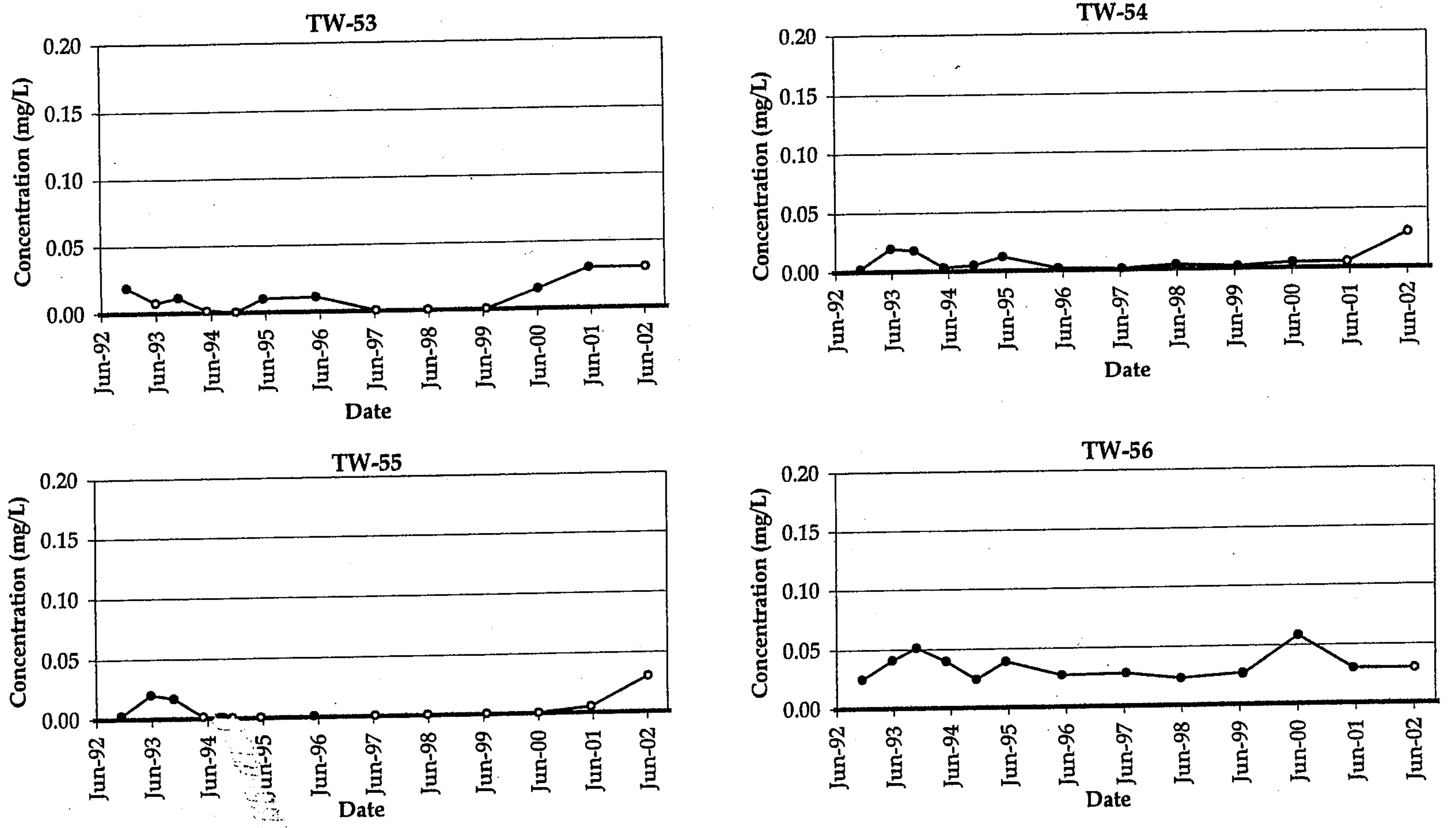
Legend

- ●— Manganese Concentration (mg/L)
- ○ Non-Detects
- — Predicted Concentration

FIGURE D-27: MANGANESE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID
913-1101.605, 11/22/02,
Manganese_AppD.xls

Golder Associates



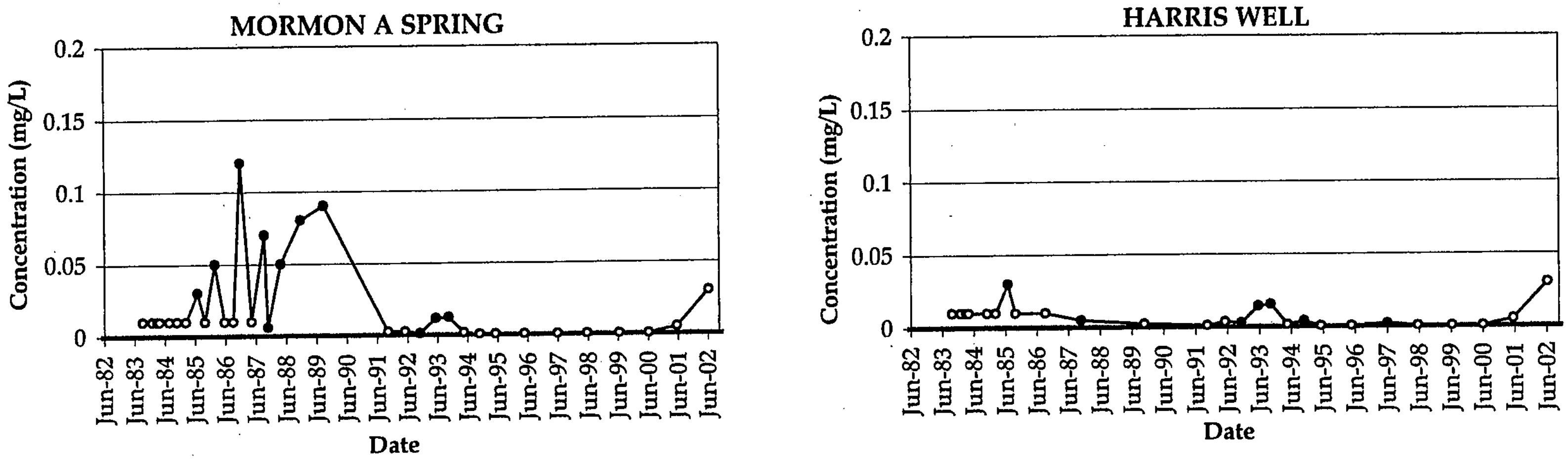
Legend

—●— Manganese Concentration (mg/L)
○ Non-Detects
—— Predicted Concentration

FIGURE D-28: MANGANESE IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID
913-1101.605, 11/22/02,
Manganese_AppD.xls

Golder Associates



Legend

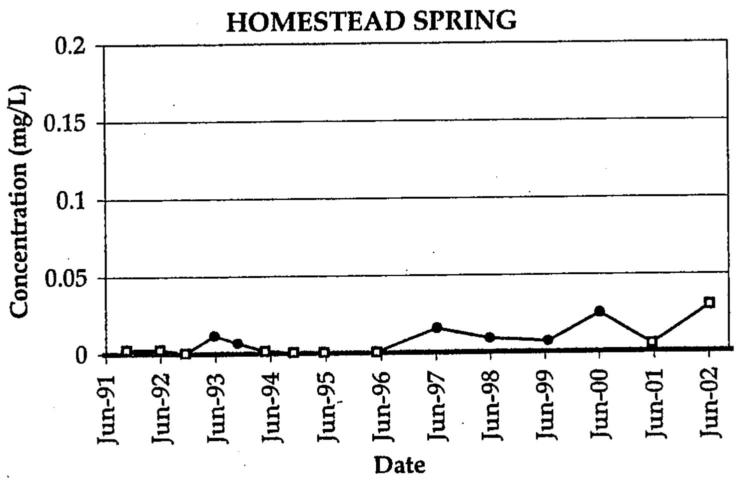
—●— Manganese Concentration (mg/L)
○ Non-Detects
— Predicted Concentration

FIGURE D-29: MANGANESE IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Manganese_AppD.xls

Golder Associates



Legend

● Manganese Concentration (mg/L)

□ Non-Detects

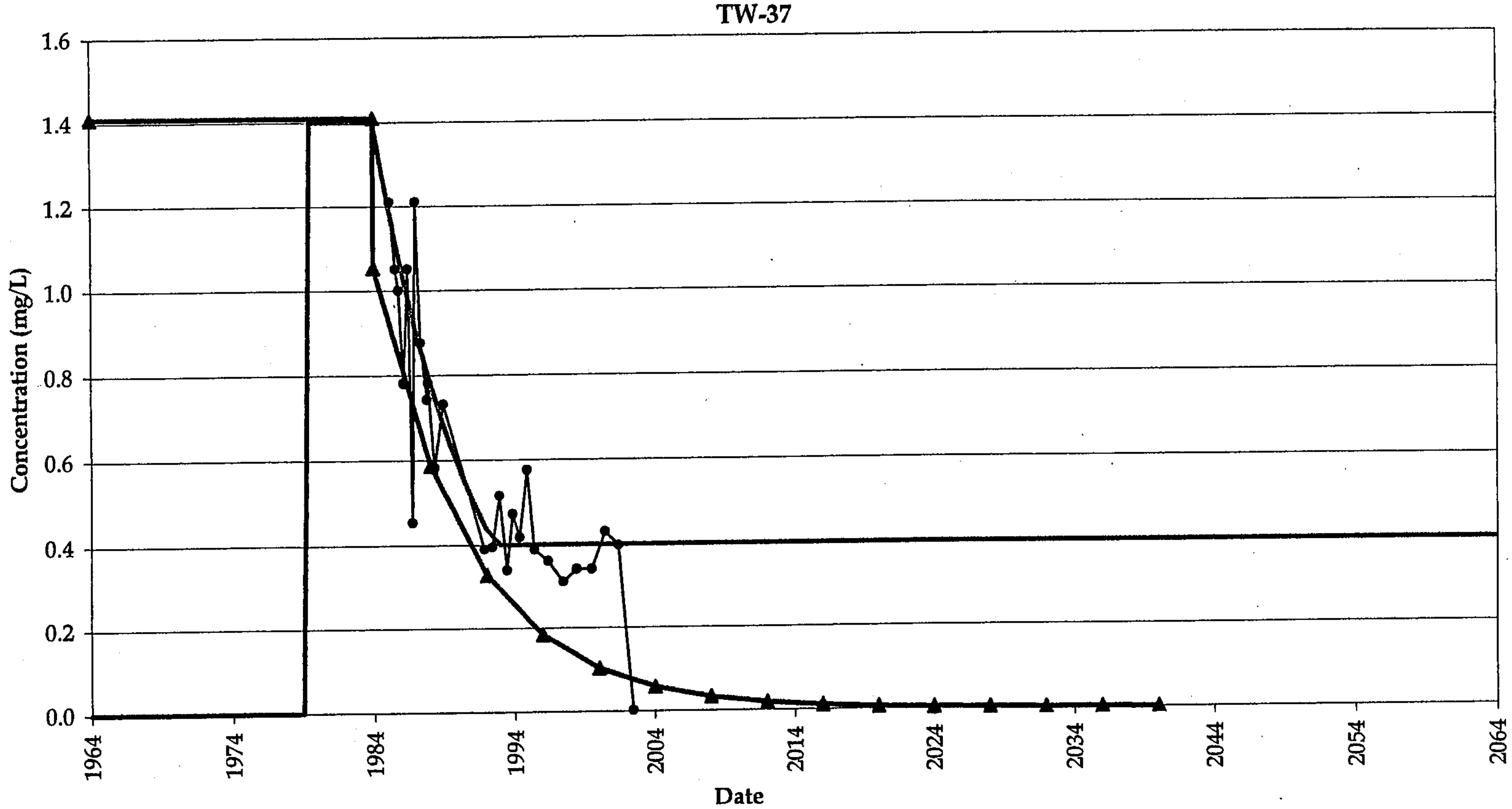
— Predicted Concentration(10,000 feet from UFS Ponds)

FIGURE D-30: MANGANESE IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Manganese_AppD.xls

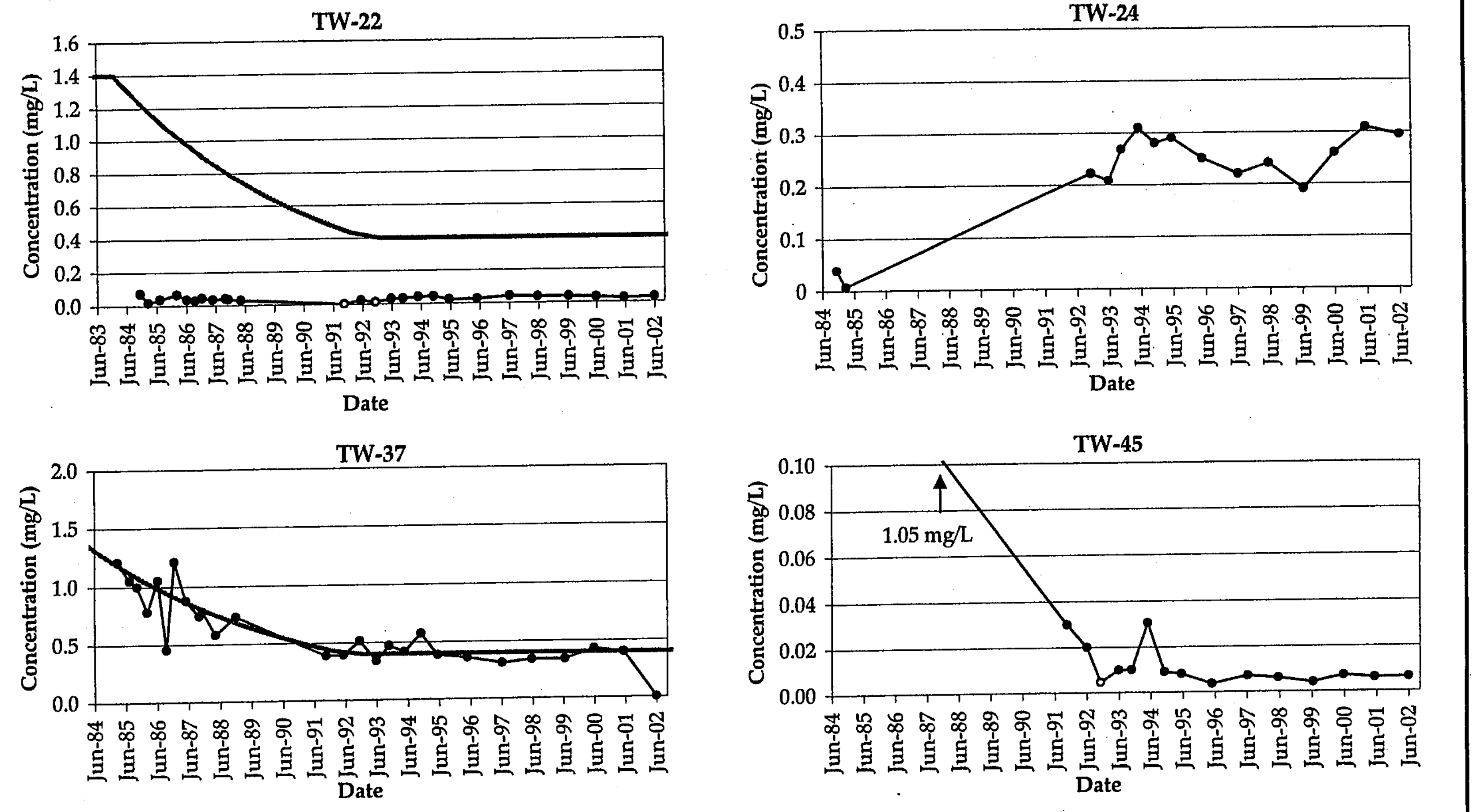
Golder Associates



Constant source concentration of 0.7 mg/l after 1994 based on observed concentrations.

FIGURE D-31: CADMIUM IN UNDERFLOW SOLIDS POND SOURCE AREA - NO SOLUBILITY CONTROL

Golder Associates



Legend

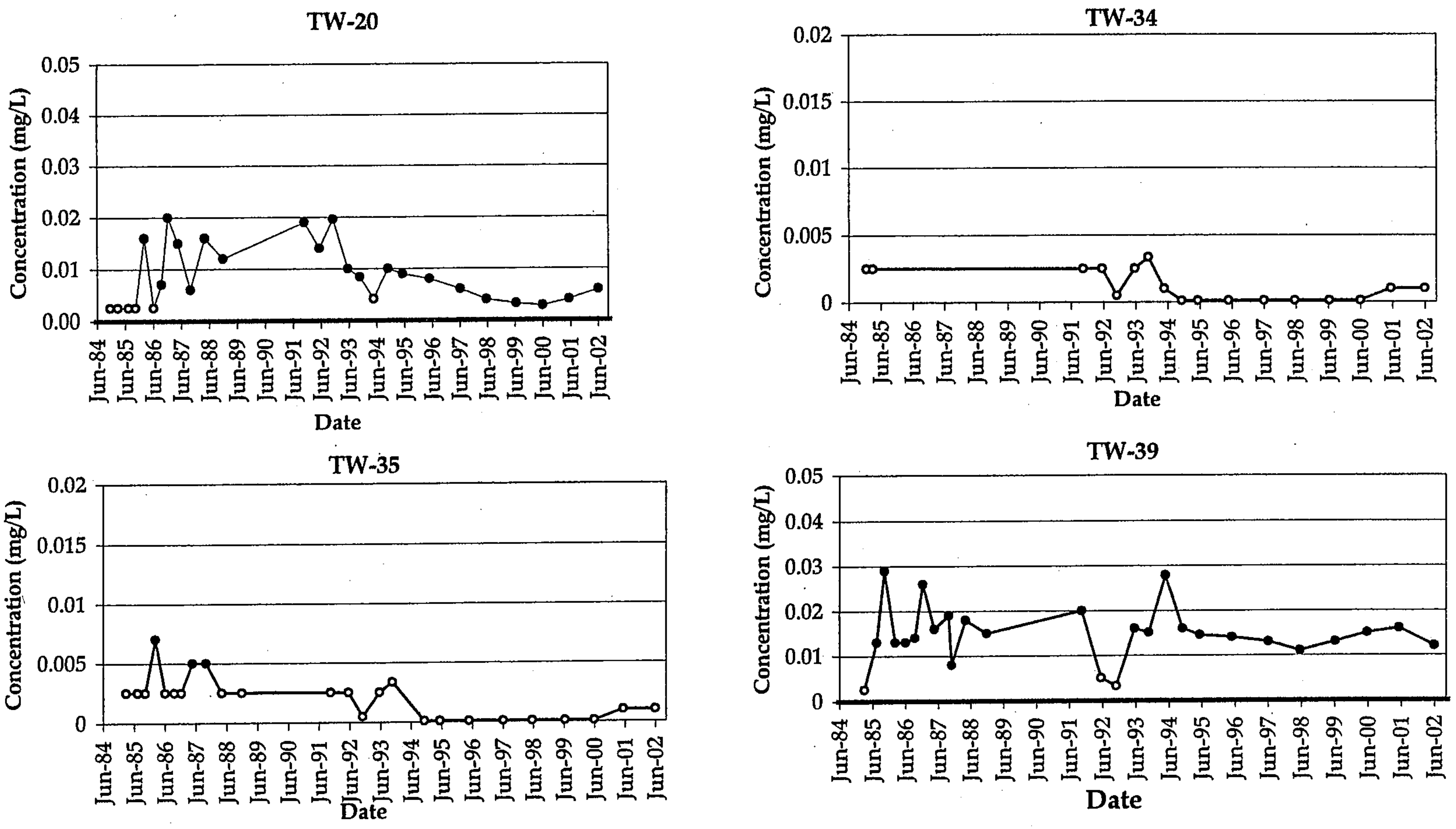
- —●— Cadmium Concentration (mg/L)
- ○ Non-Detects
- ━ Predicted Concentration

FIGURE D-32: CADMIUM IN UNDERFLOW SOLIDS POND AREA WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Legend

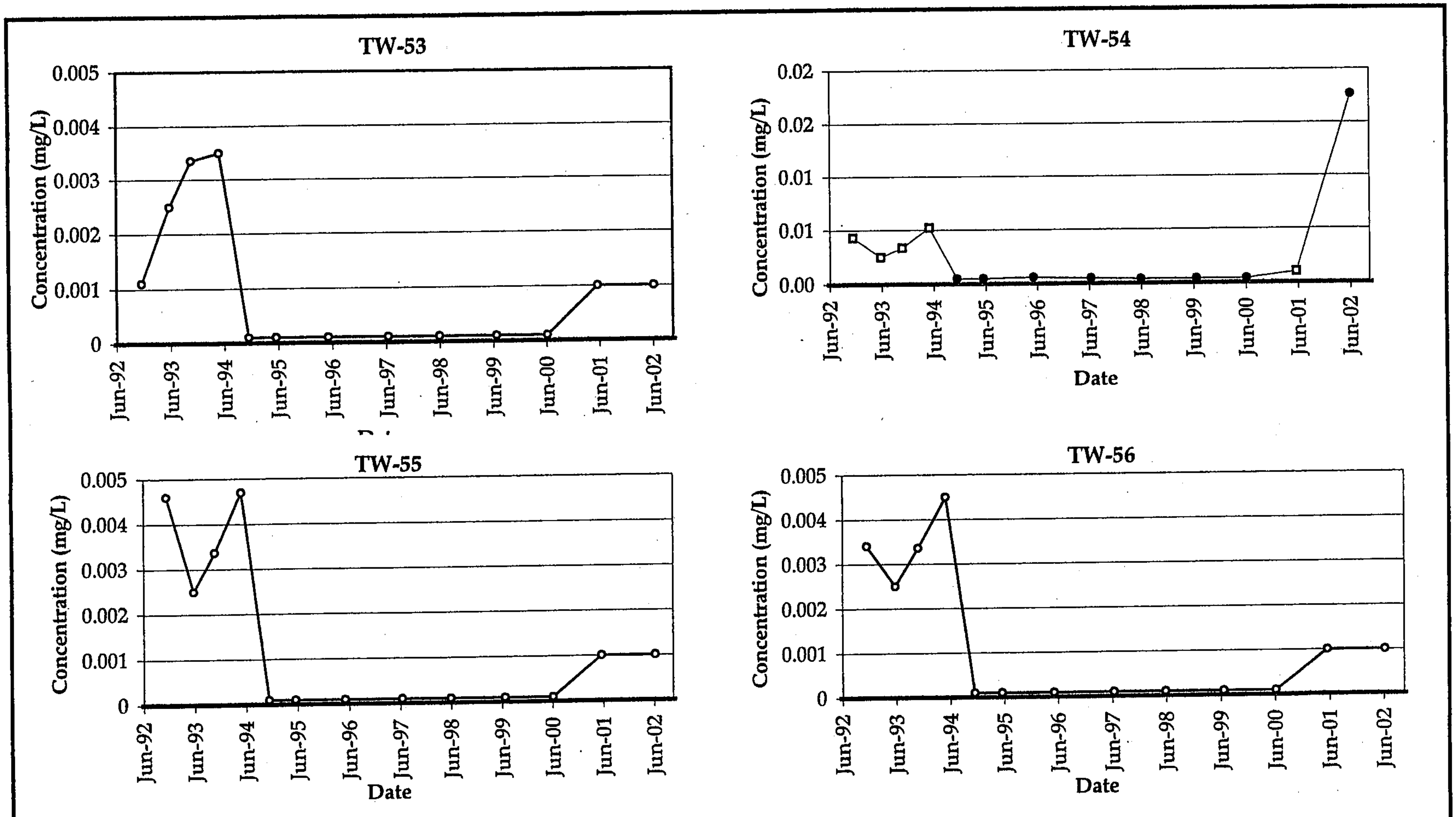
—●— Cadmium Concentration (mg/L)
○ Non-Detects
━ Predicted Concentration

FIGURE D-33: CADMIUM IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Legend

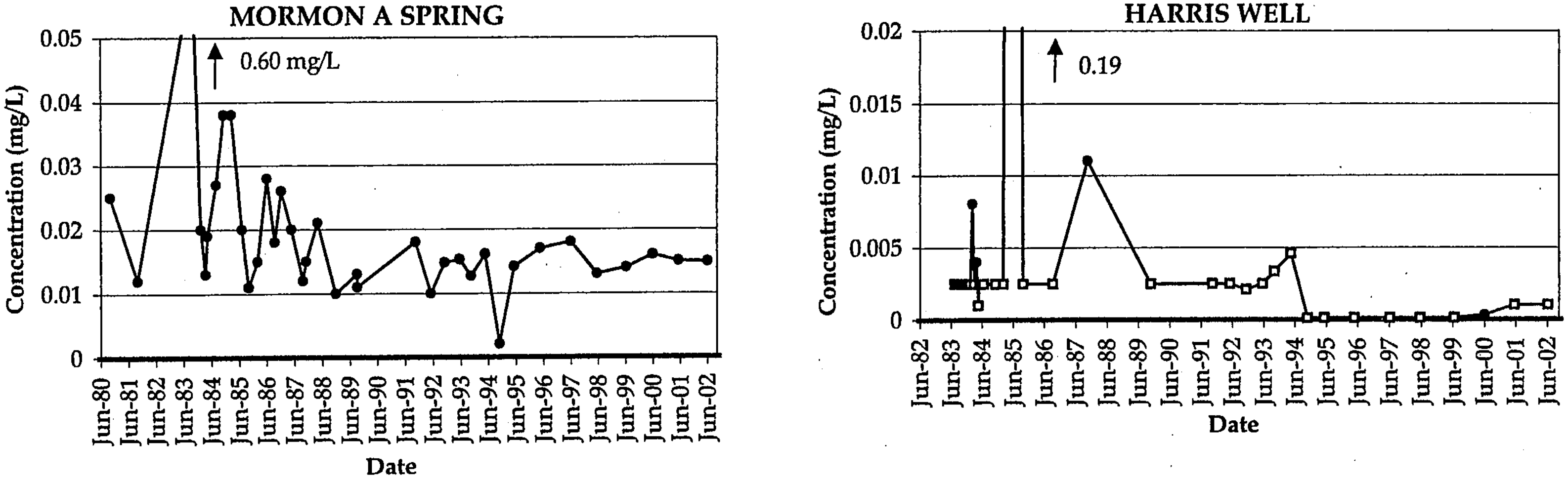
- ●— Cadmium Concentration (mg/L)
- ○ Non-Detects
- —— Predicted Concentration-No Solubility Control

FIGURE D-34: CADMIUM IN SOUTHERN BOUNDARY WELLS

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Legend

—●— Cadmium Concentration (mg/L)

○ Non-Detects

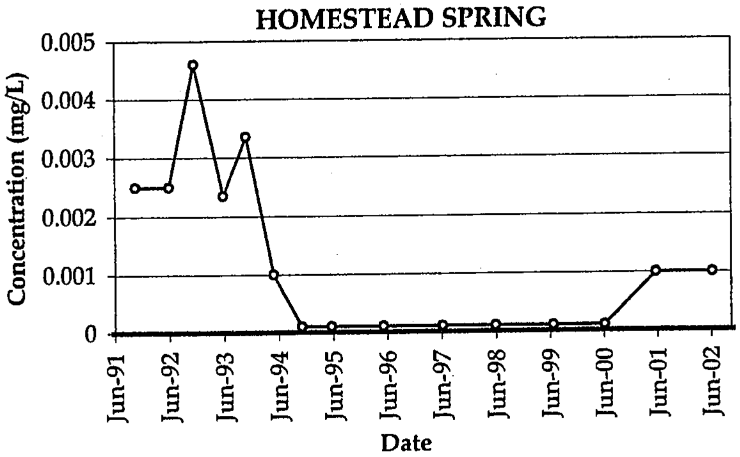
—— Predicted Concentration-No Solubility Control

FIGURE D-35: CADMIUM IN MORMON A SPRING AND HARRIS WELL

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates



Note: Concentrations at point 10,000 feet downgradient of UFS

Legend

- —•— Cadmium Concentration (mg/L)
- ○ Non-Detects
- —— Predicted Concentration-No Solubility Control

FIGURE D-36: CADMIUM IN SPRING SOUTH OF PLANT

Monsanto/Groundwater/ID

913-1101.605, 11/22/02, Cadmium_AppB.xls

Golder Associates

ATTACHMENT E

GEOCHEMICAL MODELING MEMORANDUM

TECHNICAL MEMORANDUM

TO:	Michael Klisch and David Banton	**DATE:**	May 25, 2003
FR:	Joseph McCarthy and Rens Verburg	**OUR REF:**	913-1101.605
RE:	Geochemical Modeling of Cadmium Behavior in Groundwater – Monsanto, Soda Springs Site		

INTRODUCTION

The purpose of this report is to present an assessment of the mobility of cadmium in groundwater at the Monsanto site and the influence of chloride and sulfate on groundwater transport.

Groundwater sampling at wells located downgradient from the underflow solids ponds indicate that cadmium concentrations in wells TW-20 and TW-39 reached a peak in 1992/1993 and have declined slowly (Figure 1). Concentrations in both wells are currently above the remediation goal of 0.005 mg/L.

Figures 2 and 3 show chloride and sulfate concentrations at these two wells over the same time period. Chloride and sulfate are typically conservative species and move at the overall groundwater velocity. Cadmium on the other hand is typically strongly retarded in groundwater and migrates very slowly. The question that is posed here is why is cadmium apparently migrating at the same velocity in groundwater as conservative species? It is postulated that cadmium could be complexing with existing anions (chloride and sulfate), reducing the affinity of cadmium to partition to aquifer materials thereby enhancing transport within groundwater. Elevated chloride and sulfate concentrations measured in groundwater samples could therefore be responsible for increasing cadmium mobility through complexation with dissolved cadmium.

In order to assess the effects of elevated chloride and sulfate concentrations on cadmium species present in groundwater, geochemical modeling using PHREEQC (Parkhurst and Appelo, 1999) was conducted to evaluate the cadmium species produced from the dissolution of otavite [$CdCO_3$] present in source area, over a range in chloride and sulfate concentrations. Otavite was identified in earlier studies (Golder, 1995) as a potential solubility control on dissolved cadmium concentrations. Table 1 summarizes the wells considered for geochemical modeling.

The Record Of Decision (ROD) established groundwater remediation goals for cadmium at the Monsanto site. This remediation goal is the Maximum Contaminant Level (MCL) under the Safe Drinking Water Act (0.005 mg/L). Average groundwater concentrations for each well are shown in Table 1. Values that exceed the remediation goal are noted in bold type.

TABLE 1

Downgradient Monitoring Wells and Springs

Monitoring Well	Aquifer (Upper or Lower Basalt Zone)	Average Cadmium Concentration (mg/l)
Remediation Goal		0.005
UBZ Background Concentration (Golder, 1985)		0
TW-20	UBZ2	0.003
TW-22	UBZ2	**0.02**
TW-36	UBZ2	**0.06**[b]
TW-37	UBZ2	**0.31**
TW-39	UBZ2	**0.01**
Harris Well	UBZ1	0.0006
Springs		
Mormon A		**0.01**
Calf		0.005

[a] Average concentrations calculated from the last three sampling events (2000, 2001, and 2002). Non-detect values were assumed equal to half the detection limit in statistical calculations.

[b] TW-36 has not been sampled since 1994. The values represent the average of the last three years the well was sampled (1992, 1993, and 1994).

CADMIUM MOBILITY

Review of literature reports and commonly available geochemical databases suggests a wide range of values for the solubility product of otavite. One recent article by Stipp and others (1993) suggests a log K value of -12.1, which is the value presently adopted by both the PHREEQC and WATEQ4F databases. The previous hydrological investigation performed by Golder (Golder, 1995) concluded that site groundwaters were undersaturated with respect to cadmium carbonate (otavite) by applying a solubility constant of $10^{-11.12}$ used in the WATEQF and WATEQ2 databases. Golder generated solubility curves using the solubility products proffered in the 1985 Golder report ($10^{-11.12}$), the PHREEQC database ($10^{-12.1}$), and the MINTEQA2 database ($10^{-13.7}$). The solubility curves resulting from this evaluation are presented in Figure 4. In addition, Figures 5 through 7 superimpose cadmium concentrations measured in 2002 for three wells of interest: TW-40, TW-16, and TW-37.

These plots illustrate a general trend of decreasing cadmium concentrations with increasing pH. A number of the sample points lie close to the two uppermost solubility curves, suggesting these curves may be appropriate for the Monsanto site.

Figure 8 presents cadmium concentrations for a larger number of downgradient wells to determine if the data support the solubility product constant adopted by the 1985 Golder report. As shown in this figure, nearly all the values from the downgradient wells (excluding source well TW-37) reside closer to the curves generated using the solubility product from the PHREEQC database ($10^{-12.1}$) and MINTEQA2 database ($10^{-13.7}$). Geochemical simulations conducted as part of the chloride/sulfate sensitivity analysis, therefore, used the values from both of these databases.

Cadmium in natural groundwaters and surface waters exists in the +2 valence state. Cadmium is adsorbed by oxides of aluminum, iron and manganese, and also by calcite, clay minerals, and particular organic matter. The adsorption edge for cadmium occurs at a higher pH than that of lead, copper and zinc (EPRI, 1984), with adsorption becoming effective at pH values of approximately 5 and higher. In groundwater, otavite [$CdCO_3$] precipitation may control cadmium concentrations. Dissolved cadmium may form complexes with a number of anions thereby limiting the amount of cadmium present as the free ion, and therefore the amount of cadmium available to participate in mineral precipitation and adsorption reactions. The PHREEQC and MINTEQA2 databases include association constants for complexes with chloride, hydroxide, carbonate and sulfate, although there are discrepancies between the two databases with respect to the carbonate values. The MINTEQA2 database also includes constants for cadmium complexes of fluoride, nitrate, sulfide, bromide and iodide. Although the hydrological investigation (Golder, 1985) concluded that otavite [$CdCO_3$] was not likely controlling cadmium concentrations at the Monsanto site, speciation modeling conducted as part of this study indicates that otavite may be supersaturated in some locations.

GEOCHEMICAL MODELING APPROACH

The PHREEQC models were designed to evaluate the influence of chloride and sulfate on dissolved cadmium concentrations assuming equilibrium with the mineral otavite. The basic solution chemistry was derived from the results of the most recent TW-37 water sample. A pH value of 7 was chosen based on a review of the measurements from the entire period of record. Review of the downgradient wells indicates that this pH reasonably represents the conditions at these sites over the period of record.

The Monsanto groundwater database contains all the sampling results over the past 20 years. The database was reviewed to determine the range of chloride and sulfate concentrations measured in groundwater. This range served to establish the upper and lower limits of model inputs for the sensitivity runs. Chloride model inputs ranged from 0 to 425 mg/L, while sulfate inputs ranged from

0 to 925 mg/L. Each of these parameters was incrementally (and independently) increased using steps of 25 mg/L.

Modeling results were plotted on graphs of cadmium versus chloride and cadmium versus sulfate (Figures 9 and 10, respectively). These graphs also include cadmium, chloride, and sulfate concentrations measured in downgradient groundwater to compare the model predictions against field concentrations. Non-detect values were removed for ease of interpretation. Figures 11 and 12 show the resulting speciation of cadmium for the chloride and sulfate simulations, respectively. Complexes that accounted for less than 1 percent of the total dissolved cadmium present were not included in the graphs.

DISCUSSION OF GEOCHEMICAL MODELING RESULTS

The following observations were made based on the results of the PHREEQC simulations:

- The model results using the PHREEQC database (log K -12.1) show a 64 percent increase in dissolved cadmium concentrations, while the results using the MINTEQ (log K -13.7) database show a 50 percent increase over the chloride range modeled (Figure 6). In general, the modeled trend mimics and brackets the trend of the measured values collected from the site.

- Figure 11 shows cadmium speciation for the PHREEQC chloride simulation. As expected, increases in chloride concentration result in increases in $CdCl^+$ and $CdCl_2$ complexes and a corresponding overall decline in the concentration of the free ion $[Cd^{+2}]$. For the highest chloride concentration modeled (425 mg/L), cadmium-chloride complexes account for approximately 30% of total dissolved cadmium.

- The model results using the PHREEQC database (log K -12.1) show a 125 percent increase in dissolved cadmium concentrations, while the results using the MINTEQ (log K -13.7) database show an 88 percent increase over the sulfate range modeled (Figure 10). As for chloride, in general, the modeled trend mimics and brackets the trend of the measured values.

- Figure 12 shows cadmium speciation for the PHREEQC sulfate simulation. As for chloride, increases in sulfate concentration result in increases in $CdSO_4$ and $Cd(SO_4)2^{-2}$ complexes and an overall decline in the concentration of the free ion. For the highest sulfate concentration modeled (925 mg/L), cadmium-sulfate complexes account for approximately 20% of total dissolved cadmium.

- Despite uncertainties with respect to the thermodynamic constants governing otavite solubility, the results of the sensitivity analysis strongly suggest that observed cadmium behavior in downgradient wells is consistent with complexation with sulfate and chloride.

GROUNDWATER CADMIUM TRANSPORT CONSIDERATIONS

The migration of solutes in groundwater is controlled by advection, mechanical dispersion, retardation, and diffusion. Diffusion is generally a slow process, and in areas of high groundwater flow velocities such as the Monsanto aquifer, the effect of diffusion on solute concentrations is generally masked by the effect of groundwater movement. Dissolved constituents are transported with the groundwater flow (advective transport). Differences in groundwater velocity along a flow path as well as variable flow path lengths result in dispersion. Dispersion (or mixing) results in a decrease in solute concentration. Dispersion occurs in both the direction of groundwater flow (longitudinal dispersion) and in directions normal to the groundwater flow path (transverse horizontal and transverse vertical dispersion).

The transport of solutes in groundwater may also be retarded due a number of chemical reactions and processes (e.g., sorption, mineral precipitation) as well as biological reactions. The process by which a solute becomes distributed between the groundwater and the aquifer materials is called partitioning, described by a partition, or distribution coefficient (K_d). The electrical charge of a dissolved constituent in solution significantly influences the partitioning of ions in groundwater. In general, the degree of retardation is proportional to the charge (i.e., charged particles are more likely to be adsorbed than neutral particles, and particles with higher charges will be retained more effectively than particles with a lower charge).

Complexes that are neutral will therefore typically behave conservatively, given there is little chemical propensity for interaction with aquifer materials. Complexes or ions retaining a net charge will be attracted and sorb to the aquifer material, thereby reducing their dissolved concentrations migrating downgradient. Based on the results of the speciation modeling (Figure 11 and 12), some proportion of the cadmium is present as neutral complexes (e.g., $CdSO_4$, $CdCO_3$, $CdCl_2$). These complexes will therefore not be retarded, and will be transported with the same general groundwater velocity to that of conservative species such as chloride.

Therefore, the presence of cadmium chloride and sulfate complexes in groundwater explains the arrival of a cadmium peak at TW-20 and TW-39 at the same time as the chloride and sulfate peaks. Similarly, now that there is no longer a source for chloride and sulfate from the underflow solids ponds, cadmium concentrations are expected to decrease in these and other wells. However, over the long term, cadmium present in groundwater from the dissolution of otavite in the aquifer below the underflow solids ponds will occur as a free ion [Cd2+], which will be subject to the adsorption process and will be highly retarded.

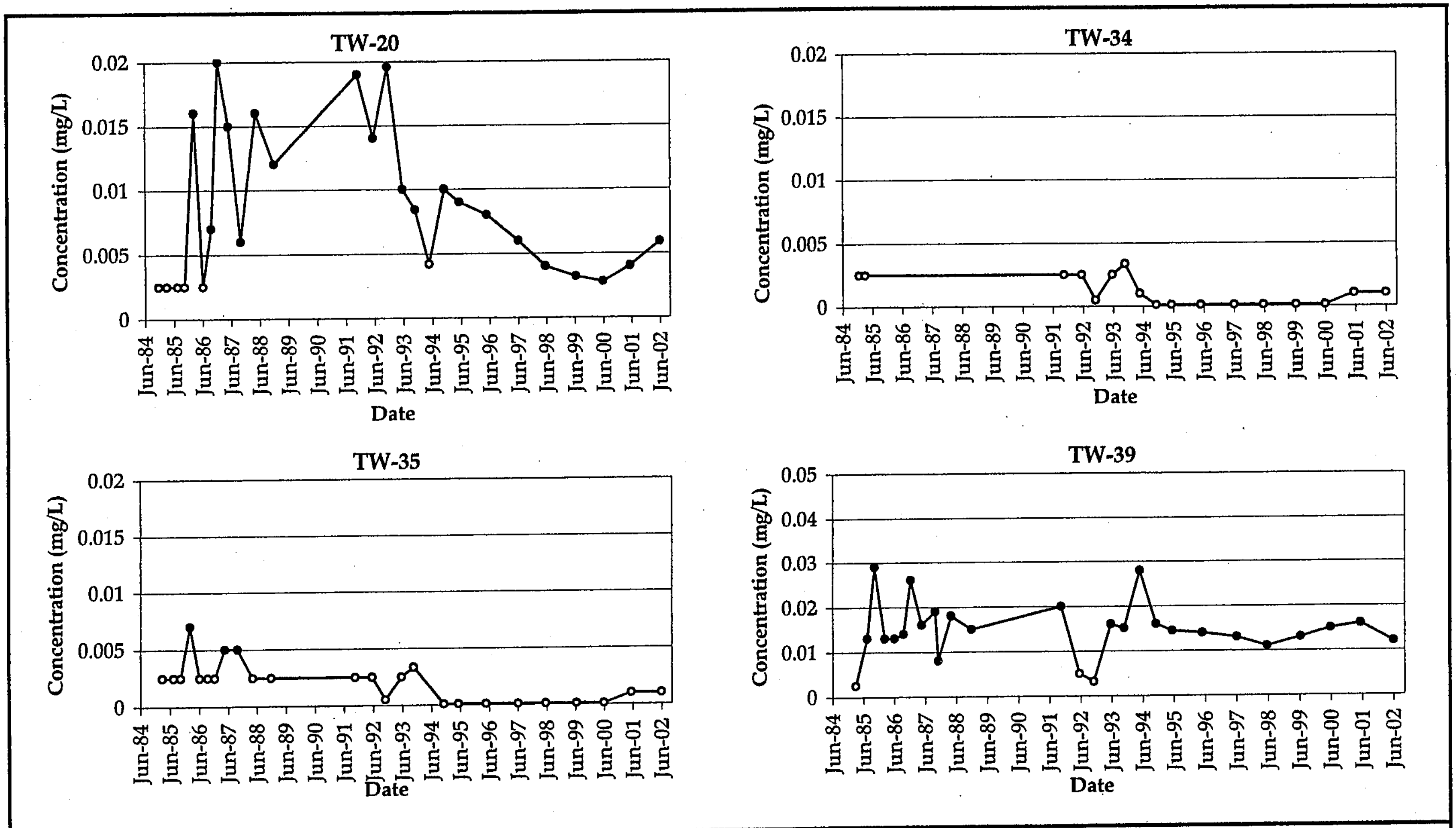
LIST OF FIGURES

REFERENCES

EPRI, 1984. Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Volume 1: A Critical Review, EPRI EA-3356.

Golder, 1995, Phase II Remedial Investigation Report for the Soda Springs Elemental Phosphorous Plant

V:\PROJECTS_1991 PROJECTS\913-1101\Monsanto Groundwater Modeling - 2002\Geochemistry\PHREEQC Chloride-Sulfate\Memo\Cadmium Behavior in Groundwater - Monsanto.doc



Legend

—●— Cadmium Concentration (mg/L)

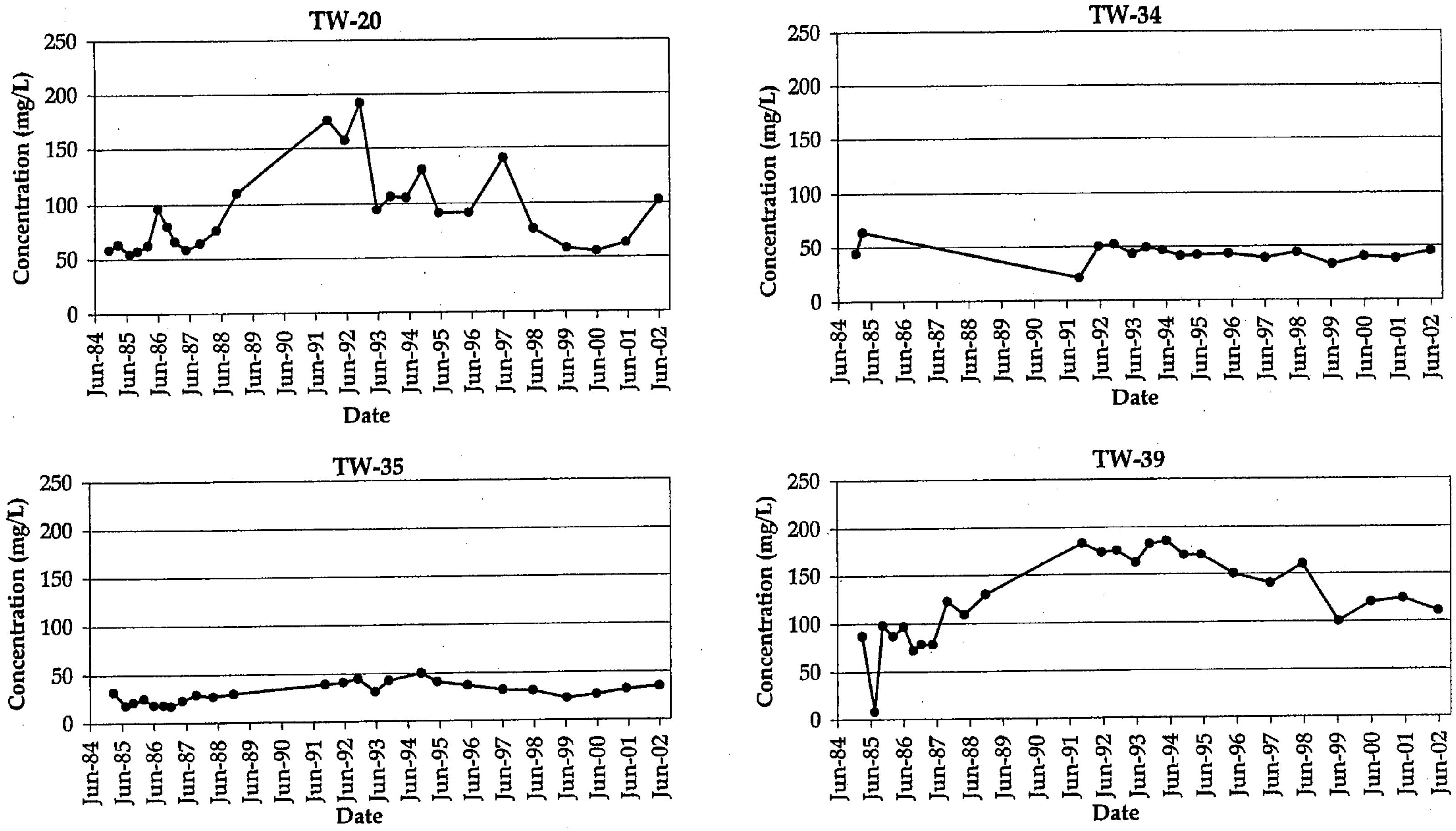
○ Non-Detects

FIGURE 1: CADMIUM IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 1,2,3 - fencline plots.xls

Golder Associates



Legend

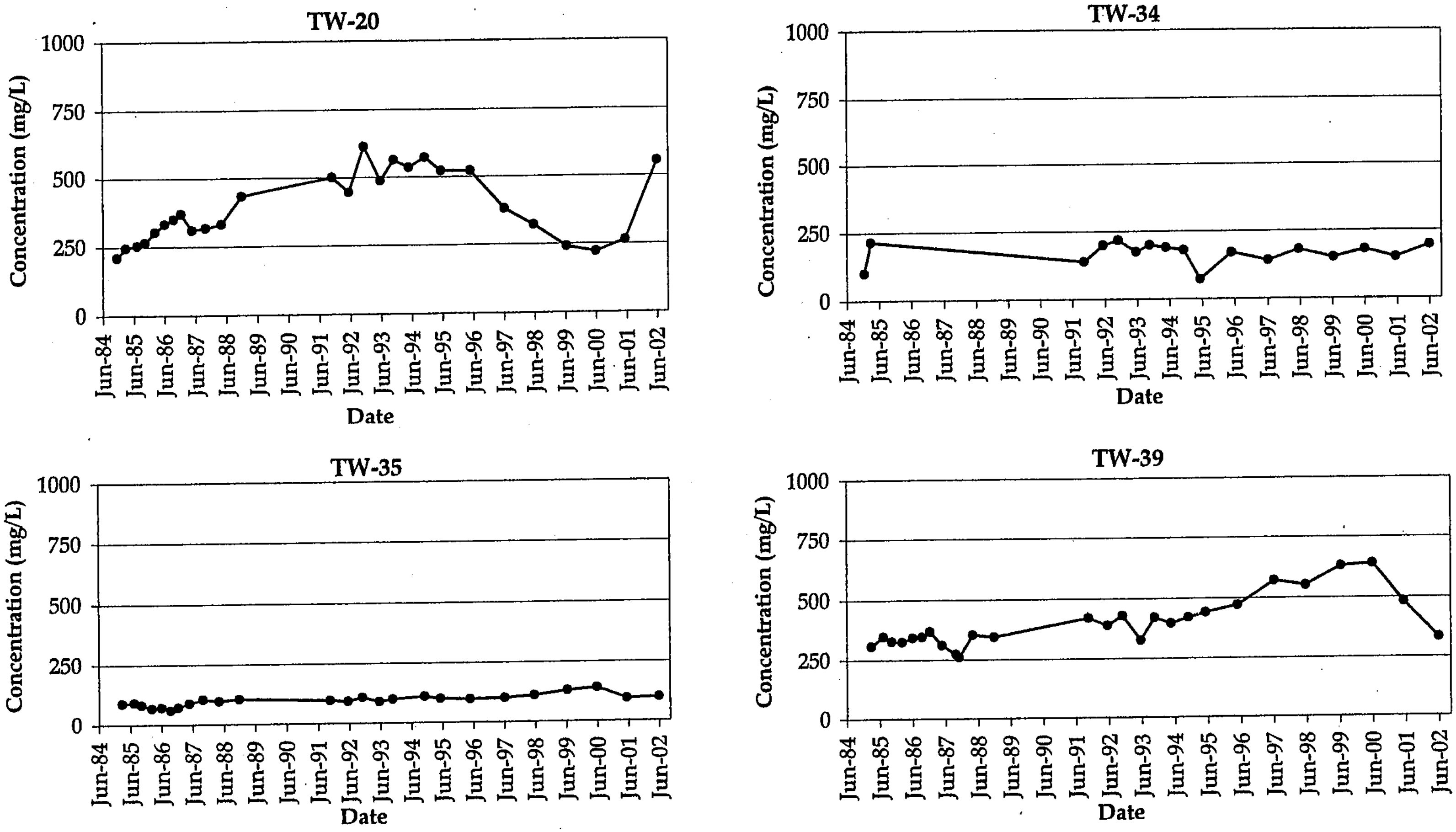
—●— Chloride Concentration (mg/L)

FIGURE 2: CHLORIDE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 1,2,3 - fencline plots.xls

Golder Associates



Legend

—●— Sulfate Concentration (mg/L)

FIGURE 3: SULFATE IN SOUTH FENCE LINE WELLS

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 1,2,3 - fencline plots.xls

Golder Associates

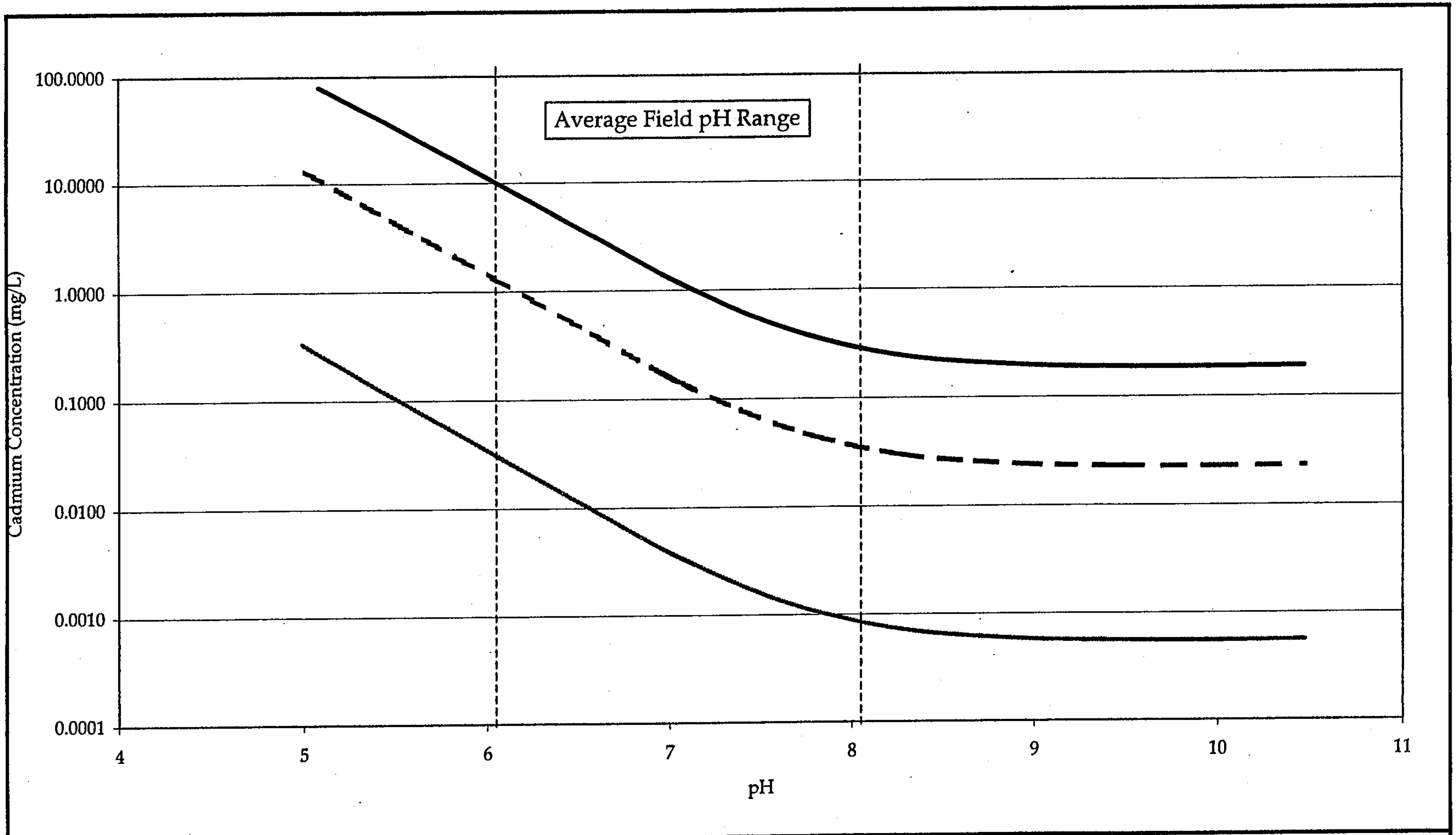


FIGURE 4: OTAVITE SOLUBILITY CURVES

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 4,5,6,7,8 - $CdCO_3$ pH Solubility plots.xls

Golder Associates

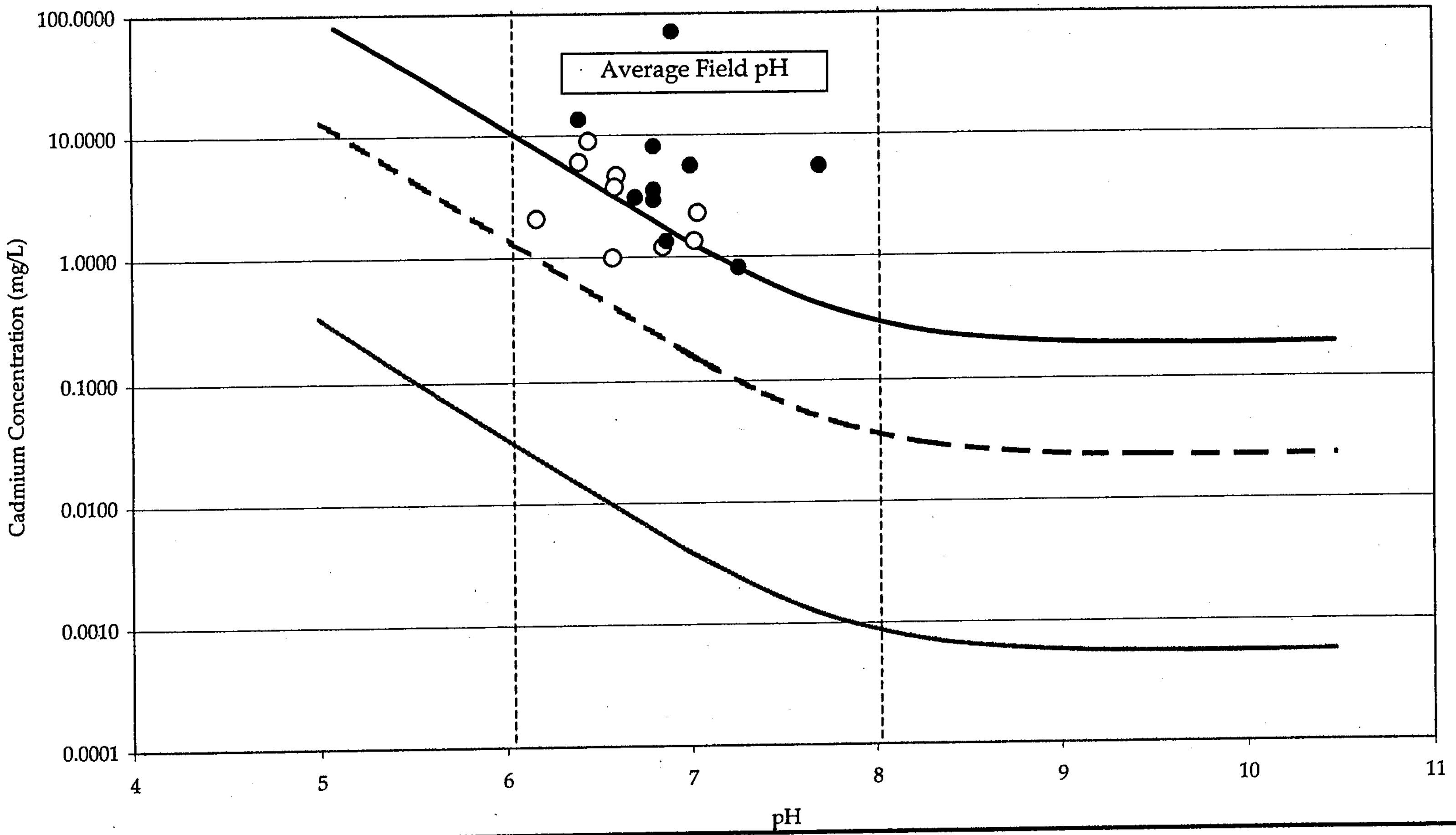


FIGURE 5: TW-40 CADMIUM VS. PH

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 4,5,6,7,8 - CdCO3 pH
Solubility plots.xls

Golder Associates

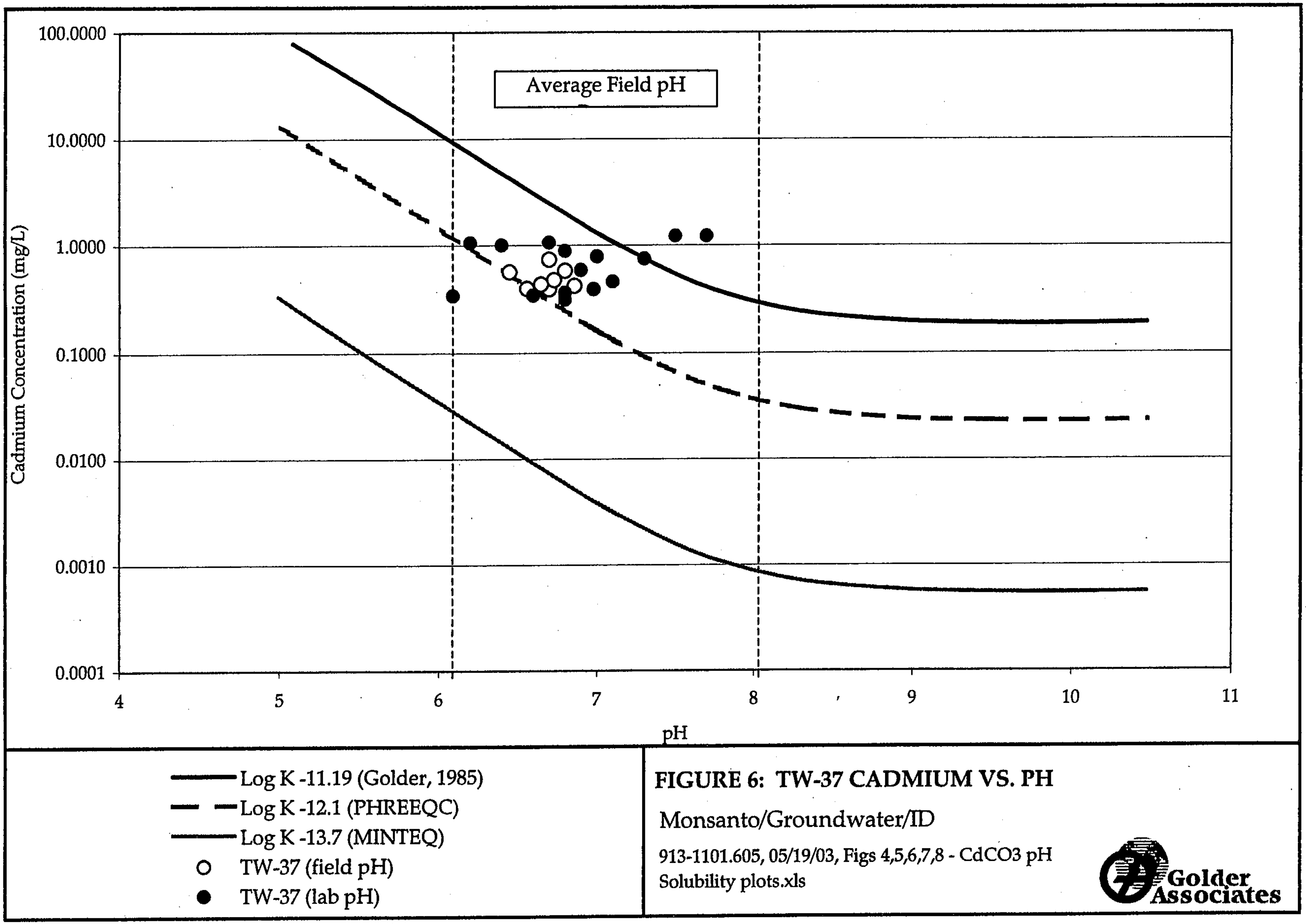


FIGURE 6: TW-37 CADMIUM VS. PH

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 4,5,6,7,8 - CdCO3 pH
Solubility plots.xls

Golder
Associates

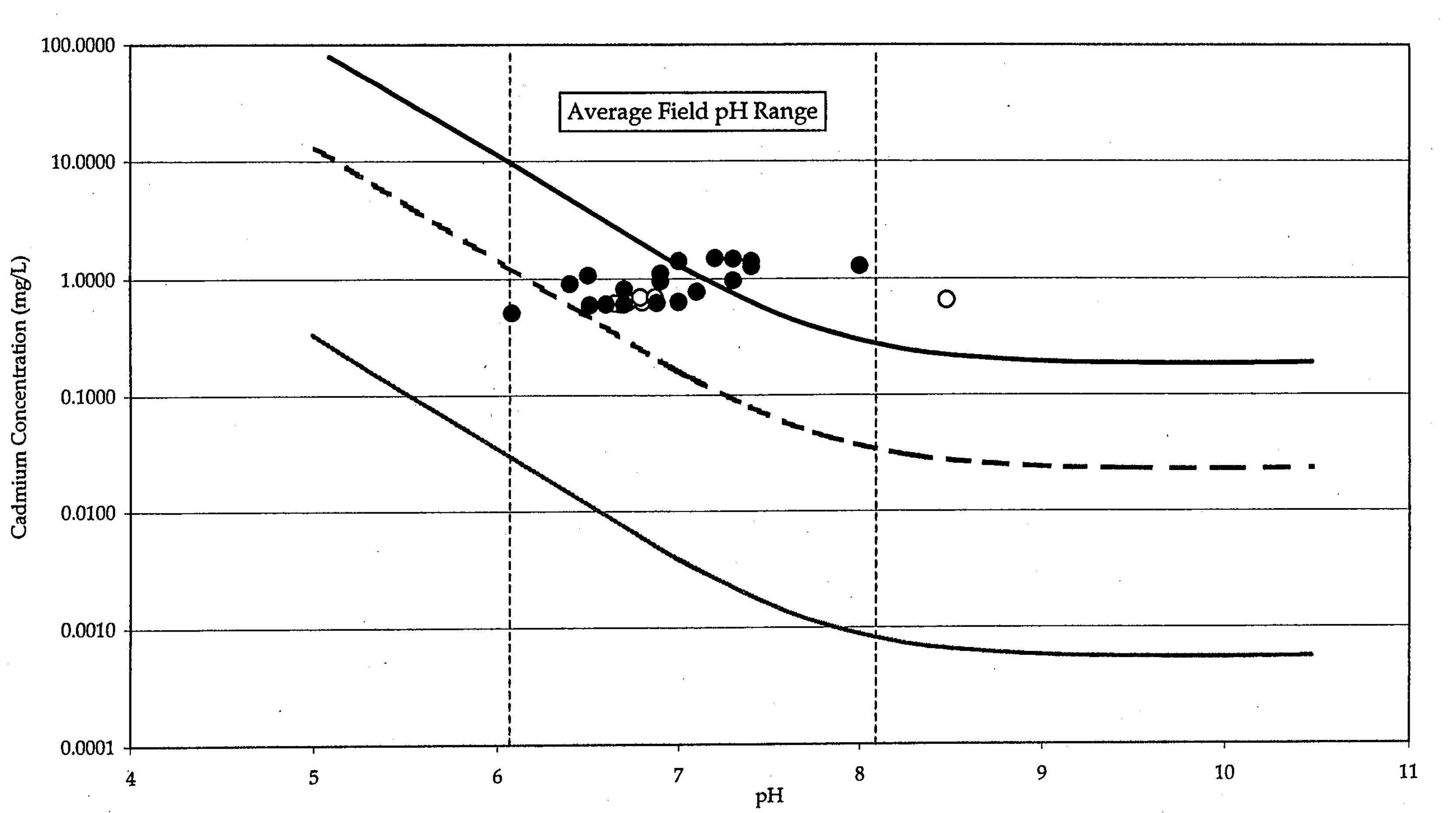


FIGURE 7: TW-16 CADMIUM VS. PH

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 4,5,6,7,8 - CdCO3 pH
Solubility plots.xls

Golder Associates

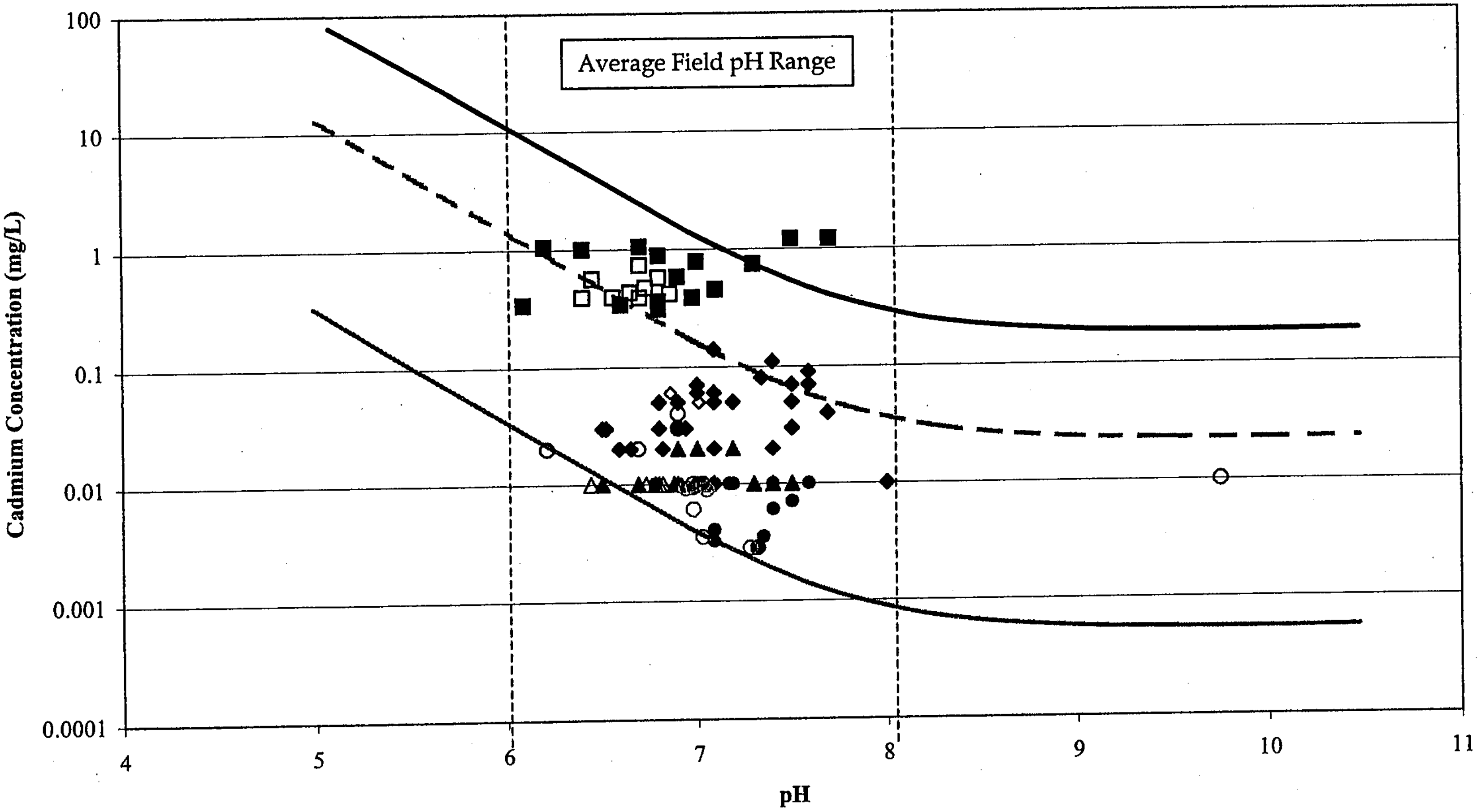


FIGURE 8: DOWNGRADIENT TEST WELLS (TW) CADMIUM VS. PH

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 4,5,6,7,8 - CdCO3 pH Solubility plots.xls

Golder Associates

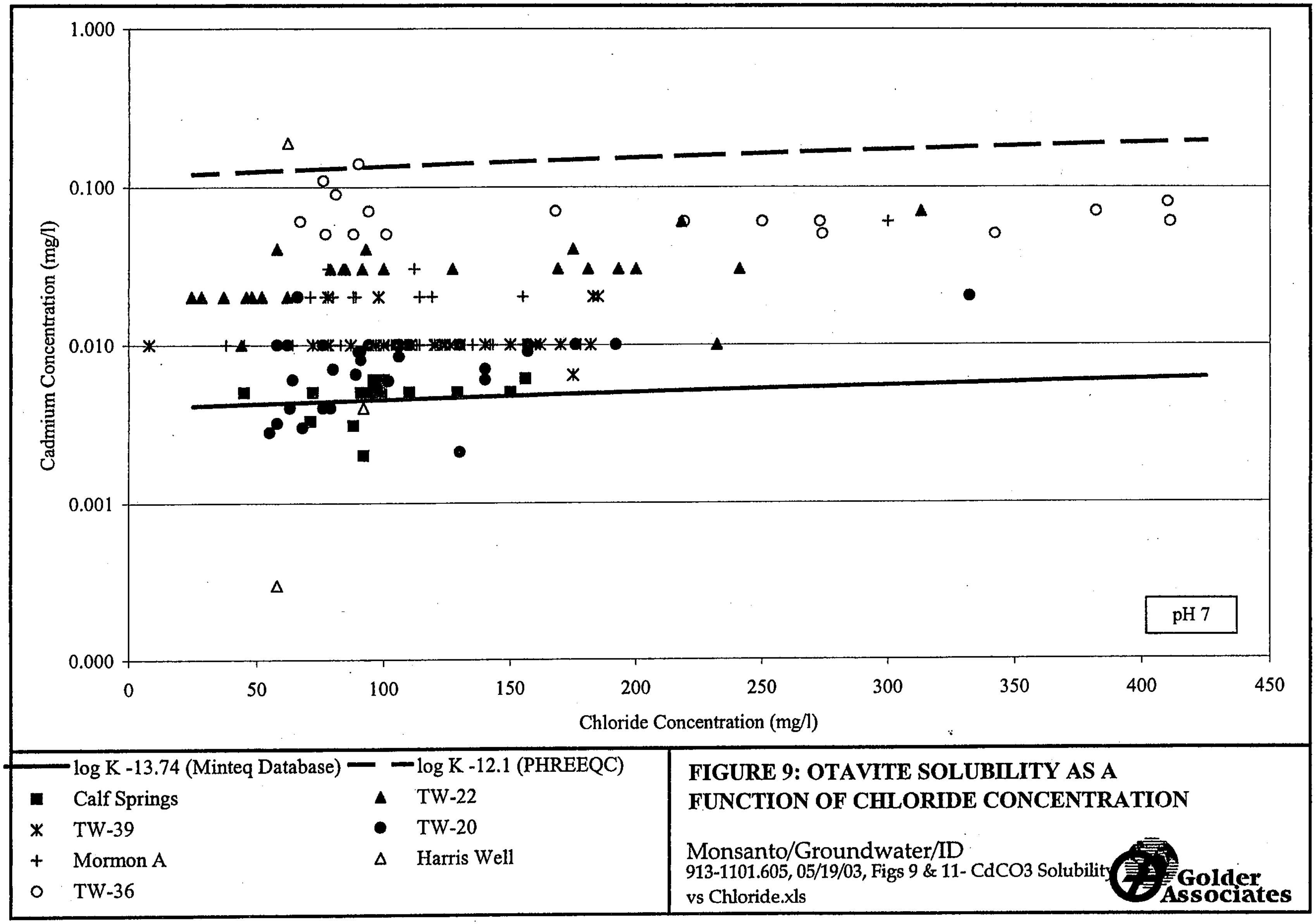


FIGURE 9: OTAVITE SOLUBILITY AS A FUNCTION OF CHLORIDE CONCENTRATION

Monsanto/Groundwater/ID
913-1101.605, 05/19/03, Figs 9 & 11- CdCO3 Solubility vs Chloride.xls

Golder Associates

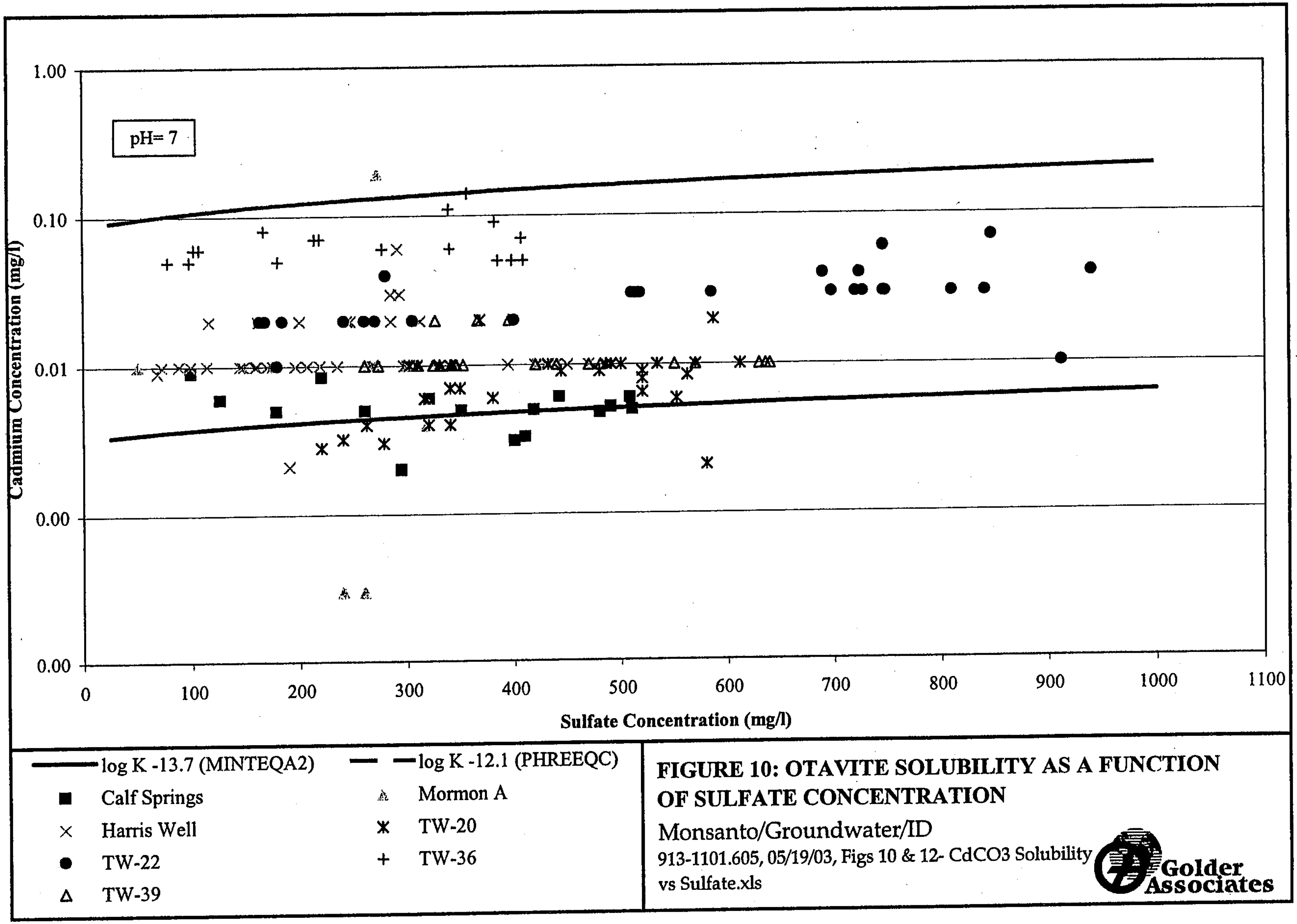


FIGURE 10: OTAVITE SOLUBILITY AS A FUNCTION OF SULFATE CONCENTRATION

Monsanto/Groundwater/ID
913-1101.605, 05/19/03, Figs 10 & 12- CdCO3 Solubility vs Sulfate.xls

Golder Associates

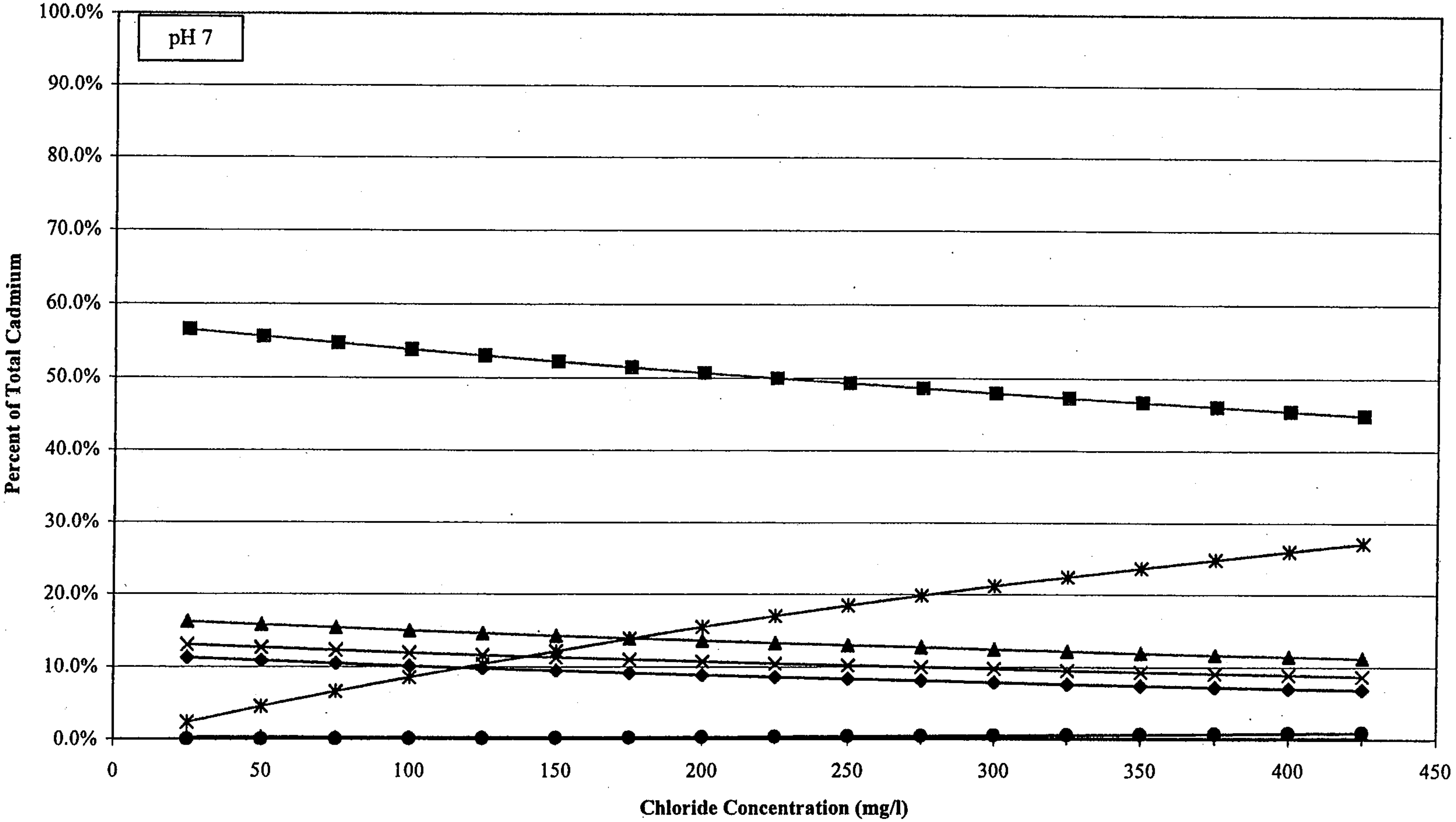


FIGURE 11: SPECIATION OF CADMIUM IN SOLUTION (CHLORIDE SIMULATION)

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 9 & 11- CdCO3 Solubility vs Chloride.xls

Golder Associates

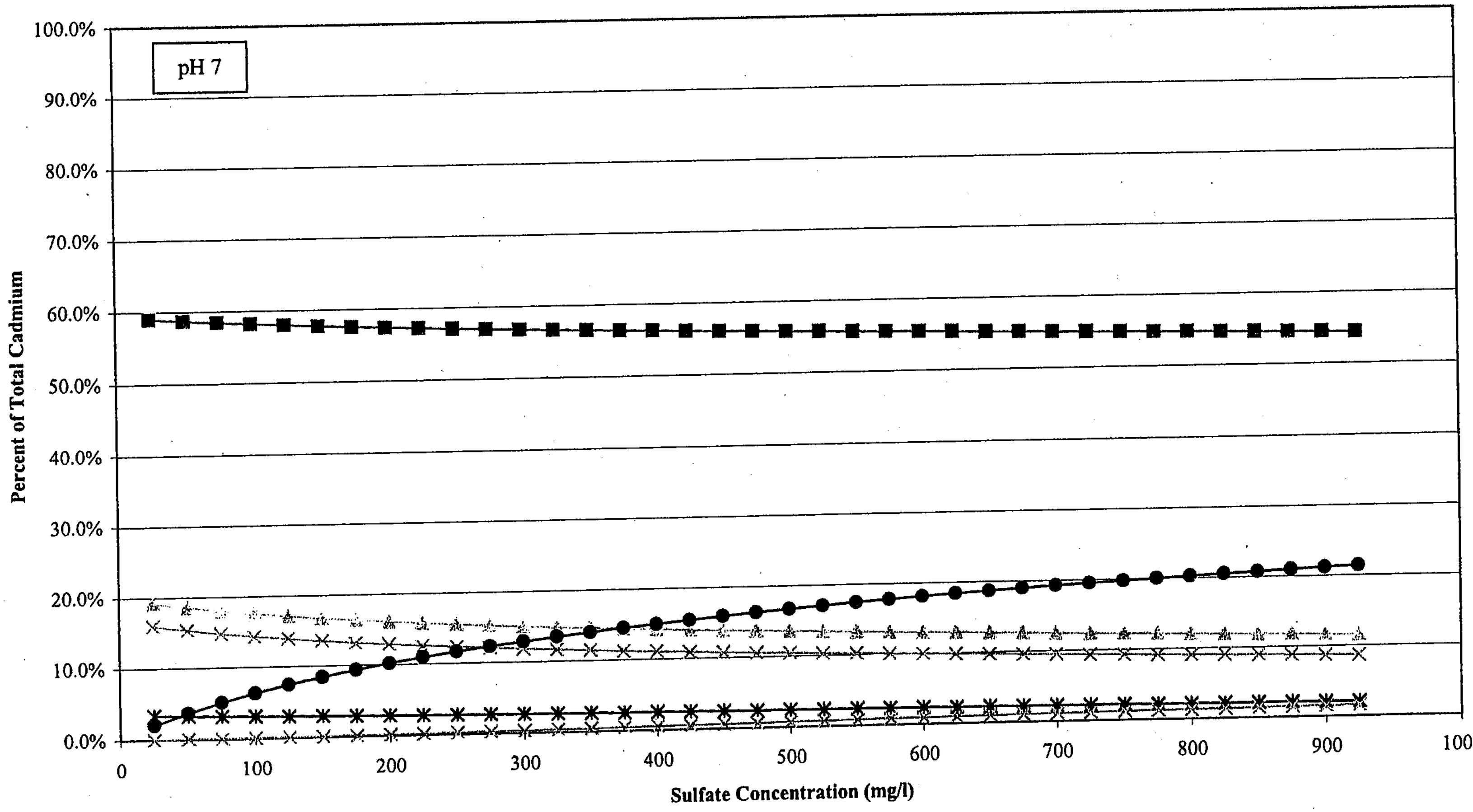


FIGURE 12: SPECIATION OF CADMIUM IN SOLUTION (SULFATE SIMULATION)

Monsanto/Groundwater/ID

913-1101.605, 05/19/03, Figs 10 & 12- CdCO3 Solubility vs Sulfate.xls

Golder Associates