



**ENVIRONMENTAL
RESTORATION
PROGRAM**

**Phase I Report on the Bear Creek Valley
Treatability Study, Oak Ridge Y-12 Plant,
Oak Ridge, Tennessee**

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LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Energy Systems Environmental Restoration Program

**Phase I Report on the Bear Creek Valley
Treatability Study, Oak Ridge Y-12 Plant,
Oak Ridge, Tennessee**

Date Issued—April 1997

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Environmental Management Activities at the
OAK RIDGE Y-12 PLANT
Oak Ridge, Tennessee 37831
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
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MASTER

PREFACE

Phase I Report on the Bear Creek Valley Treatability Study, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, Y/ER-285, was prepared to describe the activities of the Bear Creek Valley Treatability Study. This work was performed under Work Breakdown Structure 1.1.02.41.10.34.20. This document describes the results of Phase I testing and the recommendations for Phase II testing for the management of the Y-12 Plant and the Environmental Management and Enrichment Facilities organization.

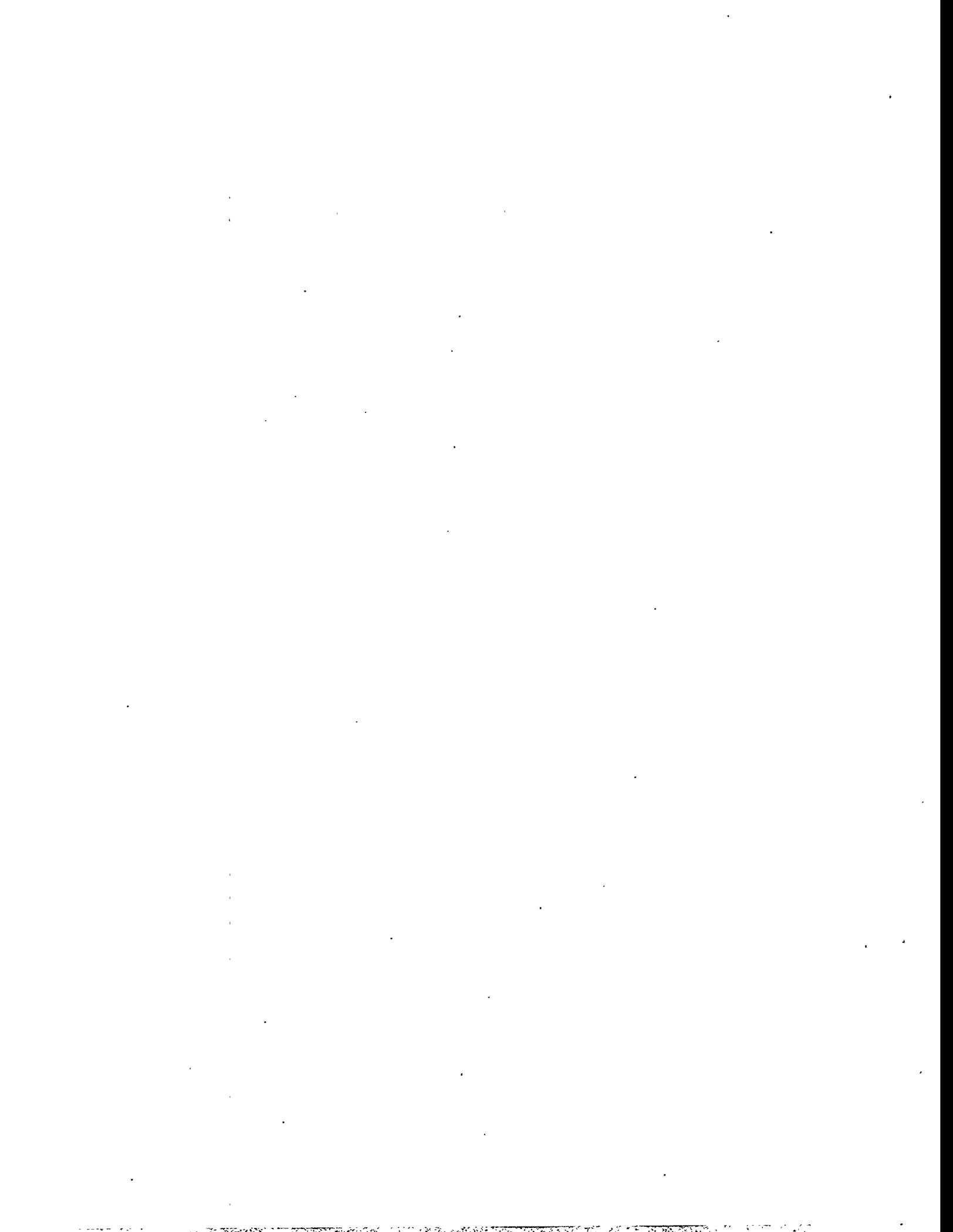


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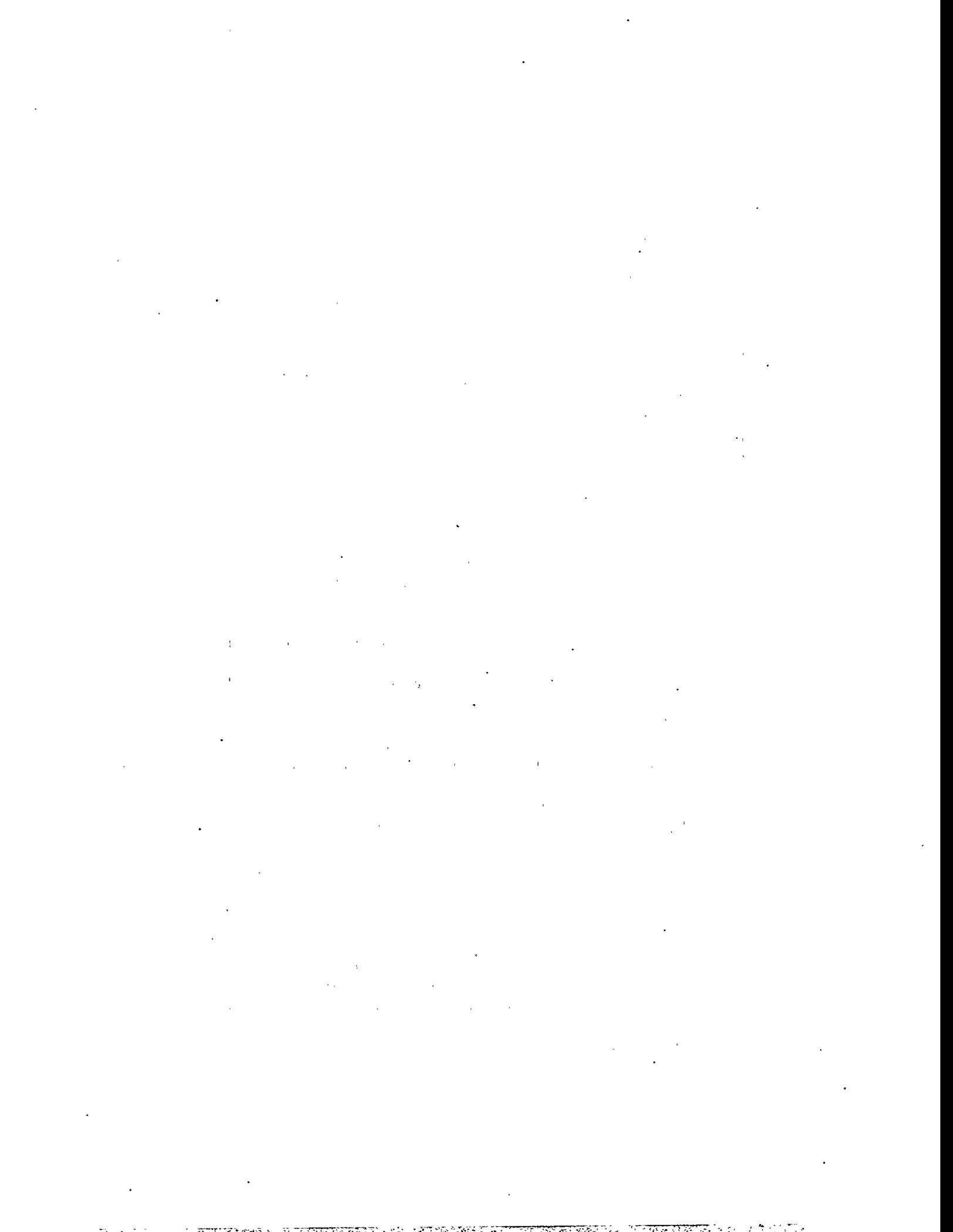
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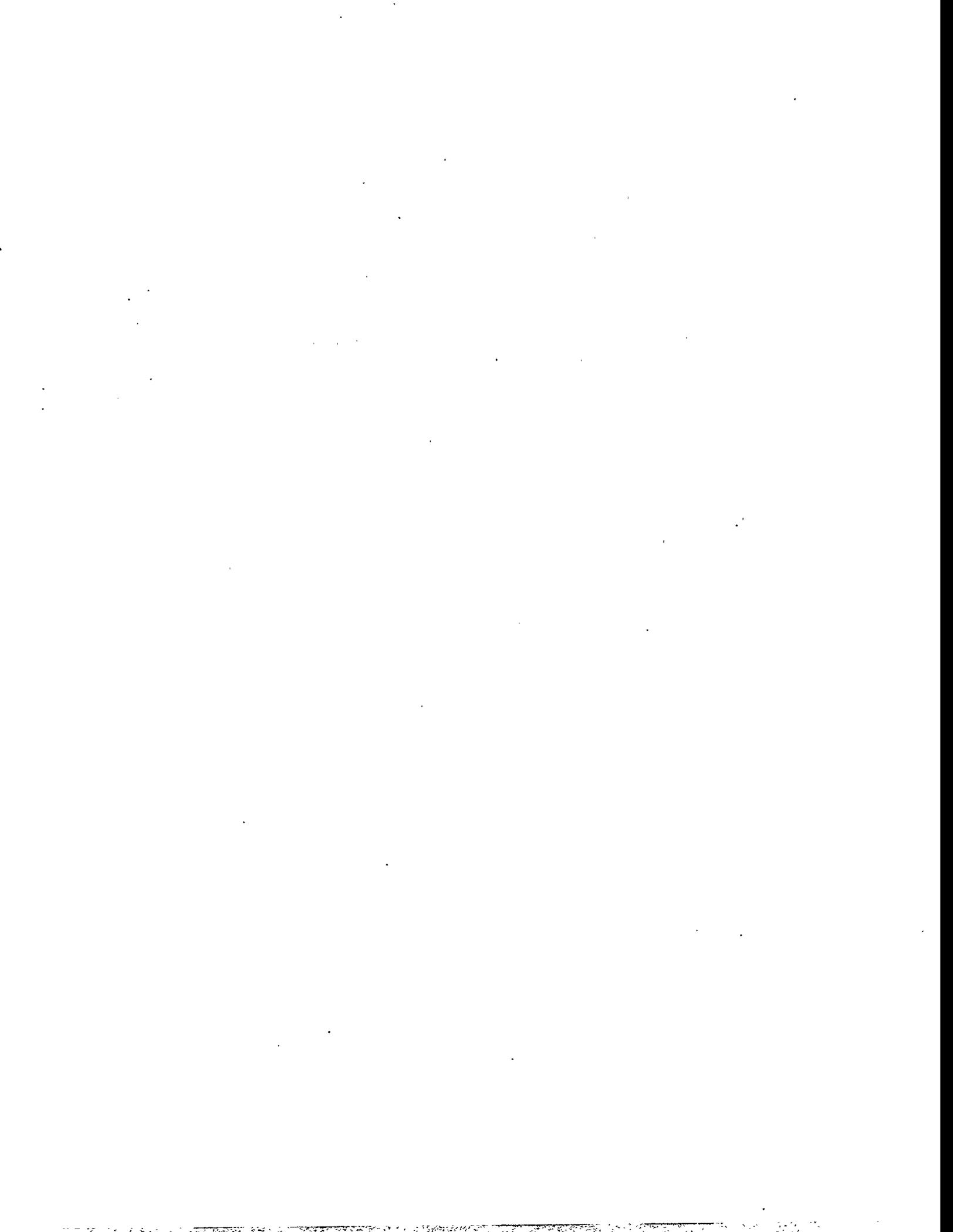
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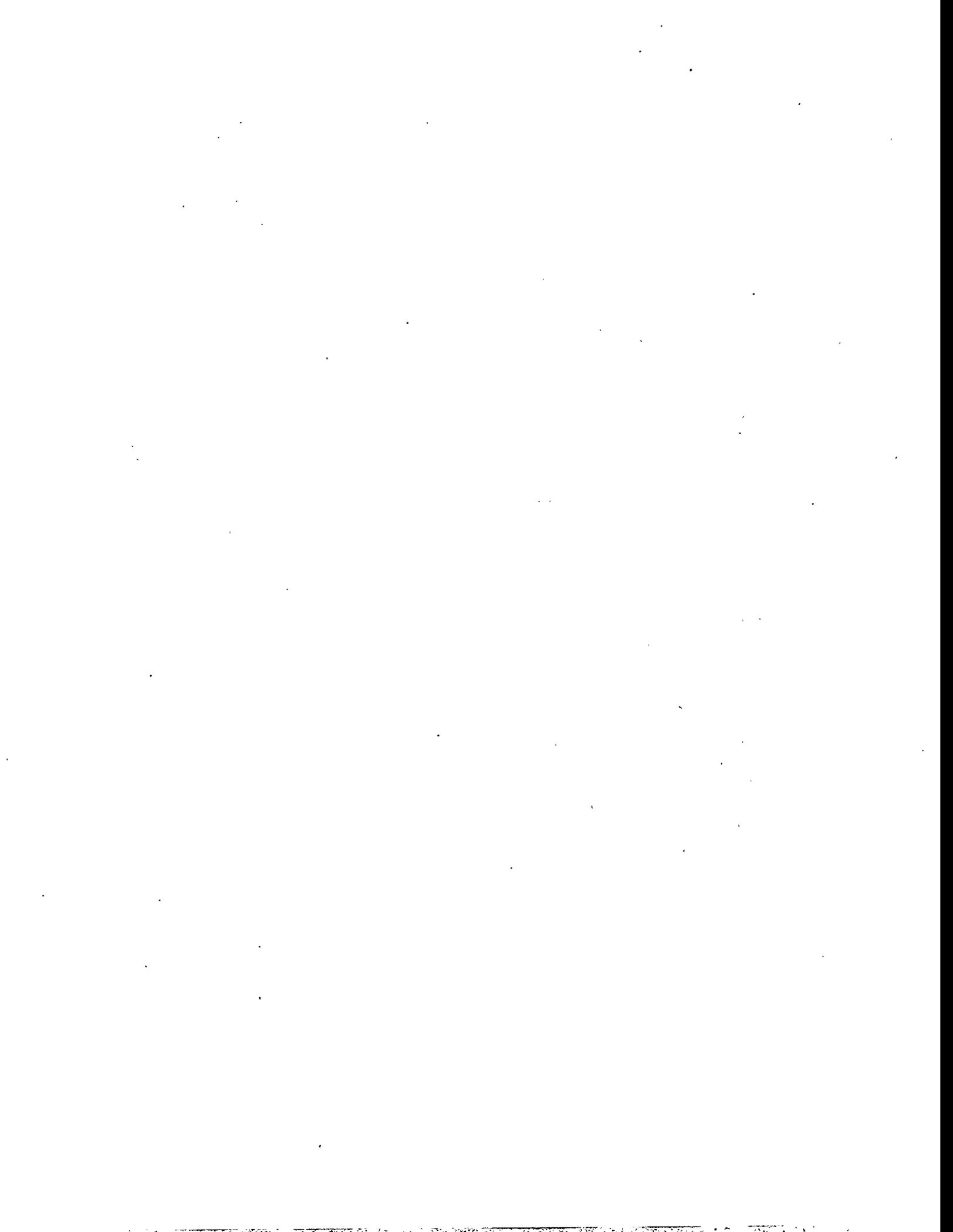
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ABBREVIATIONS

BCBG	Bear Creek Burial Grounds
BCK	Bear Creek Kilometer
BCV	Bear Creek Valley
BYBY	Boneyard/Burnyard
CA	Characterization Area
COCs	contaminants of concern
COPCs	contaminants of potential concern
DCE	dichloroethene
DOE	U.S. Department of Energy
FS	feasibility study
GAC	granulated activated carbon
HCDA	Hazardous Chemicals Disposal Area
ICP	inductively coupled plasma
IP	integration point/plane
MB	Masterbuilder, Inc.
MCL	maximum contaminant levels
NT	North Tributary
OLF	Oil Landfarm
ORR	Oak Ridge Reservation
P2	piezometer 2
PCE	tetrachloroethene
UEFPC	Upper East Fork Poplar Creek
RGOs	remedial goal options
RI	remedial investigation
SMZ	surfactant-modified zeolite
SS	South Spring
TCE	trichloroethene
TDS	total dissolved solids
TDS/TSS	total dissolved solids/total suspended solids
TRW	coal-based resin
VOCs	volatile organic compounds
ZVI	zero-valence iron



EXECUTIVE SUMMARY

Bear Creek Valley (BCV) is located within the U.S. Department of Energy (DOE) Oak Ridge Reservation and encompasses multiple waste units containing hazardous and radioactive wastes associated with past operations at the adjacent Oak Ridge Y-12 Plant. The BCV Remedial Investigation (Energy Systems 1996) determined that disposal of wastes at the S-3 Site, Boneyard/Burnyard (BYBY), and Bear Creek Burial Grounds (BCBG) has caused contamination of both deep and shallow groundwater. The primary contaminants include uranium, nitrate, and VOCs, although other metals such as aluminum, magnesium, and cadmium persist. The BCV feasibility study will describe several remedial options for this area, including both in situ and ex situ treatment of groundwater.

A Treatability Study was designed to identify passive treatment technologies capable of reducing the mass of contamination entering Bear Creek. The *Bear Creek Valley Characterization Area Treatability Study Action Plan* (SAIC 1996a) describes the three phase treatability study program. The goal of the first phase was to screen relevant technologies. The second phase is intended to test long-term on-site treatment performance of the best candidate technologies. The third phase will be implementation of an early action to reduce contamination reaching Bear Creek. This Treatability Study Phase I Report describes the results of preliminary screening of treatment technologies that may be applied within BCV.

The primary target of this study was the S-3 Site area located at the west end of DOE's Y-12 Plant, although information was collected to determine the potential for transferring this technology to the BYBY and Upper East Fork Poplar Creek (UEFPC) as well. Water samples used during testing were collected from the vicinity of North Tributary (NT)-1, Boneyard Burnyard (BYBY), and South Spring 4 (SS-4). Together these samples were considered representative of the range of contaminant characteristics that must be addressed with treatment.

Four activities were undertaken in Phase I: field characterization, laboratory screening of potential sorbents, laboratory testing of zero valent iron products, and field screening of three biological treatment systems. Each of these activities is described fully in technical memos attached in Appendices A through G. This report summarizes results as they pertain to Phase II recommendations. Major summary points include:

Field Characterization. In-stream screening of specific conductivity and nitrate revealed several contaminated seeps within the main stem of Bear Creek and in NT-1 and NT-2. Further investigation using temporary piezometers to collect groundwater allowed delineation of three main contaminant pathways from the S-3 ponds area to surface water. Sampling and analysis of additional monitoring wells and the piezometers indicate that each of these pathways is distinctly different from the others with respect to concentrations of uranium, nitrate, total dissolved solids, and hydrology.

Sorbent Technology Screening. Uranium removal was the primary measure of performance for sorbent testing, although other metals were measured as well. NT-1 and BYBY water samples produced vastly different results with a wide range of sorbent products. The high total dissolved solids content of NT-1 water greatly reduced the treatment efficiencies of all sorbents except peat moss. Most sorbents performed to expectations with BYBY water, with sorbent capacities near

4 mg of uranium per gram of sorbent tested. One product, Dowex, performed exceptionally well with all uranium doses tested in BYBY water. Dowex and peat moss were considered potential candidates for further testing.

Iron Screening. Many different iron products were tested for removal of metals and organic solvents. Products included different brands of zero valent iron (ZVI), palladium-coated ZVI, iron oxides, iron blended with silica foams, and iron oxides as pellets. ZVI products performed well with both water types, removing uranium to below maximum contaminant levels and sometimes below detection limits. Iron oxides performed best when tested as a powder, but treatment efficiency was reduced when tested in a more in-field usable pellet form. This loss in efficiency was attributed to the loss of surface area caused by pelletizing powder.

The mechanism of uranium removal by iron is somewhat unclear because the testing was completed in batch systems. Batch systems cause artifacts that would not be part of the in situ application. The apparent removal mechanism is the binding of uranium in an oxide floc. The potential mobility of the floc is uncertain. Therefore further examination of this mechanism and its long-term stability is essential to determine the ultimate feasibility of this technology.

ZVI was effective at reducing TCE and PCE from groundwater. Palladium coating of ZVI produced a small increase in efficiency, although it was not large enough to be cost effective. The fate of dechlorinated daughter products has not been fully defined and should be examined prior to implementing a full-scale system.

Biological Testing. Three different biological systems were tested: constructed wetlands, algal mats treatment system, and rhizofiltration system (also known as phytoremediation). The primary goal of testing these media was to identify toxic effects due to water characteristics that might negatively impact treatment efficiency. This was measured by observing physical changes during treatment and by measuring treatment efficiency. Each system was tested under realistic field conditions using pilot scale test systems. The wetlands system produced a trend of gradually increasing removal efficiencies for uranium and nitrate when tested with SS-4 water, but results suggested that a longer acclimation or maturation period was necessary for optimum efficiency. Algal mats removed uranium and many other metals from both NT-1 and SS-4 water, but nitrate removal was minimal. Further testing is needed to determine the reason for the loss of nitrate removal ability in the field since laboratory testing showed more positive results. Phytoremediation was successful in removing uranium in half of the tests completed on SS-4 and NT-1 water. Considering the operational requirements for each biological system, algal mats and wetlands were considered viable alternatives for on-site treatment.

The conclusions drawn from this study demonstrate the importance of site-specific testing. Different characteristics of water samples collected from within close proximity greatly influenced the treatment efficiency of most products tested. However, at least one candidate treatment medium was identified as a potential remedy for each of the three types of water in the S-3 area. The final candidates for Phase 2 testing are peat moss, Dowex, ZVI, iron oxides, algal mats, and wetlands. The greatest data gap remaining, prior to implementation of these systems, is the unknown impact of long-term exposure on different treatment agents under subsurface groundwater or surface water conditions at the S-3 Site. In Phase II of the demonstration project, these impacts will be defined and the extent of hydraulic control provided by different trench and well designs will be demonstrated.

1. INTRODUCTION

A treatability study is being conducted to support implementation of early actions at the S-3 Site in the Bear Creek Valley (BCV) Characterization Area (CA). The system will include a trench for capturing and treating groundwater by passing it through a train of individual treatment media that, together, are capable of removing some or all of the targeted contaminants of concern. The treatment objectives of the early actions are (1) to reduce concentrations of uranium and nitrate in Bear Creek to meet downstream concentration goals that will be protective of human health at a location that will be determined in the record of decision (ROD) for the BCV CA and (2) to reduce concentration of nitrate, total dissolved solids (TDS), and selected metals in NT-1 to reduce the risk to the ecology of NT-1 and upper Bear Creek. In addition, a secondary objective of the early actions will be to hydraulically contain a plume of contaminated groundwater in the bedrock of the Nolichucky Shale that is currently migrating west along geological strike from the S-3 Site. This plume discharges contaminants into NT-1 and NT-2 and the long-term effect of containment will be to reduce contaminant discharges to these two tributaries.

The treatability study has two objectives: (1) to design and implement early actions for treatment of contaminated groundwater discharge at the S-3 Site and (2) to support future decision making for the BCV CA where similar technologies may be utilized at other sites in BCV. The treatability study is being conducted in the following three phases (BCV CA Technology Demonstration Action Plan, SAIC 1996):

- **Phase I: Site characterization and preliminary investigation of treatment technologies.** The objectives of Phase I were (1) to identify and characterize possible demonstration sites near Bear Creek, North Tributary (NT)-1 and NT-2; (2) to test and select effective treatment media; and (3) to conduct initial evaluation of bioremediation technologies.
- **Phase II: In-field evaluation of treatment technologies and trench hydraulics.** The objectives of Phase II are (1) to determine efficient treatment trains for S-3 Site-specific water by conducting long-term testing of select media using water from piezometers or test trenches, (2) to evaluate hydraulics and flow rate control for treatment trenches and horizontal/inclined wells, (3) to determine the most effective design for the treatment train/groundwater capture configurations at each site, and (4) to develop optimization data for pilot-scale bioremediation technology designs.
- **Phase III: Implementation of integrated treatment system as an Early Action.** The objective of Phase 3 is to implement groundwater capture trenches and horizontal/inclined wells coupled with in situ or ex situ treatments at the S-3 Site and, if appropriate, operate them in conjunction with bioremediation technologies.

This is the second report issued describing activities related to the BCV Treatability Study. The first report described the action plan to conduct evaluation activity in three phases (SAIC 1996a). This report describes the results of Phase I testing and the recommendations for Phase II testing. Section 1 describes the BCV CA and the treatability study. Section 2 describes results of field characterization. Sections 3 and 4 describe results of treatment technology screening. Section 5 summarizes the findings, and Section 6 provides recommendations for Phase II testing.

1.1 BEAR CREEK VALLEY CHARACTERIZATION AREA

The BCV CA is located within the U.S. Department of Energy's (DOE's) Oak Ridge Reservation (ORR) in east Tennessee, about 32 km (20 miles) northwest of Knoxville. About 16.7 km (10.4 miles) long, the BCV CA extends from the east end of DOE's Oak Ridge Y-12 Plant westward to the Clinch River.

Hazardous and radioactive materials were disposed of at various sites within BCV (Fig. 1.1) throughout Y-12 Plant operation, beginning in the 1940s (Energy Systems 1996). Trenches located at the Bear Creek Burial Grounds (BCBG) and at the Boneyard/Burnyard (BYBY) received large volumes of hazardous and radioactively contaminated solid waste. The S-3 Site, Oil Landfarm (OLF), Hazardous Chemicals Disposal Area (HCDA), and BCBG received hazardous liquid waste.

Groundwater and surface water in the BCV CA have been contaminated by activities at these waste sites. The remedial investigation (RI) for the BCV CA identified that the greatest mass flux of contaminants from the various sources migrated via groundwater at the source and discharges to surface water in Bear Creek and its tributaries (Energy Systems 1996). As part of the RI, contributions of individual wastes sources to the total contaminant mass flux at a downstream location in BCV called the integration plane (IP) were calculated (Fig. 1.2). The combined mass flux of contaminants from two sites — the S-3 Site and BYBY — accounts for 75% of the cancer risk and more than 80% of the chemical toxicity to potential human receptors at the IP with uranium and nitrate contamination accounting for more than 90% of the risk and toxicity. In addition, discharge of contaminated groundwater to surface water from a plume moving west along strike from the S-3 Site has caused degradation of surface water quality in upper Bear Creek and two of its tributaries [North Tributary (NT-1 and NT-2)]. Water and sediments in these tributaries pose risk to the ecology of these streams due to high concentrations of nitrate, total dissolved solids (TDS), and metals.

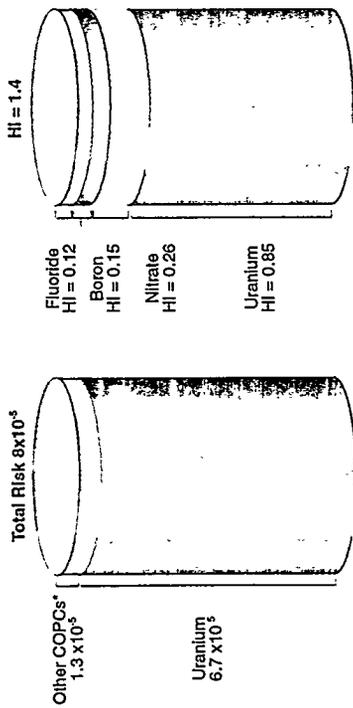
A feasibility study (FS) is currently under way but is not completed. Three of the five remedial alternatives that will be considered in the FS focus on in situ treatment of surface water or shallow groundwater to prevent migration of contaminants beyond the Bear Creek tributary streams. This emphasis on in situ water treatments is dictated to a large extent by the nature of the contaminant pathways within BCV (i.e., passive water treatment at those points at which contaminated groundwater funnels into exit pathways before or after upwelling into the Bear Creek tributaries is a reasonable remedial strategy). Thus, to support the remedial action decision-making and design process, a treatability study is being conducted within the BCV CA to evaluate the implementability and cost effectiveness of passive in situ systems that integrate multiple water treatment technologies.

1.2 IN SITU TREATABILITY STUDY

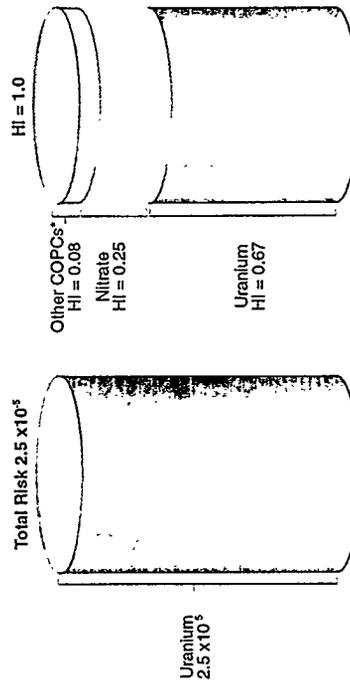
The BCV CA treatability study focuses on capture and treatment of shallow groundwater before it discharges to tributary waters. The potential objectives of treatment of this groundwater are (1) reduce the concentrations of uranium and nitrate in NT-1 and Bear Creek such that, in concert with actions taken at BYBY, the concentrations of these chemicals in surface water and groundwater at the IP are reduced to acceptable levels; (2) reduce the concentrations of nitrate

Potential Risks and Toxic Effects at the Integrator Plane

BCK 9.4/SS-5 Aggregate



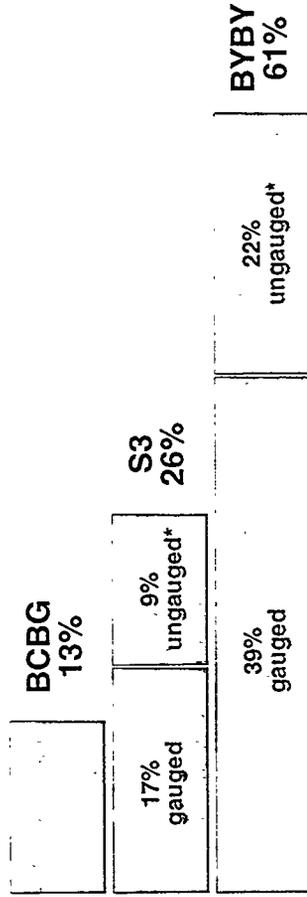
GW 684 Groundwater



*COPCs not listed individually have individual potential risk $< 10^{-5}$ or HI < 0.1

Relative Contribution of Uranium and Nitrate at the IP from Source Areas

Uranium Flux



*Assumed distribution of ungauged flux is 70% BYBY, 30% S-3 Site.

Nitrate Flux

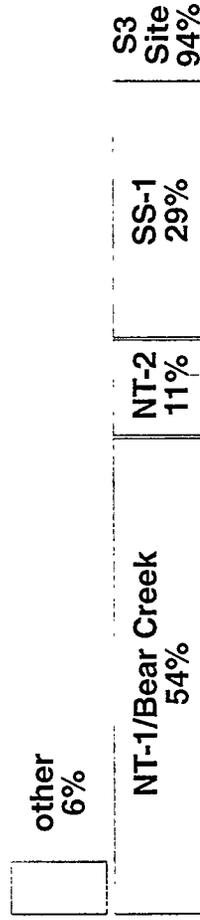


Fig. 1.2. Potential risks and hazards at the integrator point/plane and the relative magnitude of the sources for nitrate and uranium.

and metals, and reduce the overall concentration of TDS to meet ecological remedial goal options (RGOs) in NT-1 and upper Bear Creek [RGOs for the BCV CA were calculated by the BCV CA RI Report (Energy Systems 1996) (see Tables 1.2 through 1.5) and are presented in Appendix H]; and (3) hydraulically contain the plume of contaminated groundwater that is moving west in bedrock in the Nolichucky Shale along strike from the S-3 Site such that the rate of contaminant discharge to NT-2 will be reduced in the long term.

In defining these objectives it is realized that it may not be technically feasible to fully achieve objectives 2 and 3; however, technologies used in this treatability study will be considered viable if significant reductions of in-stream contaminant concentrations can be made.

Three components of this in situ treatment technology require site-specific testing:

- **Permeable treatment media.** The demonstration project tested and developed processes for applying several treatment media to a range of surface water and groundwater chemistries that are known to occur within the BCV CA. The two primary media types tested include (1) zero valence iron media and (2) sorptive media (zeolite, activated carbon, peat moss, biological sorbents).
- **Biological media.** The demonstration project tested and evaluated the ability of three different biologically derived approaches: a constructed wetlands to reduce nitrate and immobilize uranium; algal mats, which can accumulate metals, reduce nitrate, and degrade chlorinated solvents; and phytoremediation, which uses hydroponically grown plants to remove metals from water.
- **Groundwater capture and treatment trench.** The demonstration project will design, install, and operate a passive system that captures and treats groundwater by passing it through a train of treatment media that, together, are capable of removing targeted contaminants of potential concern (COPCs) found in BCV CA waters.

Table 1.1 describes each treatment technology, where it may be applied, and the advantages/disadvantages associated with each approach.

The treatability study is divided into three phases, each of which has specific objectives to test the technologies as individual and as combined treatment trains to address needs at different areas of concern:

- **Phase I: Preliminary Screening.** This phase is the subject of this report. The objectives of Phase I were to characterize the demonstration site, select effective treatment media, and conduct initial tests of bioremediation. Groundwater monitoring was performed to obtain detailed data on the hydraulics and chemistry of groundwater at NT-1 and NT-2 and the main stem of Bear Creek near the S-3 Ponds. These have been selected as the most likely demonstration sites (Fig. 1.1). Bench-scale batch and column tests were performed to determine which treatment media are most efficient for the selected water chemistries. Field and greenhouse tests were performed to determine the ability of the three wetlands applications to remove contaminants from BCV waters.

Table 1.1. Potential treatment systems for BCV waters

Treatment category	Medium	Target contaminants	Phase I sample locations	Treatment advantages	Treatment disadvantages
Zero valence metals	Zero valence iron forms, bimetallic systems	Chlorinated organics (PCE, CCl ₄ , TCA)	NT-1, east Y-12 Plant water, surrogate (BCV groundwater spiked with organics)	Potentially long life span treatment media, resulting in less secondary solid waste, destroys organics	Somewhat unproven, developed on bench scale only, potential for high iron concentrations in effluent, high nitrate levels may impact effectiveness on other contaminants
Zero valence metals	Iron filings, steel wool, modified filings/metal wool, iron based ceramic foams (Cercona foam)	NO ₃ ; metals	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Potentially long life span treatment media, resulting in less secondary solid waste	Somewhat unproven, developed on bench scale only, potential for high iron concentrations in effluent, high nitrate levels may impact effectiveness on other contaminants
Sorption	Zeolites (natural, synthetic, anion adsorbing)	Metals, organics	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Well-developed technology, good cation removal capacity	Highly specific sorptive media would require use of several different zeolites
Sorption	Surfactant enhanced zeolites	Inorganic cations and anions, organics, metals	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Potential economical alternative for wide variety of contaminants	Relatively untested
Sorption	Granular activated carbon	Metals, organics	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Well-developed technology, good adsorption capacity for BCV CA contaminants	Relatively high cost, potential buoyancy problems
Sorption	Peat	Organics, metals	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Should remove a wide range of contaminants, fairly well developed	Questionable adsorption capacities because of tendency for nonselective removal

Table 1.1 (continued)

Treatment category	Medium	Target contaminants	Phase I sample locations	Treatment advantages	Treatment disadvantages
Sorption	Ion exchange	Cations, anions, metals	NT-1, BY/BY or Burial Ground, SS-4, NT-2	Well-developed technology, depending on the media can treat for a specific contaminant or broad class of contaminants	Fairly large secondary waste streams, expensive per unit mass relative to other treatment media; interferences in natural systems
Biological	Algal mats	Metals, nitrate, organics	NT-1, SS-4, NT-2	Can treat many different contaminants, self-sustaining, very little study or operational management required	Somewhat unproven for nitrate, requires sunlight
Biological	Constructed wetlands	Nitrate, metals	SS-4	Public perception is positive, treatment capacity is large	Harvesting metals will be expensive
Biological	Phytoremediation	Metals	SS-4	Minimizes mass to dispose	Plants will have a saturation level, requires plant replacement, high M&O

Based on Phase I results, candidate media and site locations were defined for Phase II testing.

- **Phase II: Pilot-Scale Demonstration.** The objectives of Phase II are to (1) determine long-term treatment efficiency of candidate media using site-specific water and pilot-scale systems operated in the field, (2) develop optimization data for pilot-scale wetlands and algal mats design, and (3) evaluate trench and/or horizontal well hydraulics. A prototype trench and horizontal well will be constructed to evaluate trench hydrogeologic design criteria and to determine the likely range of flow rates and the impact of significant rainfall (storms) on flow and contaminant concentrations. Specific locations for the column studies and the test trench have been identified within the S-3 Site.
- **Phase III: Early Action Implementation.** The objective of Phase III is to implement an early action in the form of a passive groundwater capture and treatment system. Integrated, site-specific treatment systems will be designed, installed, and operated to determine its effectiveness in removing contaminants from BCV groundwater. As the demonstration reveals application problems, solutions will be engineered, designed, and retested.

1.3 HISTORY AND CHARACTERIZATION OF CANDIDATE SITES

Plumes of contaminated groundwater associated with individual BCV waste sites vary in chemistry of contaminants and thus may require different treatment strategies. To ensure that passive, in situ treatment systems developed for the BCV CA are capable of effectively treating BCV waters, water samples were collected or simulated to represent groundwater from the primary plumes. Groundwater in BCV falls into three water type categories based on the chemistry nature of the primary contaminants. These are: Water Type 1 — Nitrate, high TDS, metals, and ⁹⁹Tc; Water Type 2 — uranium, volatile organic compounds (VOCs), and some nitrate; and Water Type 3 — VOCs alone.

Three candidate sites within the BCV CA identified for the demonstration project are (Fig. 1.1):

- **S-3 Site**, which includes three contaminated surface water streams: NT-1 and NT-2 with Water Type 1, and Bear Creek above Bear Creek Kilometer (BCK) 12.46 with Water Type 2;
- **BYBY**, which includes two contaminated surface water streams: NT-3 and Bear Creek adjacent to BYBY with Water Type 2; and
- **SS-4**, which is a spring discharging from the Maynardville Limestone west of the BYBY that contains Water Type 2 contamination derived from S-3 Site and BYBY.

Contaminants transported via the pathways at these sites account for a large portion of the contaminant fluxes in Bear Creek and the Maynardville Limestone, with the S-3 Site and BYBY pathways accounting for more than 80% of the total.

Figure 1.3 shows the distributions of the three water types used in this study plotted on a trilinear diagram. The major ion geochemistries of representative samples from the test locations are distinctly different. With the exception of the sample from piezometer 2 (P2) (at NT-1), each of the water types is calcium bicarbonate type water. Calcium constitutes 50 to 70% of cation milliequivalent, and $\text{HCO}_3 + \text{CO}_3$ constitute >60% anion milliequivalents. The sample from P2 is a calcium nitrate type water and demonstrates the dominant role of the nitrate ion in the S-3 Ponds plume with >60% anion equivalents from nitrate.

1.3.1 S-3 Site

Four unlined ponds with a total storage capacity of approximately 40 million L (10 million gal) were constructed at the western end of the Y-12 Plant (Fig. 1.1) in 1951. Liquid wastes, composed primarily of nitric acid and acidic plating wastes contaminated with various metals and radionuclides, were disposed of in the ponds until March 1983. After in situ neutralization and denitrification of wastewater in the ponds in September 1984, the former ponds were filled and capped and are now covered with a parking lot. Sludges generated during the in situ treatment and contaminated sediments from Bear Creek remain in place below the cap.

At the S-3 Site, a groundwater plume in the Nolichucky Shale, dominated by nitrate and radionuclide contamination, discharges to surface water in NT-1 and NT-2, and the BCV main stream south of the former ponds. A complete summary of S-3 Site groundwater aggregate data is provided in Appendix H. The contaminant pathway at this site can be summarized as follows:

- The contaminated groundwater plume extends along strike in the Nolichucky Shale from the former S-3 Ponds to just west of NT-2 and along strike in the Maynardville Limestone past the BCBG. The plume in the Nolichucky Shale is oriented parallel to bedding that dips at about 45° to the south, reaching a maximum depth of more than 122 m (400 ft) at the former ponds.
- Contaminants migrate along strike in both shallow and deep intervals in the Nolichucky Shale to exit points at Bear Creek, NT-1, and NT-2. Historically declining concentrations of contaminants in the water table interval indicate that the contaminants are being flushed from the shallowest groundwater intervals; however, contaminant concentrations remain high in intermediate and deep bedrock because of the slower flushing rates in these intervals. At NT-2 concentrations of contaminants of concern (COCs) have steadily increased over the past 5 years indicating along strike movement of the contaminant plume. Groundwater in the bedrock interval is now the source of most contaminants that migrating to surface water.
- The groundwater plume at the S-3 Site is stratified, with the relative distribution of contaminants in groundwater varying as a result of geochemical reactions. Nitrate and ^{99}Tc , which are not highly particle-reactive, have the most extensive distribution, defining the outermost boundaries of the plume. Uranium and other metals, which are most particle-reactive, have more limited distributions. As a result uranium occurs primarily in the shallow groundwater intervals and nitrate and ^{99}Tc in the intermediate and deep intervals.

- P2 (NT-1)—S-3 Water Type 1
- SS-4
- △ GW-220 (UEFPC)—Water Type 3
- GW-087 (BYBY)—Water Type 2
- GW-242 (BCBG)—Water Type 2

0 1000 2000 3000 4000
 Total Dissolved Solids
 (Parts Per Million)

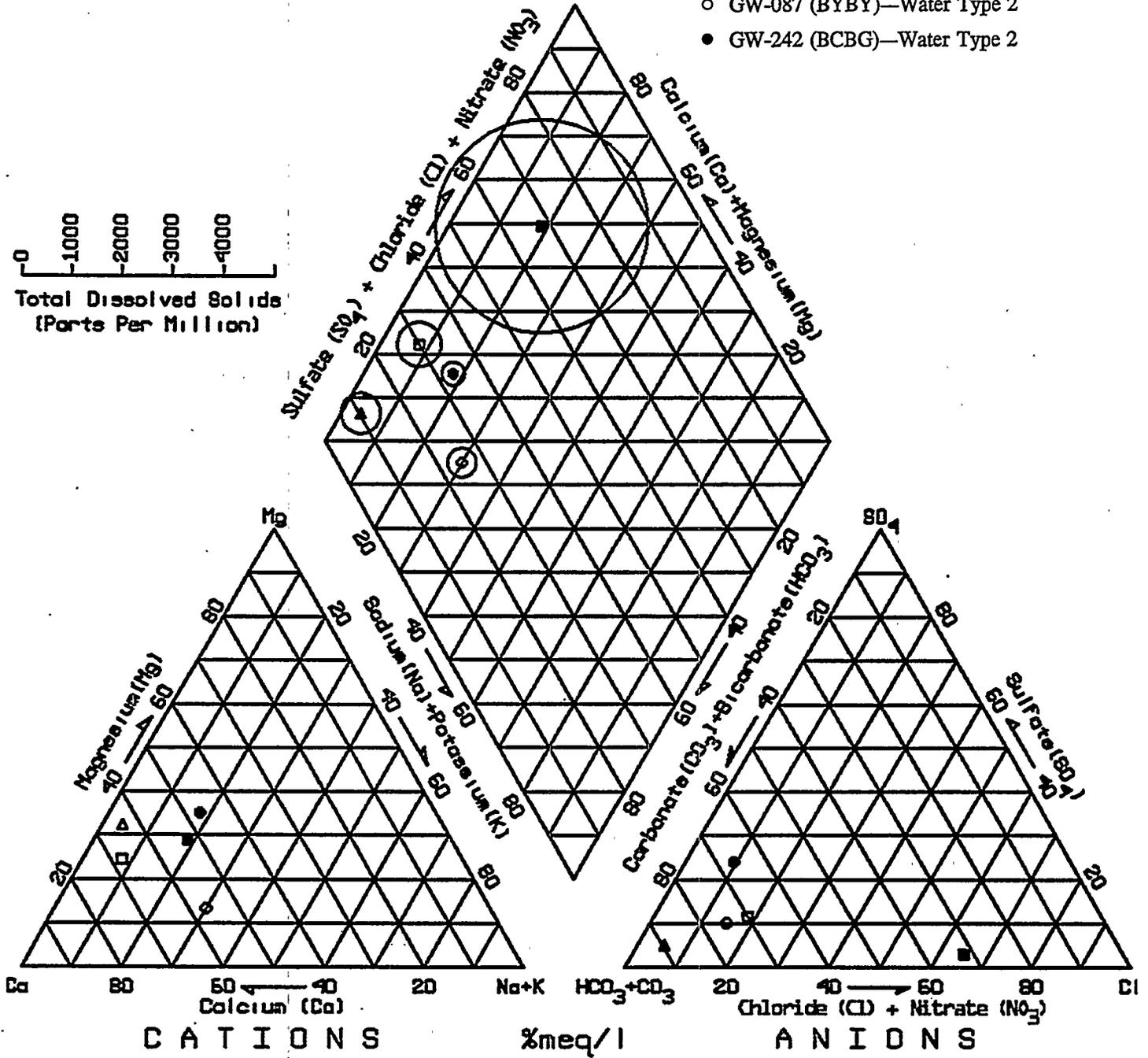


Fig. 1.3. Piper diagram plot of the proposed water types.

- Bear Creek, which receives discharge from the shallow groundwater intervals, is primarily contaminated with uranium and some metals (Water Type 2, Table 1.2), whereas NT-1 and NT-2, which receive discharge from the intermediate groundwater interval, are contaminated primarily with nitrate, high TDS, and ^{99}Tc (Water Type 1, Table 1.3).
- The TDS in the groundwater plume are highest ($>20,000$ mg/L) in the wells closest to the former S-3 Ponds, becoming more diffuse downgradient; for example, TDS >5000 mg/L occurs in the deep system 610 m (2000 ft) downgradient. TDS surface water reaches a maximum of >1500 mg/L in NT-1 and Bear Creek.
- The most widespread organic contaminants in groundwater at the S-3 Site are acetone and tetrachloroethene (PCE), which also occur in NT-1 and Bear Creek surface water.

1.3.2 Boneyard/Burnyard

The BYBY, which operated from 1943 to 1970, received an unknown volume of inert, ignitable, and radioactive wastes, including organics, metals, beryllium, acids, and debris. The HCDA, which was later built on top of the former Burnyard, received an estimated 3.8 m³/yr (5 yd³/yr) of solid, liquid, and gaseous wastes from 1975 to 1981 (Turner et al. 1991).

In shallow groundwater at BYBY, uranium and VOCs are the primary COCs that (Table 1.4), discharge to NT-3 and Bear Creek and probably also flow directly into the Maynardville Limestone. Uranium contamination, with activities exceeding 2000 pCi/L near the channel of NT-3, is derived from leaching of buried waste materials, probably below the water table, and occurs primarily in the shallow interval. The VOC contamination, dominated by PCE, trichloroethene (TCE), and 1,2-dichloroethene (DCE), occurs close to the HCDA cap and probably discharges directly to Bear Creek or the Maynardville Limestone.

1.3.3 SS-4

South Spring (SS)-4 is located downgradient of both the S-3 Site and BYBY. A portion of the contaminant flux from these sites discharges at SS-4 as one of the pathways between the source areas and the IP at BCK 9.47. Groundwater discharging at this location is contaminated with uranium, VOCs, and nitrate (Water Type 2, Table 1.5). This location represents a downstream water quality that may be treated by polishing treatment systems such as the constructed wetlands.

1.4 CONTAMINANTS TARGETED FOR REMOVAL

To meet the objectives of this treatability study (Sect. 1.2) contaminants targeted for removal are: uranium and nitrate (which constitute a Human Health risk at the BCV IP) and chemicals that occur above ecological RGOs in NT-1, NT-2, and upper Bear Creek. These contaminants are identified, with their observed concentrations and their RGO values, in Tables 1.2 through 1.5. A full list of the surface water RGOs developed by the BCV RI (Energy Systems 1996) is presented in Appendix H.

Table 1.2. Results of analysis of surface water at BCK 12.46

Analyte ^a	Freq of detect	Bkgd criteria ^b	Detects > bkgd	Min detect	Max detect	Avg ^c result	Fish and Aquatic Life Risk	RGOs ARAR
<i>Inorganics</i>								
Nitrate (mg/L)	71/ 71	0.2	71/ 71	3.8	530.0	38.8		
Aluminum (mg/L)	64/ 72	7.4	1/ 72	0.04	21.8	0.51		
Barium (mg/L)	71/ 72	0.21	1/ 72	0.044	0.928	0.092		
Beryllium (mg/L)	1/ 72	0.00072	1/ 72	0.001	0.001	0.0000		
Boron (mg/L)	72/ 72	0.062	59/ 72	0.04	0.291	0.086		
Calcium (mg/L)	72/ 72	36	72/ 72	57.2	230.0	164.5	116	
Cerium (mg/L)	1/ 72	.		0.08	0.08	0.012		
Cobalt (mg/L)	1/ 72	0.017	0/ 72	0.014	0.014	0.001		
Copper (mg/L)	3/ 72	0.0072	3/ 72	0.02	0.052	0.005		0.0118
Cyanide (mg/L)	6/ 72	.		0.002	0.003	0.001		0.0052
Iron (mg/L)	41/ 72	30	1/ 72	0.06	42.6	0.74		
Lithium (mg/L)	33/ 72	.		0.02	0.02	0.02		
Magnesium (mg/L)	72/ 72	7.2	72/ 72	7.63	37.4	23.4		
Manganese (mg/L)	72/ 72	6.1	0/ 72	0.005	0.571	0.046	6.6	
Mercury (mg/L)	18/ 72	0.0002	3/ 72	0.0	0.001	0.0000	0.126	0.000012
Nickel (mg/L)	2/ 72	0.011	1/ 72	0.009	0.03	0.005	0.015	0.158
Phosphorous (mg/L)	41/ 72	.		0.05	0.4	0.06		
Potassium (mg/L)	72/ 72	3.5	69/ 72	2.5	7.5	5.1		
Scandium (mg/L)	1/ 72	.		0.012	0.012	0.000		

Table 1.2 (continued)

Analyte ^a	Freq of detect	Bkgd criteria ^b	Detects > bkgd	Min detect	Max detect	Avg ^c result	Fish and Aquatic Life RGOs Risk	ARAR
Selenium (mg/L)	1/ 72	0.066	0/ 72	0.002	0.002	0.0010		0.005
Sodium (mg/L)	72/ 72	7.6	72/ 72	18.6	179.0	57.0		
Strontium (mg/L)	72/ 72	0.12	72/ 72	0.155	0.578	0.4230		
Thallium (mg/L)	2/ 72	.		0.001	0.005	0.001		
Thorium (mg/L)	2/ 72	0.2	0/ 72	0.01	0.01	0.006		
Titanium (mg/L)	3/ 72	.		0.01	0.19	0.01		
Total uranium (fluorometric) (mg/L)	72/ 72	0.015	72/ 72	0.129	1.04	0.621	0.142	
Vanadium (mg/L)	1/ 72	0.013	1/ 72	0.09	0.09	0.003		
Zinc (mg/L)	24/ 72	0.066	1/ 72	0.007	0.2	0.013		0.106
Zirconium (mg/L)	1/ 71	.		0.016	0.016	0.002		
Phenols (mg/L)	54/ 72	.		0.001	0.007	0.002		
<i>Organics</i>								
<i>Radioactivity</i>								
Alpha activity (pCi/L)	72/ 72	2.11	71/ 72	0.17	750.0	270.5		
Americium-241 (pCi/L)	54/ 72	.		0.0	0.93	0.18		
Beta activity (pCi/L)	72/ 72	3.75	70/ 72	0.06	360.0	164.1		
Neptunium-237 (pCi/L)	70/ 72	.		0.20	5.7	0.8		
Plutonium-238 (pCi/L)	31/ 69	.		0.0	0.41	0.08		

Table 1.2 (continued)

Analyte ^a	Freq of detect	Bkgd criteria ^b	Detects > bkgd	Min detect	Max detect	Avg ^c result	Fish and Aquatic Life Risk	Life RGOs ARAR
Plutonium-239 (pCi/L)	39/ 69	.		0.0	0.2	0.03		
Technetium-99 (pCi/L)	70/ 72		0.0	0.67	0.12		

^a Analytes detected at least once are summarized. Results reflect data validation and data usability screens.

^b For surface water, background criteria have been established using data from NT-13 published in the GWQRs (e.g., HSW 1995). Only results for unfiltered samples were used.

^c Average result reflects the arithmetic mean of the dataset, assuming non-detects are equal to one-half the detection limit for chemicals. Radionuclide data qualified as non-detect based on comparison to minimal detectable activities or counting errors are set equal to the reported value.

Table 1.3. Results of analysis for water samples from temporary piezometers P1 and P2, and the adjacent reach of NT-1, unfiltered samples

Parameter	Units	P1	Lab	P2	Lab	NT-1	Lab	Ecological RGOs	
		(2/26/96) ^a	qual ^b	(3/6/96) ^c	qual ^b	(12/14/95)	qual ^b	Risk	ARAR
<i>Inorganics</i>									
Aluminum	mg/L	90.3		81.3		1.9			
Alkalinity (total)	mg/L			160		120			
Antimony	mg/L	0.2	<						
Arsenic	mg/L	0.2	<	0.1	<	0.005	<		0.19
Barium	mg/L	5.45		20.1		0.824			
Beryllium	mg/L	0.02		0.0103		0.0007			
Boron	mg/L	0.2				0.02			
Cadmium	mg/L	0.68		0.788		0.038		0.002	0.0011
Calcium	mg/L	184		1000	>	279		116	
Cerium	mg/L	0.58	Z			0.02	Z		
Chloride	mg/L			180		23			
Chromium	mg/L	0.08		0.0758		0.006	<		0.1
Cobalt	mg/L	0.62		0.598		0.018			
Copper	mg/L	0.03	<	0.03	<	0.006	<		0.0118
Fluoride	mg/L			30.0		1.2			
Iron	mg/L	37.7		37.4		0.06	<		
Lead	mg/L	0.1	<	0.2	<				0.0032
Lithium	mg/L	0.1				0.02	<		
Magnesium	mg/L	262.0		334.0		37.9			
Manganese	mg/L	115.0		100.0	>	6.93		6.6	
Mercury	mg/L			0.0002		0.0002	<	0.126	0.00012
Molybdenum	mg/L	0.03	<	0.04	<	0.006	<		
Nickel	mg/L	3.45		3.18		0.151		0.015	0.158
Nitrate	mg/L			1919		230			
Nitrite	mg/L			16		1			
o-Phosphate	mg/L			0.12	<				
Potassium	mg/L	47.0		48.2		4.3			
Selenium	mg/L	0.5	<			0.005	<		0.005
Silver	mg/L	0.03	<	0.02	<Z	0.006	<		0.0041
Sodium	mg/L	329.0		379.0		36.3			
Strontium	mg/L	4.16	Z			0.806	Z		
Sulfate	mg/L			12					
Thallium	mg/L	0.2	<	0.135		0.03	<		
Thorium	mg/L	0.05	<Z			0.01	<Z		
Titanium	mg/L	0.41	Z			0.02	<Z		
Uranium	mg/L	0.01		0.006				0.142	

Table 1.3 (continued)

Parameter	Units	P1 (2/26/96) ^a	Lab qual ^b	P2 (3/6/96) ^c	Lab qual ^b	NT-1 (12/14/95)	Lab qual ^b	Ecological RGOs	
								Risk	ARAR
Vanadium	mg/L	0.04		0.0514		0.004	<		
Zinc	mg/L	0.19		0.225		0.01	<		0.0106
Zirconium	mg/L	0.02	<Z						
<i>Organics</i>									
1,1,1-Trichloroethane	µg/L	2	J	2	J				
1,1,2-Trichloro-1,2,2-trifluoroethane	µg/L			65	B				
1,1-Dichloroethene	µg/L	3	J	2	J				
cis-1,2-Dichloroethene	µg/L			19					
2-Butanone	µg/L			3	BJ				
Acetone	µg/L			6	BJ	4	JB		
Chloroform	µg/L	17		17		1	J		
Bromomethane	µg/L			4	J				
Methylene chloride	µg/L	27		18		2	J		
Tetrachloroethene	µg/L	260		120	B	19			
Toluene	µg/L	1	J						
Trichloroethene	µg/L	2	J	2	J				
<i>Radioactivity</i>									
Alpha Activity	pCi/L					24 ± 10	(12)		
Beta Activity	pCi/L					310 ± 42	(8.3)		
Total Strontium	pCi/L			27 ± 4.5	(13)				
Technetium-99	pCi/L			15000 ± 1500	(12)	1000 ± 110	(12)		
Tritium	pCi/L			950 ± 190	(420)				
Uranium-235	wt %	0.35		0.37					
Uranium-234	pCi/L					3.9 ± 1.1	(0.13)		
Uranium-235	pCi/L					0.18 ± 0.21	(0.16)		
Uranium-236	pCi/L					0.14 ± 0.17	(0.13)		
Uranium-238	pCi/L					8.4 ± 1.8	(0.32)		
<i>Other</i>									
pH		4.82							
Total suspended solids	mg/L			370		8			
Total dissolved solids	mg/L			13000	270				

^a Metals by method EPA 200.7.

^b < indicates that less than detection limit and detection limit is reported. Z indicates that the analyte was not included in method EPA SW846 prep method 3010.

^c Metal by method EPA SW846.

Table 1.4. Results of analysis of shallow groundwater at BYBY

Analyte ^a	Freq of detect	Freq of wells with detects	Wells with median > bkgd ^b	Min detect	Max detect	Avg ^c result	Ecological RGOs	
							Risk	ARAR
<i>Inorganics</i>								
Aluminum (mg/L)	9/9	8/8	4	0.7670	19.2000	7.3168		
Antimony (mg/L)	1/9	1/8	0	0.0339	0.0339	0.0042		
Arsenic (mg/L)	5/9	4/8	0	0.0020	0.0133	0.0030		0.19
Barium (mg/L)	9/9	8/8	0	0.0676	0.5670	0.2135		
Beryllium (mg/L)	4/9	3/8	3	0.0005	0.0017	0.0005		
Calcium (mg/L)	9/9	8/8	7	42.1000	413	157.3222	116	
Cobalt (mg/L)	6/9	5/8	3	0.0049	0.0347	0.0140		
Copper (mg/L)	3/9	3/8	4	0.0137	0.1210	0.0297		0.0118
Iron (mg/L)	9/9	8/8	5	1.5600	44.2000	16.7889		
Lead (mg/L)	8/9	7/8	5	0.0012	0.1180	0.0266		0.0032
Magnesium (mg/L)	9/9	8/8	2	8.3700	33.5000	15.1900		
Manganese (mg/L)	9/9	8/8	2	0.1470	7.5800	1.8803	6.6	
Mercury (mg/L)	9/9	8/8	7	0.0002	0.0784	0.0094	0.126	0.000012
Molybdenum (mg/L)	2/9	2/8	2	0.0155	0.1290	0.0203		
Nickel (mg/L)	9/9	8/8	6	0.0062	0.0799	0.0428	0.015	0.158
Potassium (mg/L)	9/9	8/8	3	1.4800	13.7000	6.3922		
Selenium (mg/L)	2/9	2/8	0	0.0025	0.0040	0.0019		0.005
Sodium (mg/L)	9/9	8/8	0	4.0800	15.8000	9.6744		
Thallium (mg/L)	0/9	0/8	NA ^d	0	0	0.0009		
Tin (mg/L)	0/9	0/8	0	0	0	0.0049		
Vanadium (mg/L)	6/9	5/8	3	0.0027	0.0319	0.0103		

Table 1.4 (continued)

Analyte ^e	Freq of detect	Freq of wells with detects	Wells with median > bkgd ^b	Min detect	Max detect	Avg ^c result	Ecological RGOs	
							Risk	ARAR
Zinc (mg/L)	5/9	4/8	3	0.0234	0.3240	0.0688		0.106
<i>Common Anions</i>								
Chloride (mg/L)	9/9	8/8	1	1.8000	35	10.3222		
Cyanide (mg/L)	1/9	1/8	NA ^d	0.0336	0.0336	0.0082		
Fluoride (mg/L)	4/9	4/8	3	0.1500	4	1.0417		
Nitrate (µg/L)	5/9	5/8	0	0.1100	6.7000	0.8233		
Sulfate (mg/L)	9/9	8/8	7	33	300	101.4444		
<i>Organics</i>								
1,1,2-Trichloroethane (µg/L)	2/9	2/8		3	5	2.8333		
1,1-Dichloroethane (µg/L)	4/9	4/8		2	9	3.2778		
1,1-Dichloroethene (µg/L)	2/9	2/8		5	110	14.7222		
1,2-Dichloroethane (µg/L)	2/9	2/8		6	23	5.1667		
1,2-Dichloroethene (µg/L)	3/9	3/8		3	1,100	132.8889		
Acetone (µg/L)	2/9	2/8		15	64	16.3889		
Aroclor-1254 (µg/L)	1/8	1/7		0.4500	0.4500	0.5431		
Benzene (µg/L)	3/9	3/8		1	10	3.7778		
Bis(2-Ethylhexyl)phthalate (µg/L)	2/8	2/7		1	2	4.6875		
Chloroethane (µg/L)	1/9	1/8		17	17	6.3333		
Chloroform (µg/L)	1/9	1/8		140	140	17.7778		
Di-N-Butylphthalate (µg/L)	2/8	2/7		1	1	4.5000		
Fluoranthene (µg/L)	4/8	4/7		1	4	4.1875		
Phenanthrene (µg/L)	3/8	3/7		1	3	4.3125		

Table 1.4 (continued)

Analyte ^a	Freq of detect	Freq of wells with detects	Wells with median > bkgd ^b	Min detect	Max detect	Avg ^c result	Ecological RGOs	
							Risk	ARAR
Pyrene (µg/L)	4/8	4/7		1	3	3.9375		
Tetrachloroethene (µg/L)	2/9	2/8		15	620	72.5000		
Toluene (µg/L)	3/9	3/8		1	1	2		
Trichloroethene (µg/L)	3/9	3/8		3	2,000	247.5556		
Vinyl chloride (µg/L)	2/9	2/8		9	73	13		
<i>Radionuclides</i>								
Alpha activity (pCi/L)	6/9	6/8		23	2,200	295.8889		
Antimony-125 (pCi/L)	0/9	0/8		0	0	4.3111		
Beta activity (pCi/L)	7/9	7/8		22	2,800	378.2444		
Bismuth-212 (pCi/L)	0/9	0/8		0	0	32.4478		
Cerium-144 (pCi/L)	0/9	0/8		0	0	10.5667		
Cesium-134 (pCi/L)	0/9	0/8		0	0	2.3556		
Cesium-137 (pCi/L)	0/9	0/8		0	0	5.3333		
Chromium-51 (pCi/L)	0/9	0/8		0	0	14.8889		
Cobalt-57 (pCi/L)	0/9	0/8		0	0	1.2933		
Cobalt-58 (pCi/L)	0/9	0/8		0	0	0.1667		
Cobalt-60 (pCi/L)	0/9	0/8		0	0	6.3022		
Iron-59 (pCi/L)	0/9	0/8		0	0	5.2444		
Lead-212 (pCi/L)	1/9	1/8		16	16	10.7128		
Manganese-54 (pCi/L)	0/9	0/8		0	0	0.3133		
Niobium-95 (pCi/L)	0/9	0/8		0	0	2.2933		
Potassium-40 (pCi/L)	1/9	1/8		170	170	106.3333		

Table 1.4 (continued)

Analyte ^a	Freq of detect	Freq of wells with detects	Wells with median > bkgd ^b	Min detect	Max detect	Avg ^c result	Ecological RGOs	
							Risk	ARAR
Ruthenium-106 (pCi/L)	0/9	0/8	0	0	0	24.8889		
Sodium-22 (pCi/L)	0/9	0/8	0	0	0	0.7489		
Strontium-90 (pCi/L)	0/9	0/8	0	0	0	0.3222		
Technetium-99 (pCi/L)	0/9	0/8	0	0	0	4.1222		
Thallium-208 (pCi/L)	0/9	0/8	0	0	0	12.9044		
Thorium-228 (pCi/L)	6/9	6/8		1.2000	2.3000	1.2278		
Thorium-230 (pCi/L)	6/9	6/8		1.1000	2.6000	1.3967		
Thorium-232 (pCi/L)	2/9	2/8		1	1.2000	0.5700		
Uranium-234 (pCi/L)	8/9	8/8		2.9000	1.300	207.9511		
Uranium-235 (pCi/L)	4/9	4/8		4.6000	53	8.1298		
Uranium-238 (pCi/L)	9/9	8/8		1.5000	1,800	246.5778		
Zinc-65 (pCi/L)	0/9	0/8		0	0	2.2444		
Zirconium-95 (pCi/L)	0/9	0/8		0	0	4.8111		

^a Analytes detected at least once are summarized. Results reflect data validation and data usability screens.

^b Background criteria have been established by *Determination of Reference Concentrations for Inorganic Analytes in Groundwater at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee* (Energy Systems 1996). The background value for an analyte varies depending upon the groundwater cluster that a well has been assigned to so no single background value applies to each analyte. Refer to Sect. C.2 and the above referenced document for a discussion of the approach to evaluating groundwater background, the groundwater background values, and the well cluster assignments.

^c Average result reflects the arithmetic mean of the dataset, assuming nondetects are equal to one-half the detection limit for chemicals. Radionuclide data qualified as nondetect based on comparison to minimal detectable activities or counting errors are set equal to the reported value.

^d No background value was available from the above referenced source. Values for lithium and titanium UTLs were calculated using data from 13 groundwater wells that were previously considered as reasonable background wells in the GWQRs (HSW 1995). The values are 0.071 mg/L for lithium and 0.12 mg/L for titanium. See text for further details. Niobium and thallium were not detected in 13 groundwater wells that were previously considered as reasonable background wells and the background UTL values was, therefore, assumed to be less than the detection limit and detected values are considered as above background.

Table 1.5. Results of analysis of water from SS-4 between March 1994 and January 1995

Analyte ^e	Freq of detect.	Bkgd criteria ^b	Detects > bkgd	Min detect	Max detect	Avg result ^c	Ecological Risk	RGOs ARAR
<i>Inorganics</i>								
Chloride (mg/L)	26/ 26	21	17/ 26	2.3	41.5	25.91		
Fluoride (mg/L)	26/ 27	0.55	2/ 27	0.2	0.6	0.3619		
Nitrate (mg/L)	26/ 27	2.7	26/ 27	3.12	67.6	31.58		
Sulfate (mg/L)	26/ 27	19	21/ 27	11.3	45	27.7		
Aluminum (mg/L)	19/ 27	2.4	1/ 27	0.028	2.98	0.3362		
Antimony (mg/L)	1/ 13	0.05	0/ 13	0.0028	0.0028	0.0010		
Barium (mg/L)	27/ 27	0.34	0/ 27	0.0545	0.24	0.1482		
Boron (mg/L)	14/ 14	0.028	13/ 14	0.015	0.26	0.1104		
Calcium (mg/L)	27/ 27	60	24/ 27	16.3	140	100.2	116	
Copper (mg/L)	4/ 27	0.012	0/ 27	0.0044	0.0066	0.0024		0.0118
Iron (mg/L)	23/ 27	4.6	0/ 27	0.035	3.72	0.4613		
Lead (mg/L)	1/ 12	0.0096	0/ 12	0.0047	0.0047	0.0022		0.0032
Lithium (mg/L)	7/ 7	^d		0.0214	0.0356	0.0293		
Magnesium (mg/L)	27/ 27	36	0/ 27	2.94	26	20.27		
Manganese (mg/L)	26/ 27	0.13	7/ 27	0.0075	0.809	0.1371	6.6	
Mercury (mg/L)	3/ 24	0.0003	0/ 24	0.0001	0.0002	0.0001	0.126	0.000012
Nickel (mg/L)	3/ 27	0.02	1/ 27	0.003	0.022	0.0048	0.015	0.158
Potassium (mg/L)	26/ 27	5	1/ 27	1.6	5.4	2.996		
Silicon (mg/L)	3/ 3	9	0/ 3	3.6	4.1	3.867		
Silver (mg/L)	1/ 27	0.006	1/ 27	0.0065	0.0065	0.0026		0.0041
Sodium (mg/L)	27/ 27	9.7	21/ 27	1.32	25	15.79		
Strontium (mg/L)	14/ 14	0.079	14/ 14	0.093	0.42	0.2329		

Table 1.5 (continued)

Analyte ^a	Freq of detect	Bkgd criteria ^b	Detects > bkgd	Min detect	Max detect	Avg result ^c	Ecological Risk	RGOs ARAR
Vanadium (mg/L)	1/ 27	0.0044	0/ 27	0.0044	0.0044	0.0019		
Zinc (mg/L)	12/ 27	0.041	0/ 27	0.0022	0.02	0.0056		
Total-Uranium (Fluorometric) (mg/L)	14/ 14	0.005	14/ 14	0.04	0.285	0.1356	0.142	
Organics								
1,1,1-Trichloroethane (µg/L)	2/ 27	.	.	1	.1	2.481		
1,1-Dichloroethene (µg/L)	3/ 27	.	.	2	3	2.574		
1,2-Dichloroethene (µg/L)	21/ 27	.	.	1	21	7.704		
Carbon disulfide (µg/L)	1/ 27	.	.	2	2	2.574		
Trichloroethene (µg/L)	26/ 27	.	.	3	23	8.759		
Radionuclides								
Alpha Activity (pCi/L)	27/ 27	.	.	15.3	130	52.94		
Beta Activity (pCi/L)	26/ 26	.	.	20.6	143	82.29		
Technetium-99 (pCi/L)	2/ 3	.	.	102	220	136.6		
Thorium-230 (pCi/L)	1/ 3	.	.	0.114	0.114	0.0581		
Uranium-233/234 (pCi/L)	13/ 13	.	.	6.76	37.3	27.26		
Uranium-235 (pCi/L)	10/ 13	.	.	1.04	3.62	1.568		
Uranium-238 (pCi/L)	13/ 13	.	.	12.2	82.6	57.59		

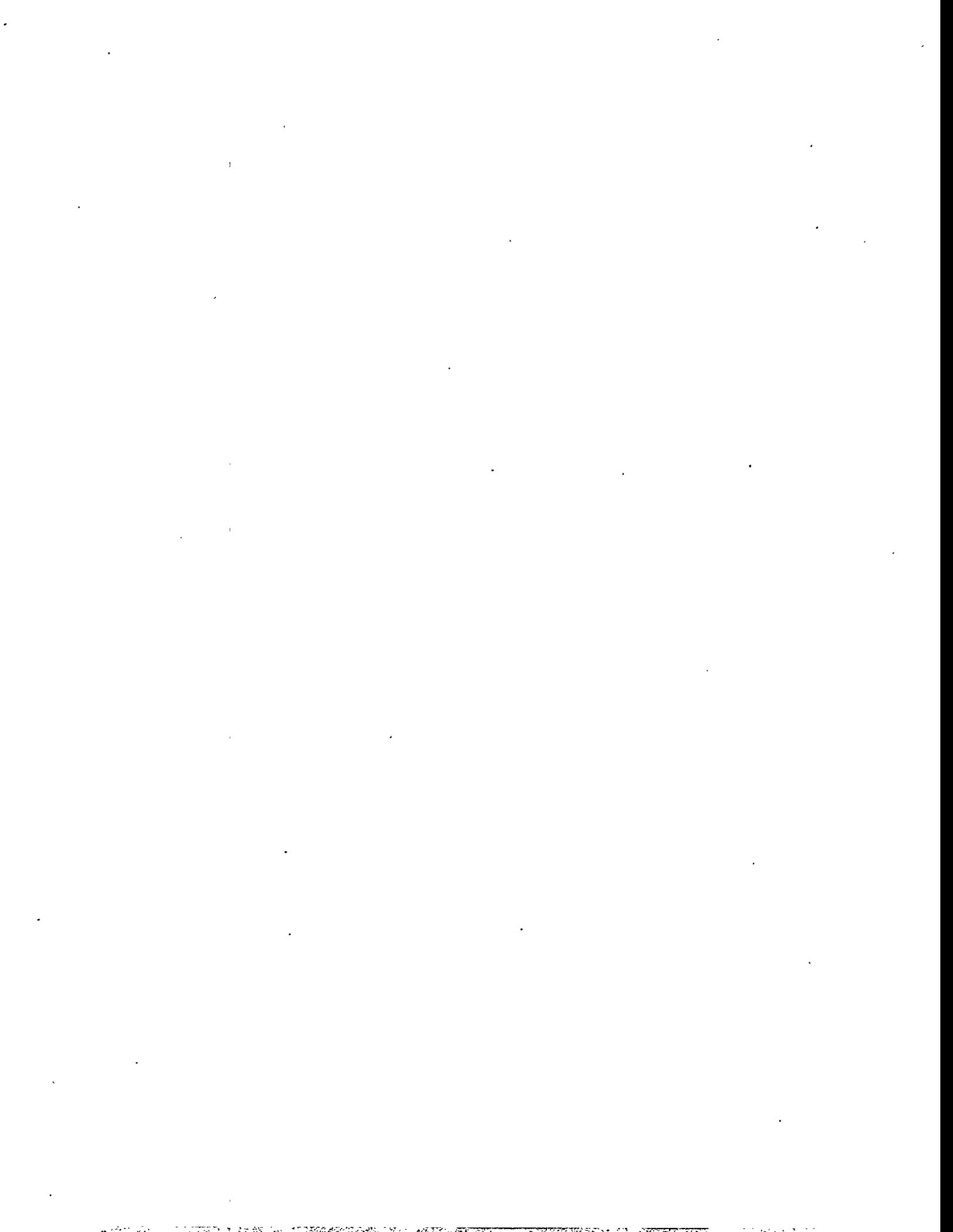
^a Analytes detected at least once are summarized. Results reflect data validation and data usability screens.

^b For springs, background criteria have been established by *Determination of Reference Concentrations for Inorganic Analytes in Groundwater at the Department of Energy Y-12 Plant, Oak Ridge, Tennessee* (Energy Systems 1996). Geochemistry of uncontaminated springs (SS-8 and SS-6) was allocated into cluster 4 in this study using the surrogate cluster analysis technique (see text). Background values from cluster 4 were therefore used as background for spring water.

^c Average result reflects the arithmetic mean of the dataset, assuming non-detects are equal to one-half the detection limit for chemicals. Radionuclide data qualified as non-detect based on comparison to minimal detectable activities or counting errors are set equal to the reported value.

^d No background value for lithium was available from NT-13 (Energy Systems 1996). The value of the lithium UTI was calculated using data from 13 groundwater wells that were previously considered as reasonable background wells in the GWQRs (HSW 1995) and is 0.071 mg/L. These data were used as background for surface water as the best available data that represent background for lithium in BCV. See text for further details.

In addition, because surface water in Bear Creek recharges groundwater in the Maynardville Limestone, where possible, RGOs for groundwater will be achieved in surface water to be protective of downstream groundwater. A list of groundwater RGOs from the RI Report is also included in Appendix H.



2. FIELD CHARACTERIZATION

2.1 INTRODUCTION

To successfully complete the treatability study, it is important to understand both the in situ chemical characteristics of the water to be treated and the hydraulics of the collection system. Field characterization activity was used to develop a database needed to understand the nature and extent of groundwater and surface water contamination and its effects on in situ treatment technologies. Geochemical data and the impact of seasonal fluctuation will be critical to successful system design. Appendix A presents the field characterization activities in Phase I.

2.2 OBJECTIVES

The field characterization activity was designed to provide site-specific data related to the flow of contaminants through the unconsolidated zone and to determine the impact of these flowpaths on the tributaries under low- and high-flow conditions.

The objectives of the field activities included the following:

- determine the discrete locations where contaminants are entering Bear Creek main stem, NT-1, and NT-2, the surface water quality at these locations, and the temporal changes in surface water flow and water quality;
- determine subsurface geologic, hydraulic, and geochemical conditions where contaminants are entering Bear Creek, NT-1, and -2, such as determining depth to bedrock, hydraulic conductivity, gradients, porosity, probable variations of groundwater inflow rates to the tributaries, spatial and temporal groundwater quality variations, and impact of storm events and seasons on groundwater flow and quality (i.e., evaluate shallow stormflow impact); and
- obtain representative groundwater samples from BYBY and S-3 Plume (NT-1) for the principal investigators to test during Phase I laboratory work.

2.3 APPROACH

The investigation approach of the site characterization was designed to determine the following (SAIC 1996b):

- Locate the discrete points of groundwater discharge in tributaries NT-1 and NT-2 and Bear Creek adjacent to the S-3 Site through surface water sample collection and screening.
- Determine contaminant geochemistry of surface water and selected seeps along these reaches.
- Analyze groundwater field parameters near discharge points, and identify locations of groundwater contaminant pathways.

- Provide site-specific groundwater and geotechnical data for the Phase I laboratory testing of potential treatment media.
- Obtain sufficient data on site hydrogeology to support Phase I laboratory testing and Phase III location selection of the groundwater capture and treatment trench.

2.4 RESULTS

2.4.1 Surface Water Field Screenings

Surface water grab samples were collected at 73 locations to locate the discrete points of groundwater discharge along reaches of NT-1, NT-2, and Bear Creek. Recognition of seepage areas was done visually (by noting obvious wet areas) and by observing trends in field measurements. In stream changes in conductivity, nitrate, and pH consistently marked the impact of visible seep locations (Fig. 2.1).

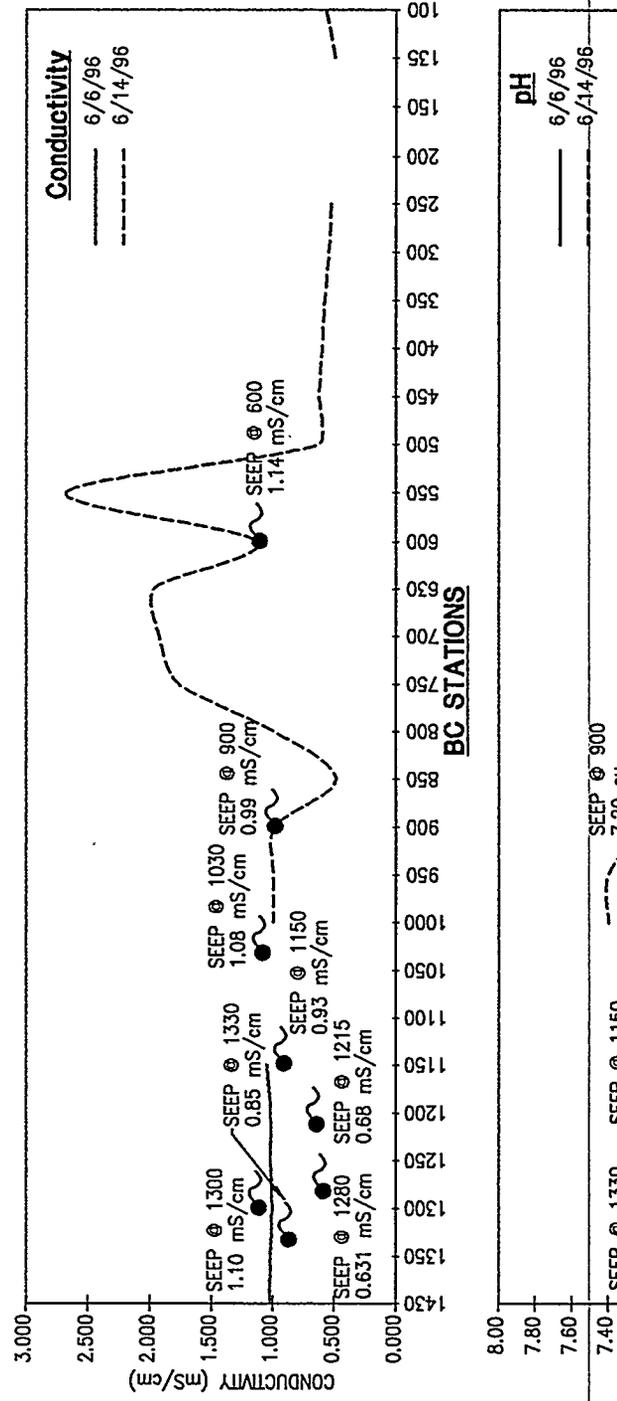
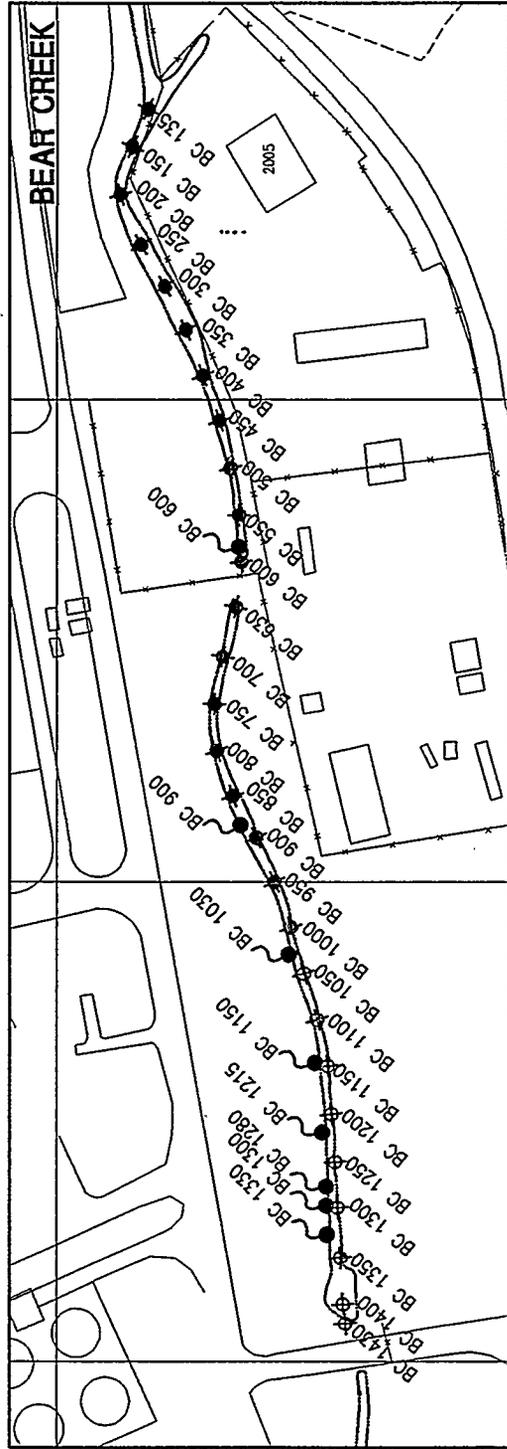
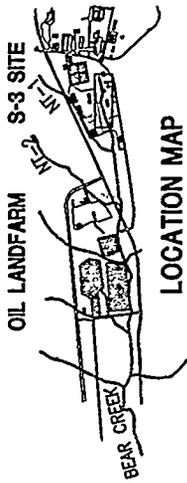
Surface water (seep) samples were collected from the most active or significant seeps based on the results of field screening. These samples were analyzed for: volatile organics, inductively coupled plasma (ICP) metals, radiochemistry (including fluorimetric uranium and tritium), anions, alkalinity, mercury, bicarbonate, and total dissolved solids/total suspended solids (TDS/TSS).

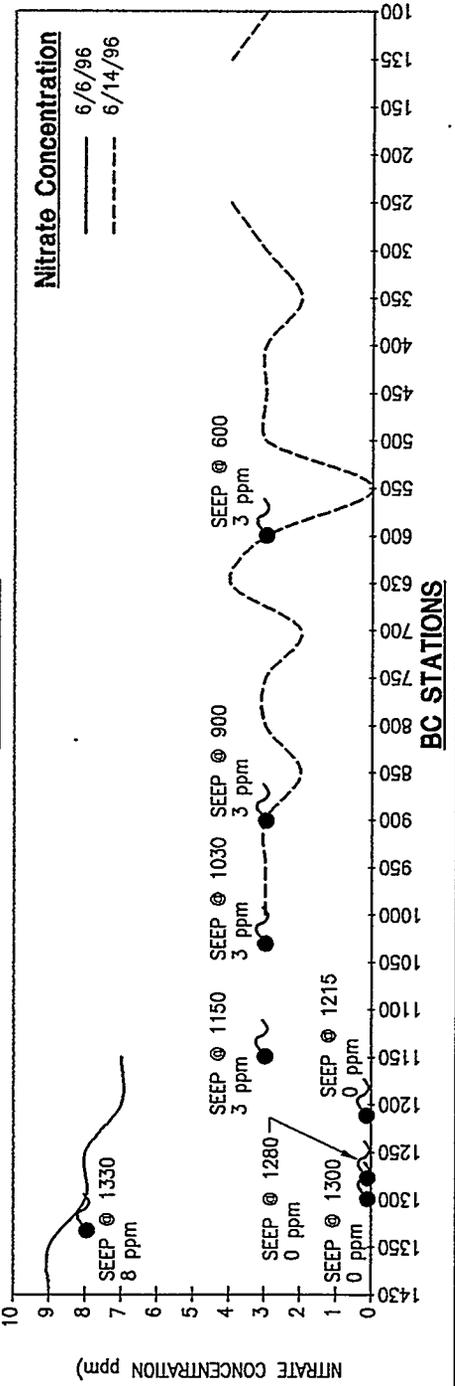
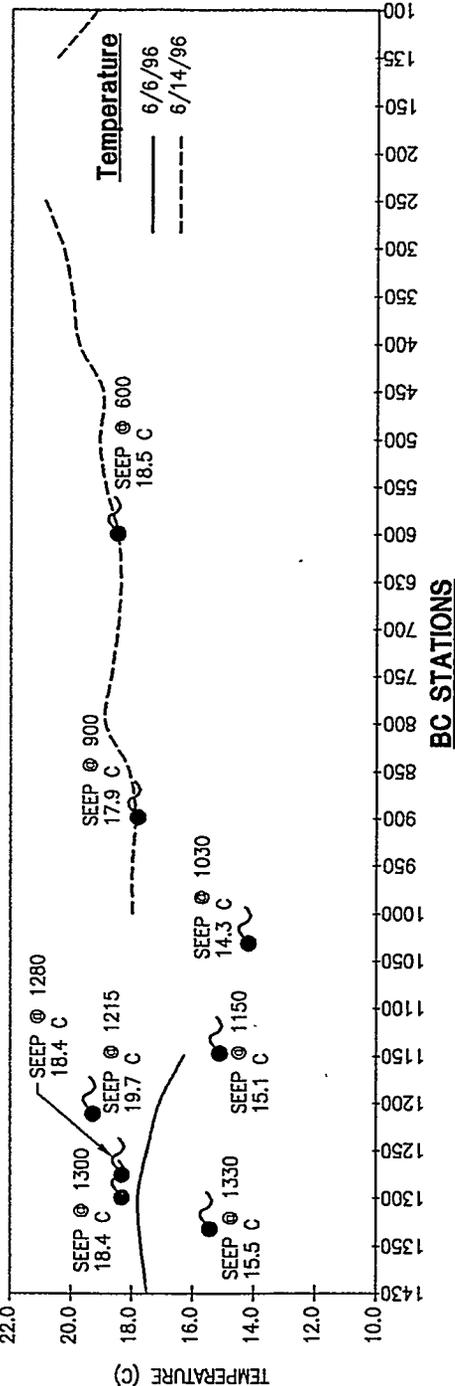
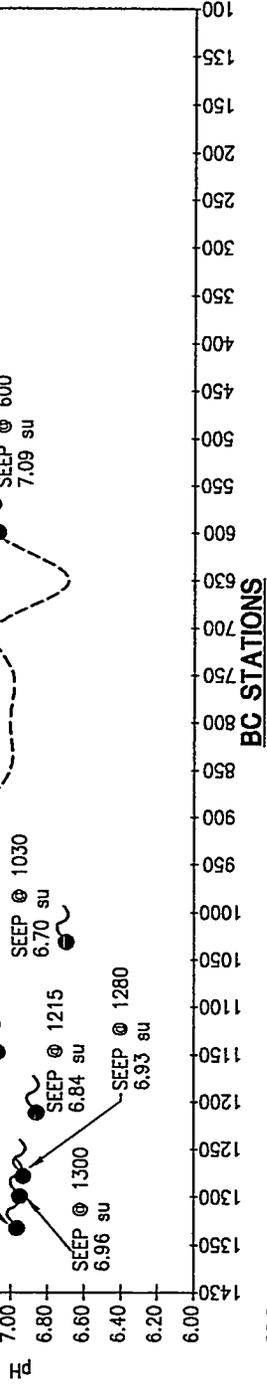
The following information summarizes observations by location:

Bear Creek

- Eight seeps were identified along Bear Creek: BC 600, BC 900, BC 1030, BC 1150, BC 1215, BC 1280, BC 1300, and BC 1330. During summer baseflow (June 6, 1996), stream flow began at Station 1030 (Fig. 2). Following a period of rain prior to June 14, 1996, water was present in the previously dry reach of Bear Creek upstream of Station BC 1030 (summer high flow) and allowed identification of seeps at BC 600 and BC 900.
- In-stream values for pH (7.0 to 7.4) and temperature (16° to 19°C) were similar along the reaches of upper Bear Creek sampled during high and low flow periods. A short reach with significantly higher specific conductivity water was observed between Stations BC 500 and 750 during the high flow period measured on June 14, 1996 (Fig. 2). In-stream values for specific conductance outside this short reach were similar during high and low flow periods (~1.0 mS/cm M).
- In-stream nitrate concentrations were 2 to 3 times higher in the low flow period compared to the high flow period.
- Identified seeps upstream of BC 1030 (summer high flow period only) generally had screening values similar to adjacent in-stream values for specific conductance, pH, and temperature. Identified seeps downstream of and including BC 1030 (summer low flow period only) fit two patterns compared with adjacent in-stream values: (1) similar nitrate concentrations and lower temperature (BC 1030, 1150, and 1330) and (2) nondetectable

Y-12 PLANT NORTH





PROJECT NO.	96030		BEAR CREEK VALLEY S-3 AREA
DRAWING NO.	/DWGS/525BCV.DWG		
REVISION DATE	REV. 1 / 11-18-96		
XREF. FILES	94020/XREF/XRBCV14	LEGEND: ROADS BEAR CREEK & TRIBUTARIES TRIBUTARIES SAMPLE STATIONS ⊕ 1300 STREAM (6/6/96) ⊕ 1300 STREAM (6/14/96) ● BC 900 SEEP	

Fig. 2.1. Bear Creek surface water sample locations and field screening results.

nitrate concentrations and slightly higher temperature (BC 1215, 1280, and 1300). For seeps below BC 1030, pH values were generally lower than in-stream values.

- Uranium concentrations in seeps upstream of BC 1030 (high flow period) were 2 to 3 times higher than those seeps downstream of and including BC 1030 (low flow period).

No single seep can account for uranium contamination in upper Bear Creek. Contamination is likely derived from more diffuse seepage of groundwater into the channel of Bear Creek above BCK 12.46. Identifiable seeps may define the discharge points of preferential groundwater flow path(s). The occurrence of a groundwater discharge point adjacent to the location where dry weather flow starts in Bear Creek may indicate that this seepage area (BC 1030) is connected to this pathway(s).

NT-1

- Three active seeps were identified in NT-1: NT1 075, NT1 200, and NT1 390.
- Seeps at NT-1 are characterized by higher specific conductivity and nitrate concentrations and lower pH compared to adjacent in-stream values (Fig. 2.2).
- The in-stream concentration of nitrate increases downstream from ~10 ppm at NT1 500 to >50 ppm at NT1 250 where the concentration exceeded the upper limit of the in-field analytical method (50 ppm). Concentrations of nitrate at seeps NT1 200 and NT1 390 measured in the laboratory were 1800 and 720 ppm, respectively (September 19, 1996). The concentration of nitrate and the specific conductance at seep NT1 390 varied between sampling events (June 4 and September 19, 1996): nitrate concentration increased from 20 to 720 ppm and specific conductance increased from 1.07 to 17.4 mS/cm.
- Coincident with the increase of nitrate concentration, pH of in-stream flow decreases downstream from NT1 390. This is consistent with the additive discharge of groundwater with lower pH from the seeps to NT-1 along this reach.
- Conductivity measured while collecting a surface water sample at Station NT1 390 on September 19, 1996, was significantly higher (17.4 mS/cm) than during the Task 1 field screenings on June 4, 1996 (1.07 mS/cm). The only other surface water sample location with higher measured conductivity was Station NT1 075 (22.3 mS/cm).

No single seep can account for contamination observed in NT-1. However, NT-1 is contaminated by discharge from a zone extending from ~NT1 500 to NT1 50. Within this zone, identifiable seeps are located at sites with higher flux of groundwater discharge (NT1 75, 200, and 390) and may indicate preferential groundwater flow paths. These seeps probably account for a large proportion of the total contaminant influx into NT-1.

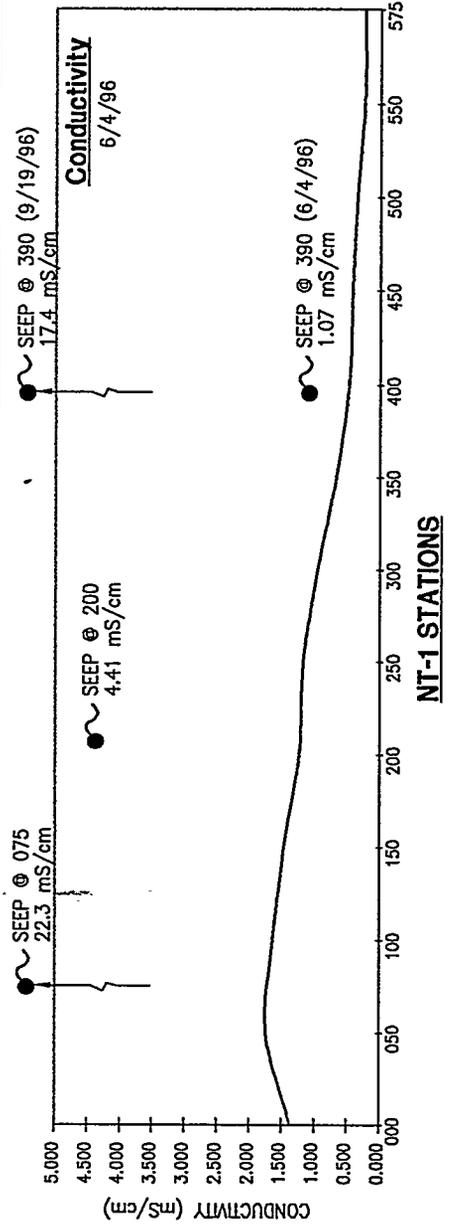
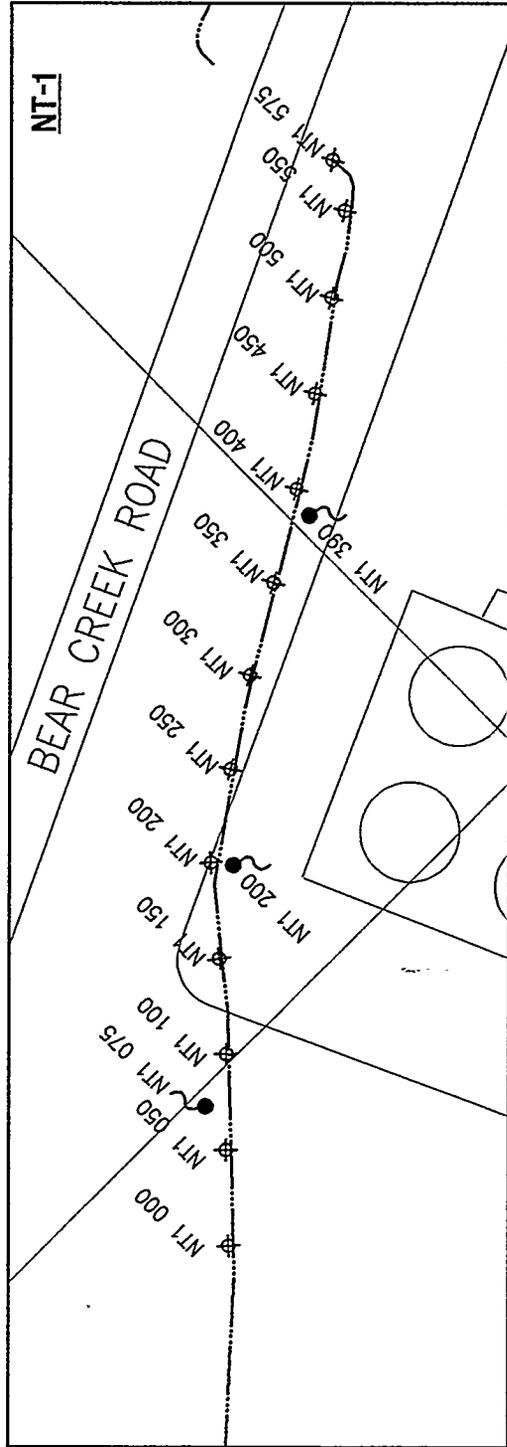
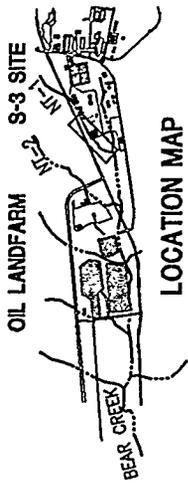
NT-2

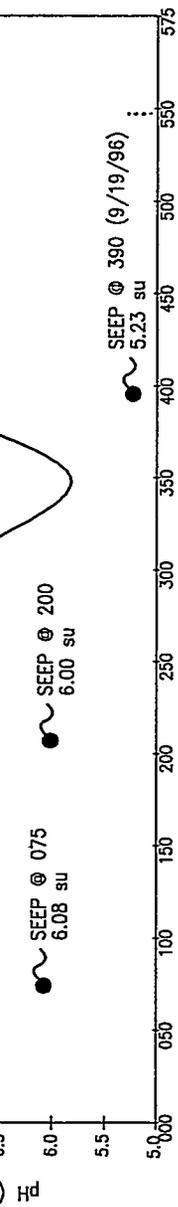
- Two active seeps were identified in NT-2: NT2 645 and NT2 970.

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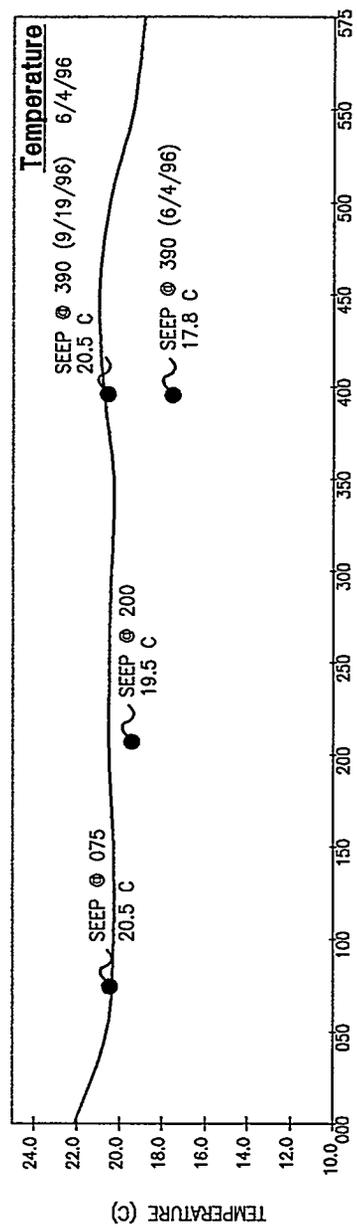
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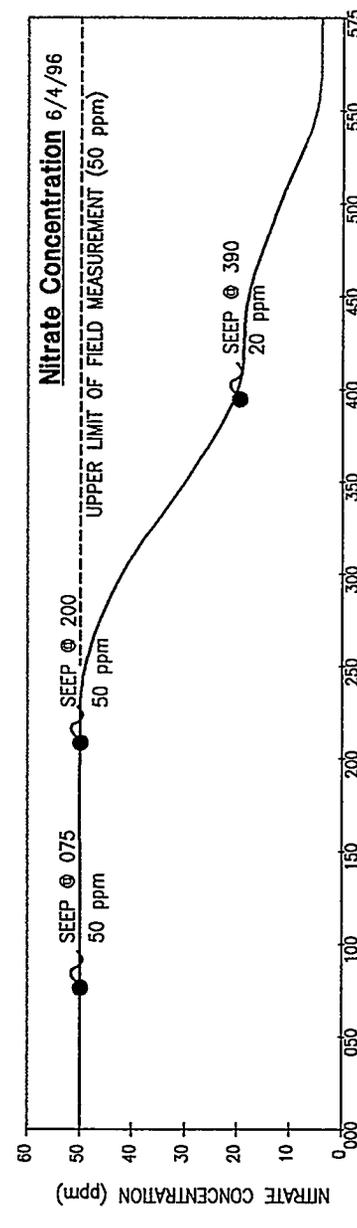




NT-1 STATIONS



NT-1 STATIONS



NT-1 STATIONS

PROJECT NO.	96030		NORTH TRIBUTARY 1 BEAR CREEK VALLEY
DRAWING NO.	/DWGS/525NT1.DWG		
REVISION DATE	REV. 0 09/24/96		
XREF. FILES	94020/XREF/XRBCV14		

LEGEND:

- ROADS
- BEAR CREEK & TRIBUTARIES
- SAMPLE STATIONS
- ⊕ NT1 150 STREAM
- NT1 075SEEP

Fig. 2.2. North Tributary 1 (NT-1) surface water sample locations and field screening results.

- Seeps at NT-2 are characterized by higher conductivity and nitrate concentrations and lower pH compared to values measured in the adjacent stream (Fig. 2.3).
- The in-stream nitrate concentration increases from <20 ppm to >50 ppm between NT2 1000 and NT2 950. This is coincident with the seep at NT2 970 which had nitrate concentration of 1000 ppm on September 12, 1996.

No single seep can account for contamination observed in NT-2. However, this stream is contaminated by discharge from a zone extending from ~NT2 645 to NT2 970. Within this zone, two identifiable seeps are located at sites with higher flux of groundwater discharge (NT2 645 and 970) and indicate preferential groundwater flow paths. Of these two seeps, NT2 970 appears to account for the largest proportion of the total contaminant influx into NT-2.

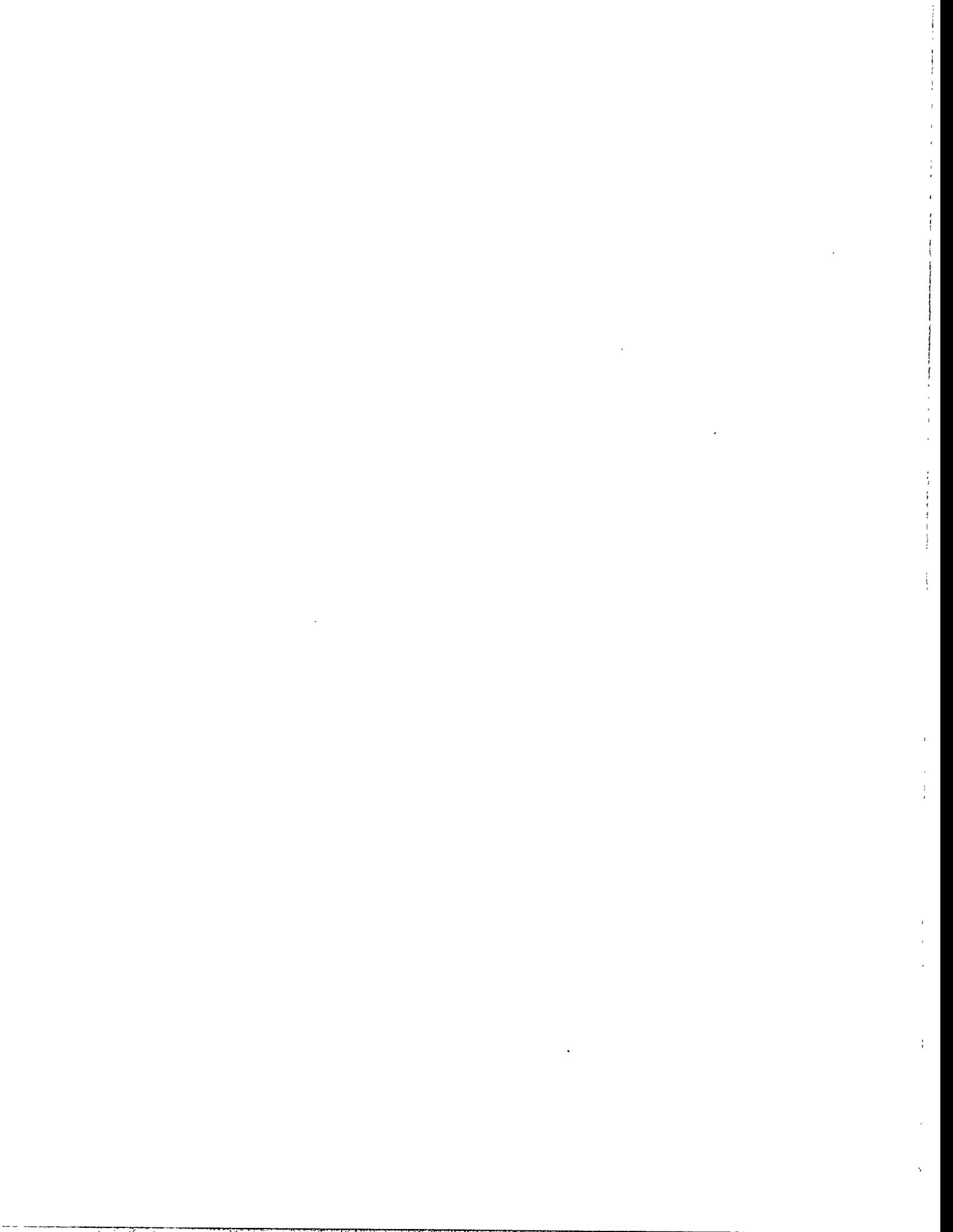
2.4.2 Piezometer Installation and Groundwater Sampling

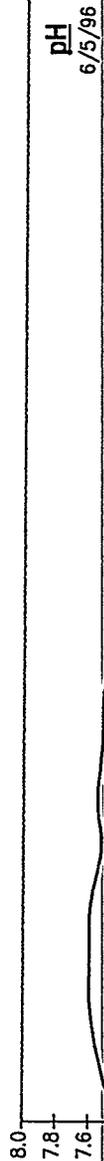
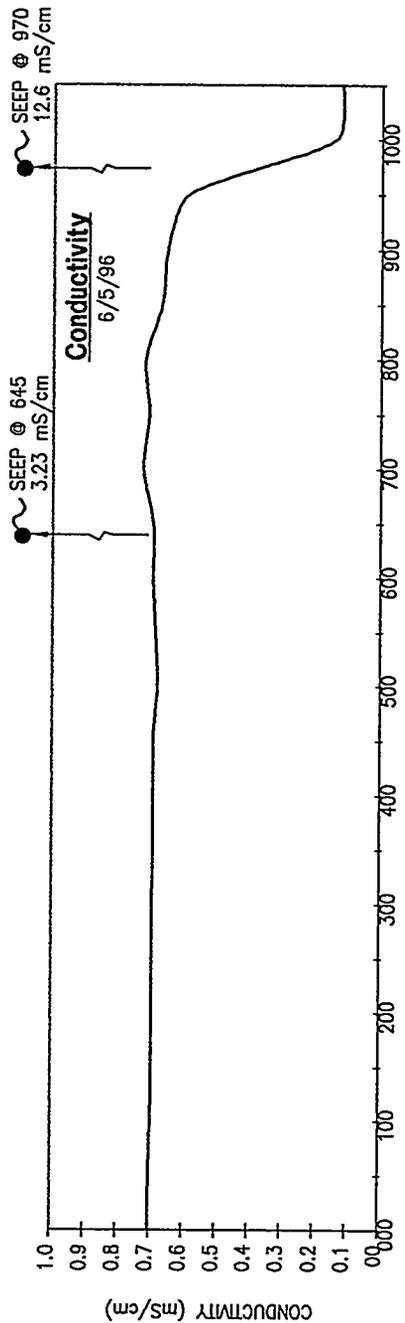
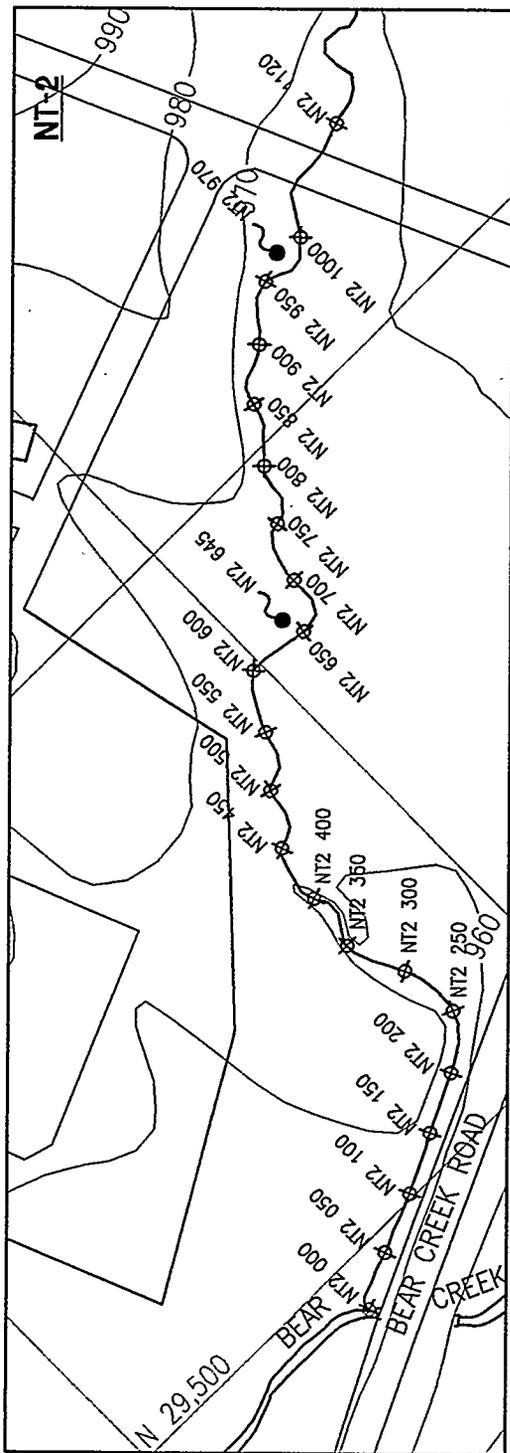
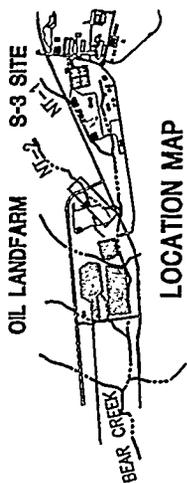
To identify groundwater contaminant pathways, temporary piezometers were installed at locations of active groundwater discharge recognized in the previous tasks. To provide the initial delineation, 25 temporary piezometers were installed using push probe (Geoprobe) drilling methods (TPB-01, -02, -04 through -06, and -08 through -27) (Fig. 2.4). Data gathered from samples of these wells were used to locate four augered piezometers (GW 834-837, Fig. 2.5). These temporary piezometers were placed to intercept active contaminated groundwater flow identified from results of the first phase.

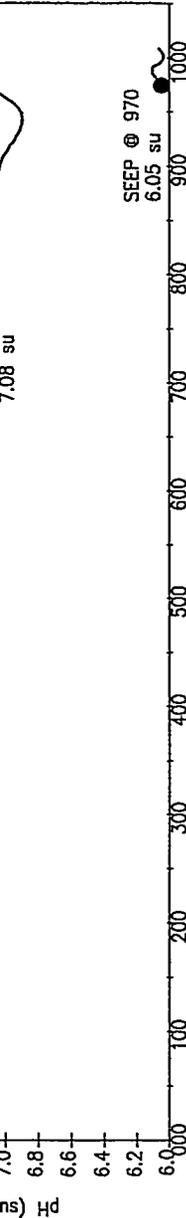
To better delineate groundwater contaminant pathways, four additional temporary piezometers were installed at the end of the second phase using push probe (air hammer) techniques. The locations of these additional piezometers are shown on Fig. 2.5 (TPB-28 through -31). Samples collected from these wells were analyzed for the same parameters as the previous wells.

Screening results of groundwater from the temporary push-probe piezometers were consistent with the screening results from the active seeps (groundwater discharge points) recognized during the surface water screenings. By using a staged approach in installing these piezometers, locations of groundwater contaminant pathways during the summer baseflow period have been delineated. Three principal migration pathways have been identified and are shown in Fig. 11. The screening results from push probe piezometers characterizing these pathways are summarized below:

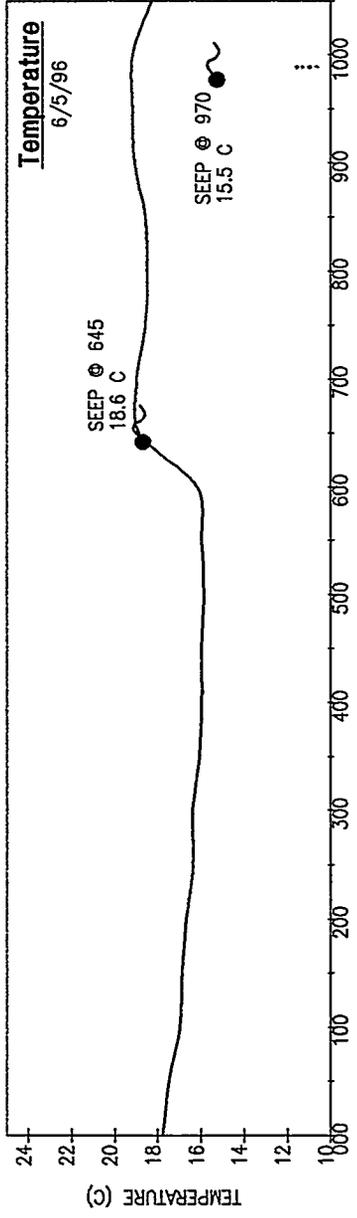
- Migration pathway 1:** to Bear Creek south of the S-3 site; shown in TPB-09 and TPB-19 by elevated conductivity, nitrate concentrations, uranium concentrations, and gross alpha and beta activity and by a decrease in pH.
- Migration pathway 2:** to Bear Creek through the area where TPB-07, -08, -15, and -16 are located; shown by elevated uranium concentrations and gross alpha and beta activity in these piezometers. Nitrate concentrations in these piezometers were not elevated.



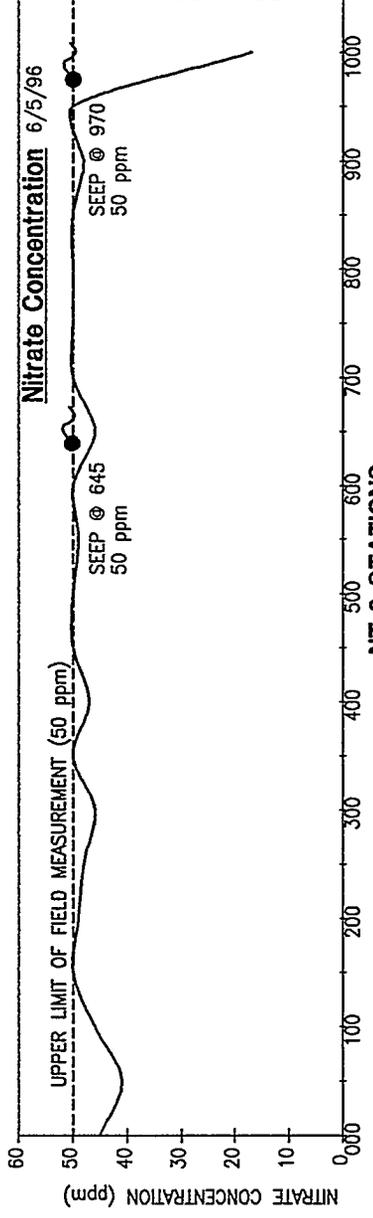




NT-2 STATIONS



NT-2 STATIONS



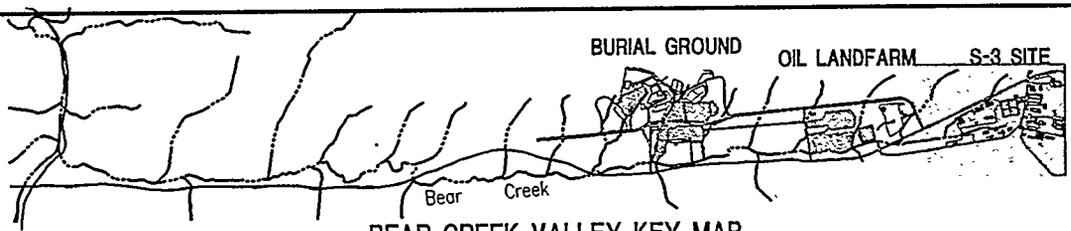
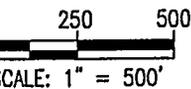
NT-2 STATIONS

PROJECT NO.	94020		<p>NORTH TRIBUTARY 2 BEAR CREEK VALLEY</p>
DRAWING NO.	/DWGS/525NT2.DWG		
REVISION DATE	REV. 0 09/24/96		
XREF. FILES	94020/XREF/RRBCV14		

LEGEND:

- ROADS
- BEAR CREEK & TRIBUTARIES
- SAMPLE STATIONS
- ⊕ NT2 150STREAM
- NT2 970SEEP

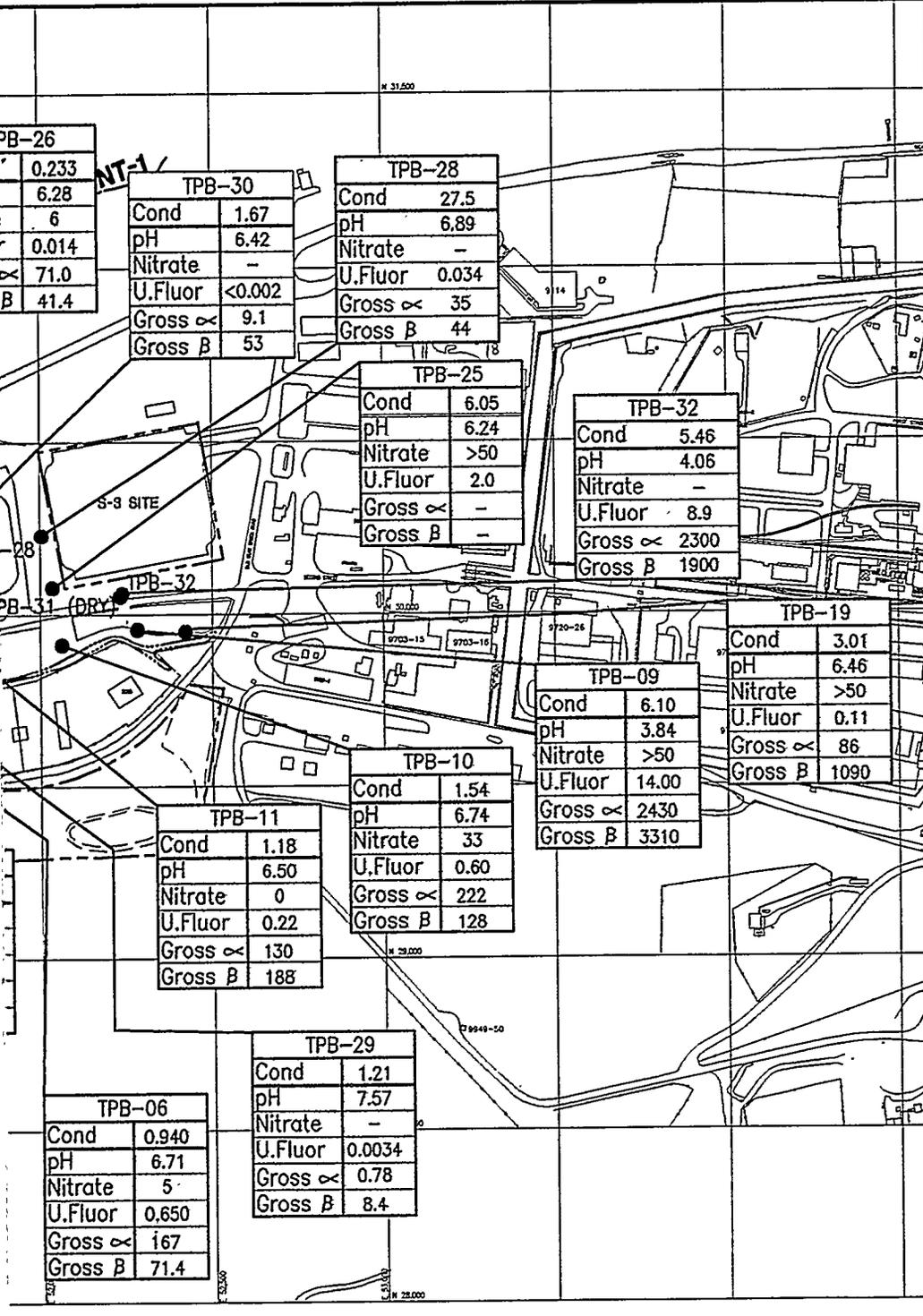
Fig. 2.3. North Tributary 2 (NT-2) surface water sample locations and field screening results.



BEAR CREEK VALLEY KEY MAP

LEGEND:

- ROADS
- BEAR CREEK & TRIBUTARIES
- WASTE AREA BOUNDARY



TPB-19	
Conductivity	mS/cm
pH	
Nitrate	ppm
Total Uranium Fluorimetric	ppm
Gross α	pCi/L
Gross β	pCi/L

TPB-19	
Conductivity	3.01
pH	6.46
Nitrate	>50
U.Fluor	0.11
Gross α	86
Gross β	1090



PROJECT NO.	96030
DRAWING NO.	/DWGS/525_TB1.DWG
REVISION DATE	REV. A 12/31/96
XREF. FILES	94020/XREF/XRBCV11, XRBCV12, XRBCV13, XRBCV14, XRBCV15

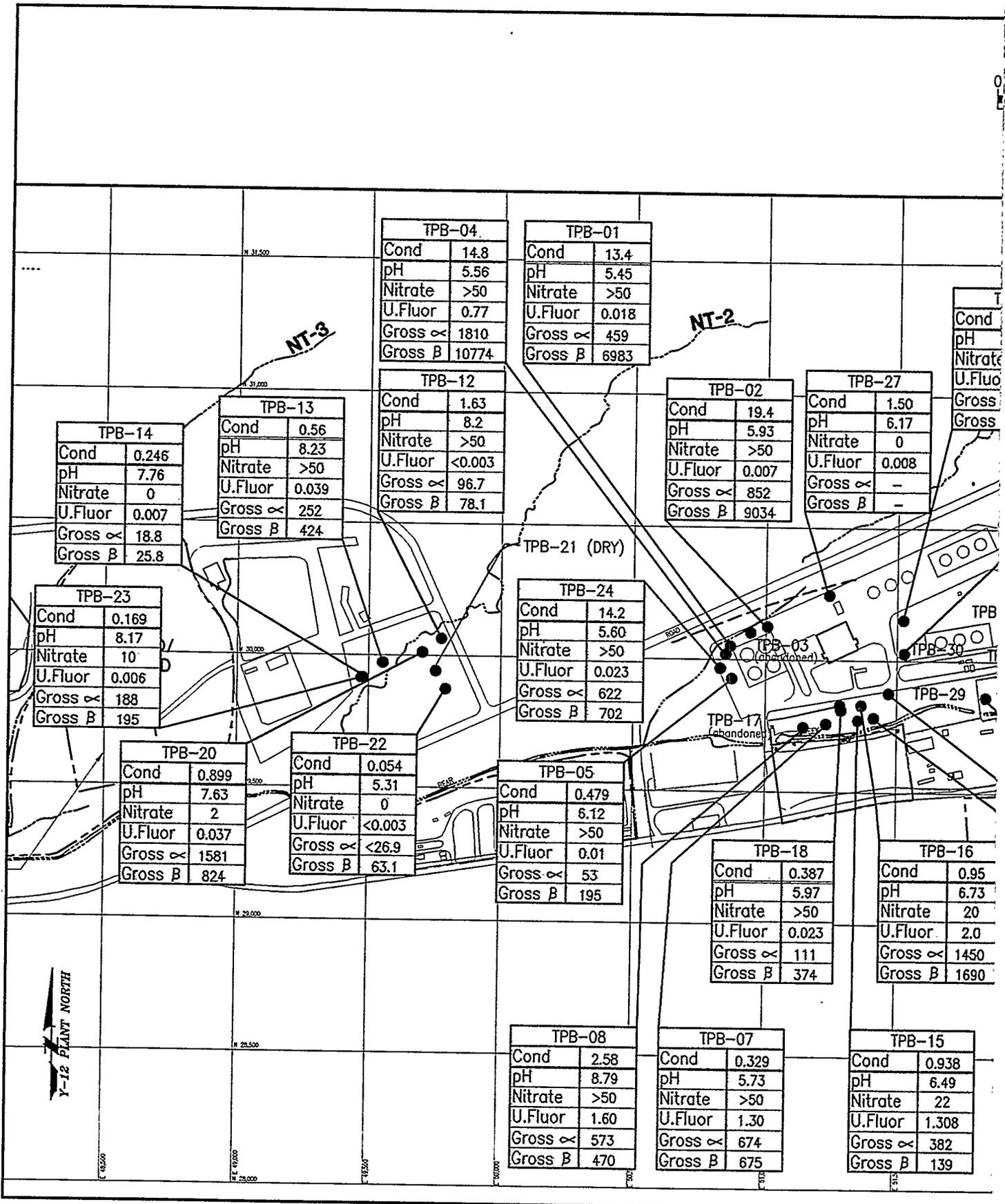


Fig. 2.4. S-3 Area Local

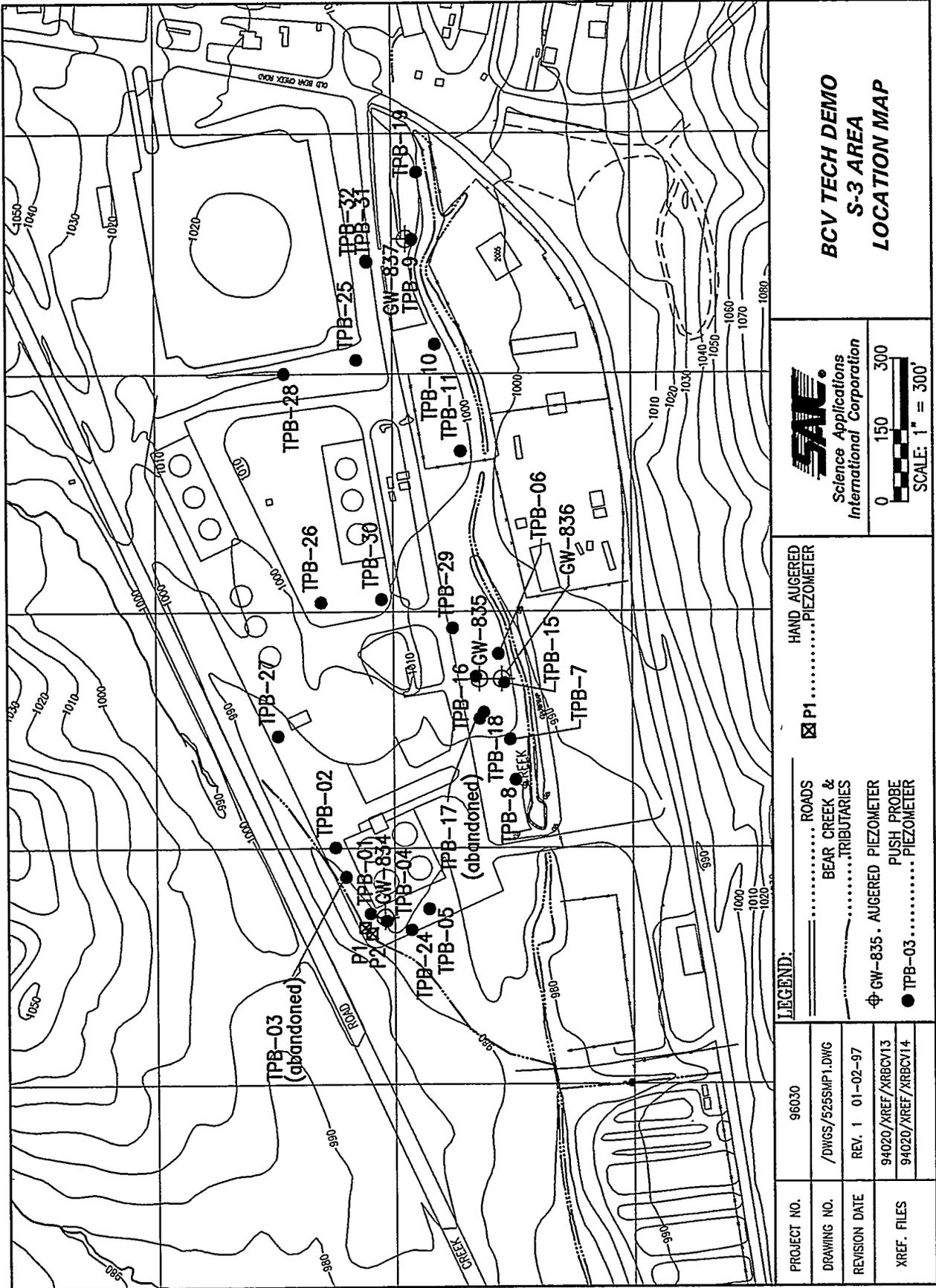


Fig. 2.5. BCV treatability study S-3 area location map.

Migration pathway 3: along NT-1 and extending to NT-2; shown by elevated conductivity, nitrate concentrations, and gross alpha and beta activity in TPB-01, -02, -04, and -24. Uranium concentrations are relatively low overall. This pathway also discharges to NT-2 further along stratigraphic strike. At NT-2, it is characterized by elevated conductivity in Piezometer TPB-12 and elevated gross alpha and beta activity in Piezometers TPB-13 and -20.

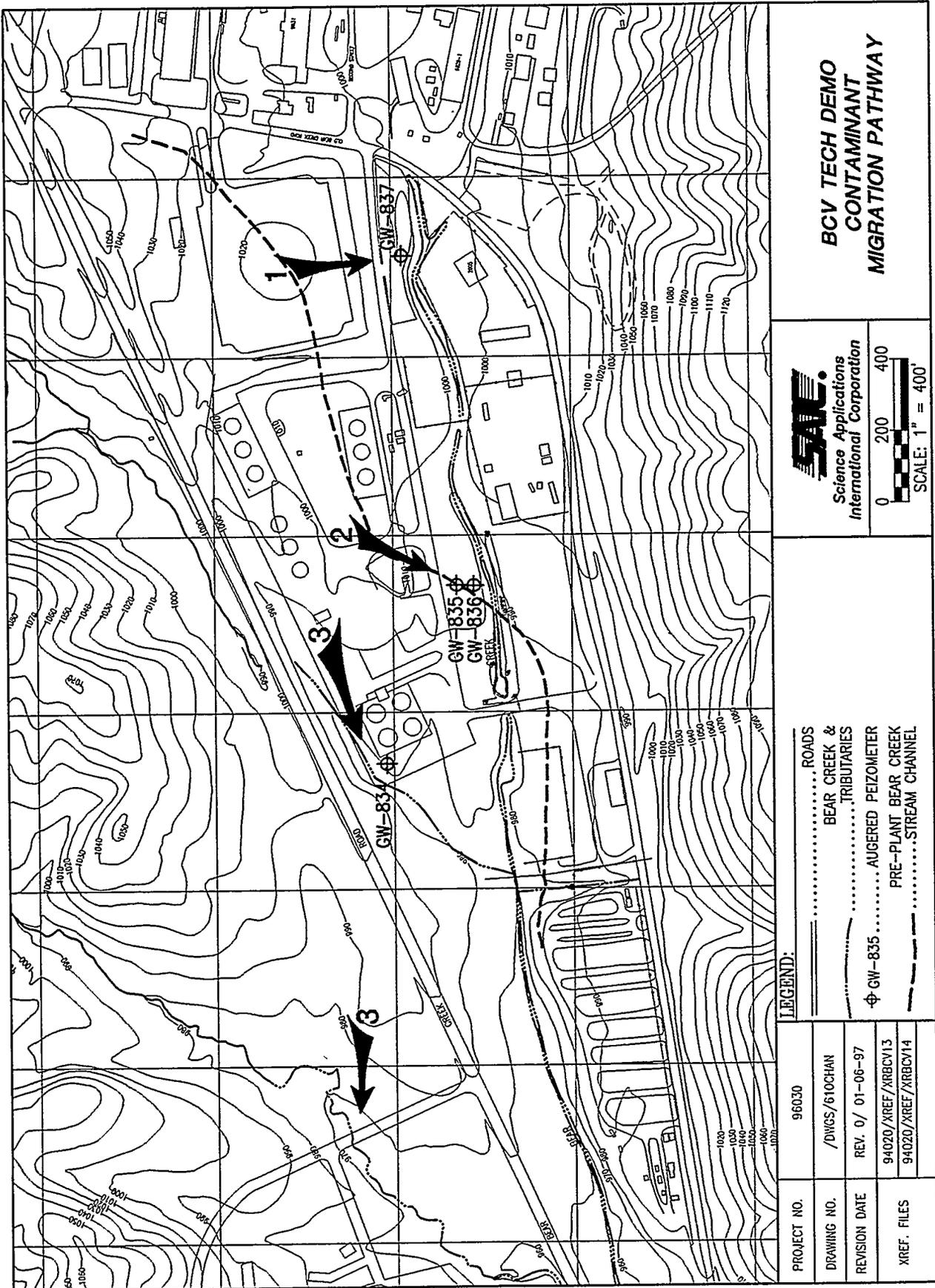
Augered piezometers are located within one of the three contaminant pathways recognized along NT-1 and Bear Creek (Fig. 2.6). An evaluation of the analytical results of groundwater collected from the augered piezometers GW-834, -835, and -837 shows the values to be consistent with the push-probe piezometers field screening results. The analytical results are summarized in Table 2.1.

2.4.3 Hydraulic Testing

A pumping test was conducted at GW-835 to assess the potential for this piezometer to provide continuous flow needed to complete Phase II media testing. Prior to this test, water levels in the observation piezometers were monitored for one week (Fig. 2.7). GW-835 was pumped at a rate of ~6 L/min for 9 hours and drawdown was observed in only one piezometer, TPB-18. Based on the results observed, the following conclusions were made (refer to Appendix B for details):

- GW-835 may be capable of producing groundwater at the rate of up to 6 L/min based on the relatively constant water level observed in the piezometer following initial drawdown.
- The screened interval in GW-835 appears to be connected to a highly transmissive zone or interval. The groundwater discharge rate into GW-835 during the test was relatively high and recovery of the water level to pre-test level at termination of the test was very rapid (~5 mins).
- GW-835 is completed in an interval that is probably not in direct hydraulic connection with the observation piezometers. This was shown by the lack of significant change in water levels in the observation piezometers during the test.
- There was little chemical variation in the groundwater collected during the test.

Historical information may explain the heterogeneous nature of the unconsolidated zone in the vicinity of the pumping test. Surface water drainage patterns were altered due to activities at the Y-12 Plant and, specifically, construction of the S-3 Ponds (Sutton 1995). Interpretation of preconstruction aerial photographs shows a section of the original stream channel of Bear Creek to be north of the present channel (Fig. 2.6). The S-3 Ponds appear to have been constructed over this filled stream channel. The stream channel continued to the southwest from this point and through the site of the pumping test. This trend appears to agree with the interpreted trend of contaminant migration pathway 2. The trace of the original channel then intersects the current channel of Bear Creek in the vicinity of stream flow initiation observed during the summer baseflow period.



**BCV TECH DEMO
CONTAMINANT
MIGRATION PATHWAY**

SAC.
Science Applications
International Corporation

0 200 400
SCALE: 1" = 400'

PROJECT NO.	96030
DRAWING NO.	/DWGS/610CHAN
REVISION DATE	REV. 0/ 01-06-97
XREF. FILES	94020/XREF/XRBCV13
	94020/XREF/XRBCV14

Fig. 2.6. Contaminant migration pathways.

Table 2.1. Survey coordinates of sample locations Y-12 Plant grid

Location ID	East coordinate	North coordinate	Surface elevation (ft-AMSL)	TOC elevation (ft-AMSL)
GW-834	50855.00	30020.30	991.93	995.04
GW-835	51358.36	29822.02	997.94	1000.91
GW-836	51356.24	29774.56	997.97	1001.00
GW-837	52281.57	29969.06	1005.22	1007.96
TPB-01	50862.26	30050.68	990.33	994.12
TPB-02	51002.32	30123.76	991.72	995.00
TPB-04	50846.69	30017.36	990.30	992.35
TPB-05	50872.25	29928.39	991.20	994.33
TPB-06	51410.93	29781.15	998.17	1000.28
TPB-7	51229.86	29757.29	996.63	999.48
TPB-8	51144.29	29745.83	988.87	991.64
TPB-9	52281.32	29958.44	1004.51	1006.78
TPB-10	52062.66	29911.55	1005.04	1007.16
TPB-11	51838.90	29858.65	1003.08	1005.53
TPB-12	49773.83	30063.55	975.63	978.82
TPB-13	49551.56	29970.97	969.94	972.73
TPB-14	49478.25	29912.20	971.70	973.73
TPB-15	51349.84	29768.96	997.91	1000.27
TPB-16	51363.03	29828.61	998.21	999.44
TPB-18	51286.82	29812.18	997.30	999.97
TPB-19	52420.49	29948.10	1001.36	1004.01
TPB-20	49702.40	30009.87	975.75	978.33
TPB-21	49752.14	29940.63	980.97	983.44
TPB-22	49791.72	29873.18	980.13	982.51
TPB-23	49471.15	29914.63	972.76	975.00
TPB-24	50827.71	29965.39	991.53	994.34
TPB-25	52029.77	30074.96	1007.68	1009.03
TPB-26	51520.13	30151.23	1000.36	1003.21
TPB-27	51237.66	30244.31	998.72	1001.49
TPB-28	52001.47	30228.20	1010.69	1012.76

Table 2.1 (continued)

Location ID	East coordinate	North coordinate	Surface elevation (ft-AMSL)	TOC elevation (ft-AMSL)
TPB-29	51465.49	29876.85	999.88	1003.11
TPB-30	51526.39	30024.42	1000.06	1003.72
TPB-31	52234.25	30052.04	1007.42	1011.00
TPB-32	52236.31	30053.34	1007.29	1010.35
BC-135	52261.33	29923.70	996.53	NA
BC-200	52240.08	29933.36	996.45	NA
BC-300	52162.31	29907.52	995.34	NA
BC-400	52071.93	29875.86	996.47	NA
BC-500	51968.83	29838.67	995.75	NA
BC-600	51867.33	29824.86	996.18	NA
BC-700	51730.22	29835.68	993.34	NA
BC-800	51664.16	29851.77	991.97	NA
BC-900	51568.14	29805.42	989.50	NA
BC-1000	51486.31	29769.34	988.55	NA
BC-1030	51413.51	29756.01	986.95	NA
BC-1100	51395.34	29753.24	986.50	NA
BC-1200	51278.20	29717.51	982.42	NA
BC-1300	51175.68	29704.18	981.37	NA
BC-1400	51080.55	29706.77	978.81	NA
NT1-000	50684.39	29892.57	977.70	NA
NT1-075	50735.25	29964.66	977.44	NA
NT1-100	50768.49	29962.8	978.63	NA
NT1-200	50813.92	30054.54	978.90	NA
NT1-300	50912.64	30105.66	980.37	NA
NT1-390	50993.64	30143.47	982.71	NA
NT1-400	51002.03	30159.45	982.65	NA
NT1-500	51086.34	30222.79	985.40	NA
NT1-575	51145.17	30275.04	989.48	NA
NT2-000	49204.42	29474.25	958.46	NA

Table 2.1 (continued)

Location ID	East coordinate	North coordinate	Surface elevation (ft-AMSL)	TOC elevation (ft-AMSL)
NT2-100	49310.73	29519.52	959.06	NA
NT2-200	49385.56	29551.56	959.63	NA
NT2-300	49425.94	29632.27	961.61	NA
NT2-400	49412.26	29715.58	962.51	NA
NT2-500	49441.54	29794.90	962.85	NA
NT2-600	49484.70	29859.36	963.31	
NT2-645	49510.40	29896.11	963.98	
NT2-700	49572.13	29881.54	964.97	NA
NT2-800	49607.18	29971.78	965.29	NA
NT2-900	49656.14	30045.32	967.94	NA
NT2-970	49717.68	30092.01	967.88	NA
NT2-1000	49746.42	30094.82	968.01	NA
NT2-1120	49878.94	30154.55	969.96	NA

It is possible that GW-835 was completed within the original stream channel. Associated fluvial lag deposits and/or coarse fill material could provide the observed interval of high hydraulic transmissivity. Confinement of this relatively high transmissive interval within the original stream channel boundaries could also explain the heterogeneous nature and the lack of response in the observation piezometers located outside the boundaries.

2.5 CONCLUSIONS

Field characterization efforts have delineated three primary pathways for contaminated groundwater at the S-3 Site to discharge to surface water (Fig. 2.6):

- Two pathways were identified for uranium-contaminated groundwater to the main stem of Bear Creek adjacent to the former S-3 Ponds. These two pathways were characterized by 4 in. piezometers and are named the GW-835 and GW-837 sites. Groundwater in the shallow pathway to Bear Creek closest to S-3 ponds (GW-837) also is contaminated with nitrate, ^{99}Tc , and some elevated levels of metals, and groundwater in GW-835 is primarily contaminated with uranium.
- One deeper pathway was identified along strike flow path for uranium, nitrate, PCE, ^{99}Tc , metals, and high TDS contaminated groundwater to NT-1. This deeper along strike flow path extends to NT-2 although, at NT-2, the contaminants are predominantly nitrate, elevated TDS, metals, VOCs, and ^{99}Tc .

Permeability and groundwater flow rates in these pathways have not been defined; however, piezometers located in the two pathways for uranium to Bear Creek showed lower than expected drawdown during well development indicating that these zones may have relatively higher permeability than the surrounding formation. Single well pumping tests have shown that GW-835 can sustain a pumping rate of up to 6 L/min, whereas GW-837 can only sustain 60 mL/min, and GW-834 a 100 mL/min pumping rate. GW-835 probably intersects a groundwater pathway with relatively high hydraulic conductivity and of limited extent which may be related to the presence of a former stream channel for Bear Creek. This stream channel was apparently filled during construction of the S-3 Ponds and the other facilities in this location, and has probably provided a preferential pathway for contaminants to migrate from the S-3 Ponds to Bear Creek.

3. TECHNOLOGY SCREENING

Three categories of technologies were screened during Phase I: sorbents, iron filings, and biological treatment. The specific agents tested within each grouping are described in greater detail in the previously published action plan (SAIC 1996a). This section describes results obtained from each of the three groupings and an interpretation of results for Phase II applications. Details of the screening process and data are provided for each category in Appendices B through G.

3.1 TEST WATER SAMPLE CHARACTERISTICS

For the purposes of media screening, aliquots of water samples from BYBY (GW-087) and NT-1 were provided to the different research groups to use as consistent test water. Results of analyses of these samples are shown in Table 3.1.

3.2 SORBENT TECHNOLOGY TESTING

3.2.1 Introduction

Ionic sorbents have been used to remove metals from many different waste streams. Each sorbent behaves differently for a given waste stream, depending on the characteristics of the water. Sorbent performance can be influenced by characteristics that are not related to the contaminants of concern. The target water used in this study presented some particularly harsh characteristics that may cause complications in sorbent application; therefore, it was imperative that screening be completed before choosing a sorbent to treat metals in water.

To evaluate the range of applicable sorbents, a series of batch equilibrium studies were completed using the two water types. Once screening was completed, selected sorbents were further tested for their loading capacity under batch conditions. The results are reported in Appendix B and summarized below. The primary measure was uranium removal, but removal of other metal constituents was also included in the screening process.

3.2.2 Approach

The following sorbents were tested:

- peat moss,
- activated carbon,
- Dowex resin 21K,
- iron oxides,
- Amberlite IRC-718,
- zeolites,
- coal,
- biobeads,

Table 3.1. Chemical analysis of test water samples

Analyte	BYBY		Analyte	NT-1	
	Sample conc. (mg/L unless otherwise noted)	Qualifier		Sample conc. (mg/L unless otherwise noted)	Qualifier
Ag	<0.02	U	Ag	<0.02	U
Al	1.67 (est)	D	Al	81.3	D
As	<0.10	U	As	<0.1	U
B	NA		B	NA	
Ba	0.0939	D	Ba	20.1	D
Be	<0.001	U	Be	0.0103	D
Ca	30.4	D	Ca	>1000	D
Cd	<0.020	U	Cd	0.788	D
Cr	<0.020	U	Cr	0.0758	D
Fe	3.42	D	Fe	37.4	D
K	4.47	D	K	48.2	D
Mg	7.16	D	Mg	334	D
Mn	0.923	D	Mn	>100	C
Na	14.4	D	Na	379	D
Ni	0.0596	D	Ni	3.18	D
Pb	<0.20	U	Pb	<0.2	U
Se	NA		Se	NA	
Sb	NA		Sb	NA	
Si	NA		Si	NA	
Tc	-40		Tc	15000 pCi/L	D
Ti	NA		Ti	NA	
Tl	NA		Tl	NA	
U	0.0001	D	Tritium	950 pCi/L	D
V	<0.01	U	U	0.006	D
Zn	0.0858	D	V	0.0514	D
Zr	NA		Zn	0.225	D
Tritium	-180	U	Zr	NA	
Alkalinity	90	D	Methylene		

Table 3.1 (continued)

Analyte	BYBY		Analyte	NT-1	
	Sample conc. (mg/L unless otherwise noted)	Qualifier		Sample conc. (mg/L unless otherwise noted)	Qualifier
Fluoride	<0.05		Chloride	0.018	D
Nitrate	1		cis-DCE	0.019	D
Nitrite	<0.05		Chloroform	0.017	D
Sulfate	26		PCE	0.12	D
Total radioactive Sr	-0.28	U	Alkalinity	160	
Total dissolved solids	160	D	Fluoride	30	D
Total suspended solids	22	D	Nitrate	8500	D
pH	5.89		Nitrite	16	D
			Sulfate	12	D
			pH	NA	
			Total radioactive Sr	27 pCi/L	D
			Total dissolved solids	13000	D
			Total suspended solids	370	D

NA = Not applicable.

U = Undetected.

D = Detected.

C = Possible contamination.

- phosphate rock, and
- Ionac.

Water samples from BYBY and NT-1 were tested in small batch tests containing 0.25 grams of sorbent and 50 mls of water in a flask. Soluble metals were measured before and after a 24-h exposure to the sorbent.

3.2.2.1 Results of sorbent screening for uranium uptake

Results from the initial screening studies using water from the BYBY area suggest that most of the sorbents effectively removed >90% of the uranium in the water (Figs. 3.1 and 3.2). The biological materials (biobeads and algal mats) produced ~50% uranium removal. The zeolite and cercona zeolite removed <20%.

The same sorbents tested with NT-1 water produced different results. There were only two products that removed >90% of the uranium: peat moss and TRW (Figs. 3.3 and 3.4). Algal mats removed 40% of the uranium, and all others removed <30%. The NT-1 water is known to have high conductivity, including high aluminum, calcium, and magnesium. This may have interfered with uranium sorption.

The screening study rapidly narrowed the list of candidates to be considered; however, the loadings chosen were somewhat arbitrary. The next criterion for advancement was the isotherm study, indicating how much uranium could be sorbed by a given mass of sorbent. Isotherms are shown in Appendix B. Table 3.2 summarizes the preliminary uranium loading estimates for those sorbents tested. The loading capacity of Dowex was so high that the experiments could not quantify it. Peat moss had the next highest loading rate in both water samples, although the loading rate at NT-1 (.9 mg U/g) was much lower than at BYBY (4 to 5 mg U/g). TRW exhibited approximately half of the capacity of peat moss. The relationship between sorption, uranium concentration, and cost were ultimately used to determine which candidates would be carried to the next phase.

Table 3.2. Estimated uranium loading rates based on isotherm studies

Sorbent	NT-1	BYBY
	mg U/g Sorbent	
Peat Moss	.9	4 - 5
TRW	.6	1.5 - 2
Phosphate Rock	NA	.3
SMZ	NA	.8
Dowex	NA*	NA*
GAC	NA*	NA*

NA = Data not available.

* exceeded loading rates tested

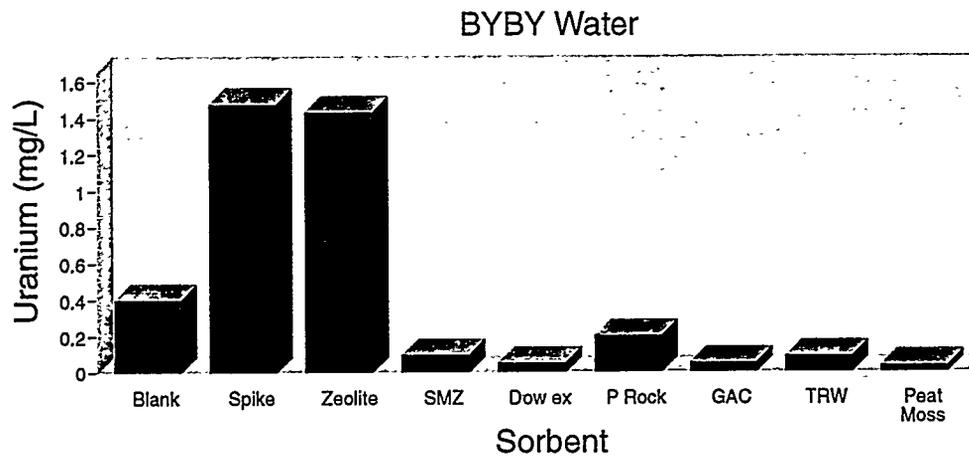


Fig. 3.1. Screening study with various sorbents in BYBY water. In this study, several of the sorbents [granulated activated carbon (GAC), coal based resin (TRW), peat moss, Dowex anion 21K exchange resin, phosphate rock (P rock), and surfactant-modified zeolite (SMZ)] worked well with the BYBY water.

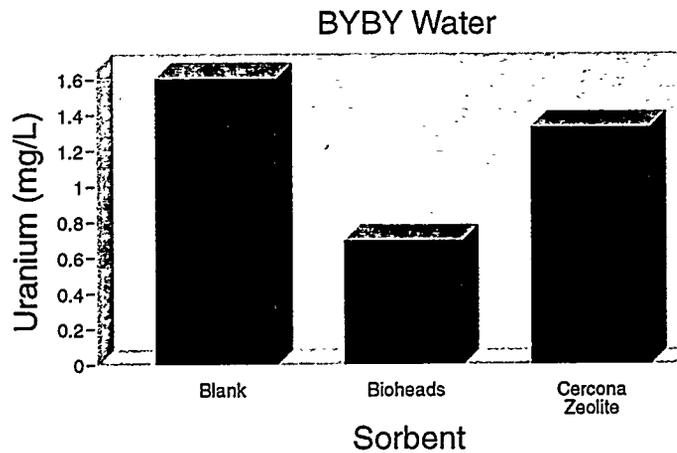


Fig. 3.2. Screening study with various sorbents in BYBY water. In this study, the biobeads (with *Pseudomonas aeruginosa*) worked to some extent, but none of the sorbents worked very well.

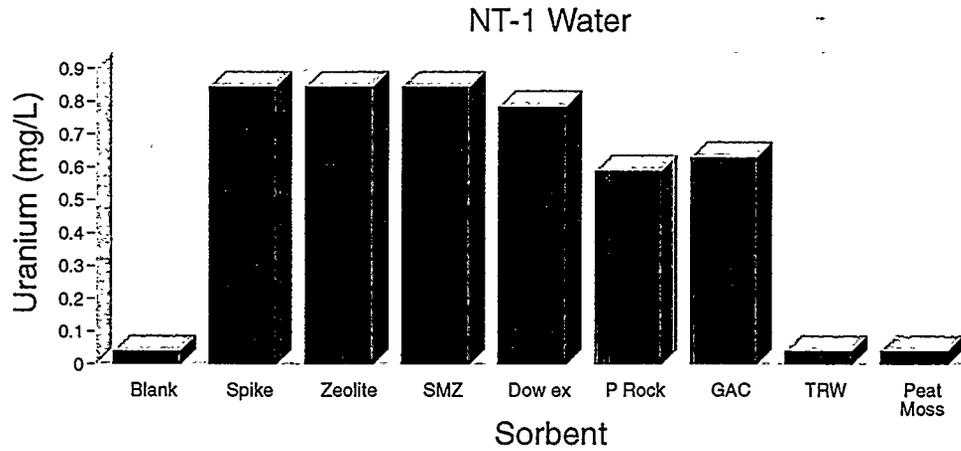


Fig. 3.3. Screening study with various sorbents in NT-1 water. As noted, the TRW (coal-based sorbent) and the peat moss worked well for the NT-1 water.

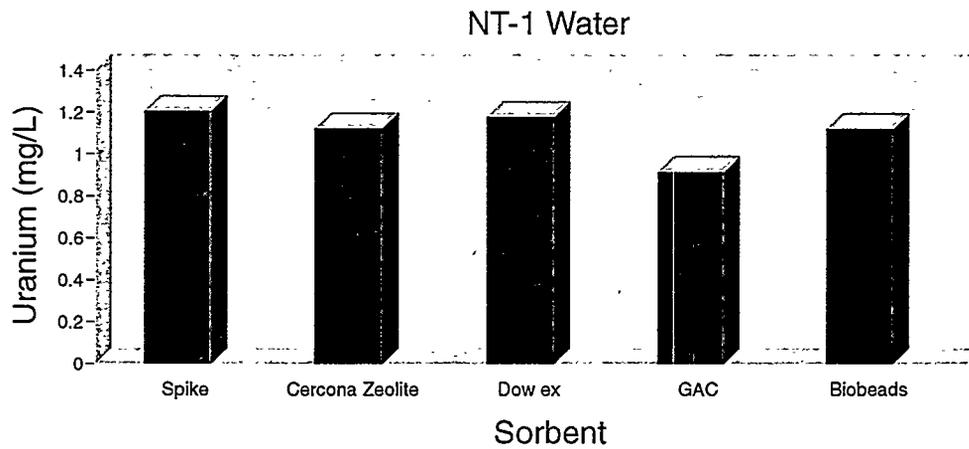


Fig. 3.4. Screening study with various sorbents in NT-1 water. As noted, none of the sorbents worked very well. (Some of the data are repeats from previous experiments.)

3.2.2.2 Results of sorbent screening for uptake of other metals in NT-1

Other metals were also monitored during screening studies to determine if any of the sorbents provided additional metal removal capacity. Amberlite IRC-718 effectively removed more than 90% of zinc, nickel, and cadmium from NT-1 water samples. Amberlite also removed significant percentages (>35%) of silver, aluminum, arsenic, and manganese. Algal mats removed aluminum, beryllium, and cadmium from NT-1 water. The lack of removal could be due to the excessively high concentrations of calcium and sodium. The results of various sorbents on other metals in water samples from NT-1 after 24 h of contact with the sorbent were poor.

The same sorbents performed better with other metals in the BYBY water samples. Table 3.3 lists those metals that were impacted by sorbents. Peat moss provided the best removal rates, with more than 80% removal for six of the non-rad metals. TRW was second, providing more than 70% removal of seven metals. Phosphate rock and algal mats were effective on fewer metals, with removals in the range of 40 to 89%. Other sorbents (including Amberlite IRC-718) had minimal impact on metals.

3.2.2.3 Results of sorbent uptake of organic solvents

As a secondary effort, removal of TCE and PCE was tested using four different sorbents: GAC, TRW, SMZ, and peat moss. Screening results are shown in Figs. 3.5 and 3.6. The best removal was observed in the samples treated with GAC and peat moss. These results strengthen these sorbents as candidates for further testing since some site water will be impacted with TCE and PCE.

3.2.3 Conclusions of Sorbent Screening and Recommendations for Phase II

The best candidates for uranium removal are Dowex, algal mats, and peat moss. However, each of these media have specific issues to be defined prior to application in a full-scale system. Phase I studies were unable to determine the loading capacity of Dowex; therefore, it is impossible to predict breakthrough for a continuous flow system. The algal mats showed uranium removal, but the viability of algal mats in high TDS systems is still unknown. Finally, there is some concern as to the physical stability of peat moss over a long period of time. All of these issues and a gauge of overall in-field performance will be resolved during Phase II testing.

3.3 ZERO-VALENCE IRON TECHNOLOGY TESTING — IMPACT ON ORGANICS

3.3.1 Introduction

Dehalogenation of chlorinated solvents by zero-valence iron (ZVI) has recently become the subject of intensive research and development as a cost-effective, passive treatment for contaminated groundwater. This treatment process is based on the fact that ZVI is an effective reducing agent relative to many redox-reactive species. Although detailed reaction pathways and mechanisms have not been determined, the reaction is believed to be a ZVI surface reaction. As such, degradation rates vary among iron filings obtained from different sources, probably due to differences in surface characteristics.

Table 3.3. Metals removed by sorbents

Metal	% removed by sorbent ^a									
	Zeolite	SMZ	Dowex	Phosphate Rock	GAC	TRW	Peat	Mats	Amberlite	SR-4
Barium	56	43		65		86	85	64		
Boron					68					
Cadmium				87	47	97	91	49		
Iron	78	78	74	72	78	78	54			
Magnesium						52	39			
Manganese				40		79	85	89		
Nickel				54		80	80	70		
Zinc	39			85		91	87	54		
Aluminum								96		
Beryllium							32	71		
Barium					51	48				74
Cadmium								56		96
Manganese										55
Nickel										98
Zinc										92

^aonly metals with > 35% removal are listed

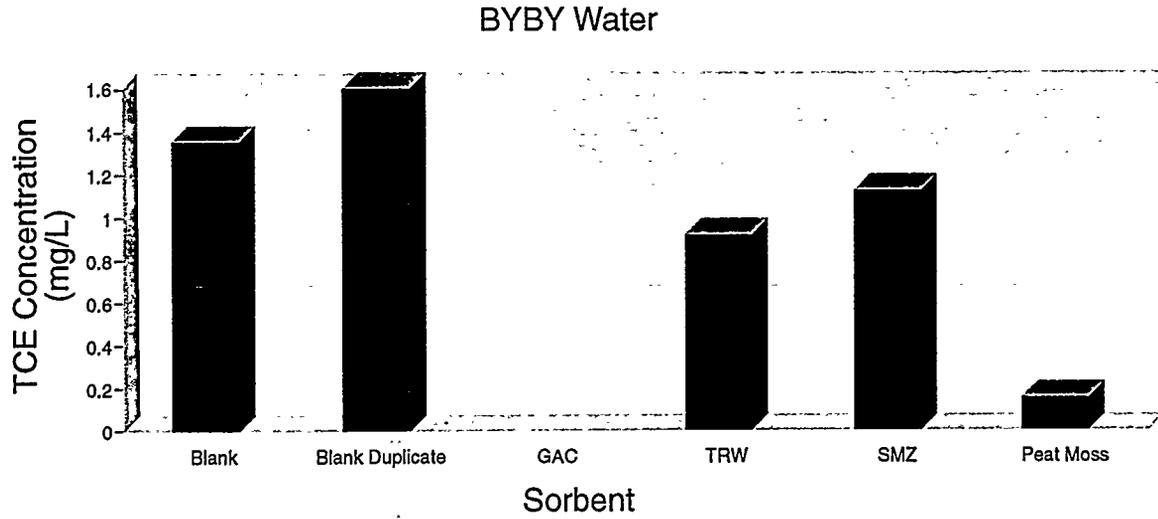


Fig. 3.5. Screening study with various sorbents in BYBY water. In this study, two of the sorbents [granulated activated carbon (GAC) and peat moss] worked well for removing TCE. The duplicate blank provides an indication of error in analysis.

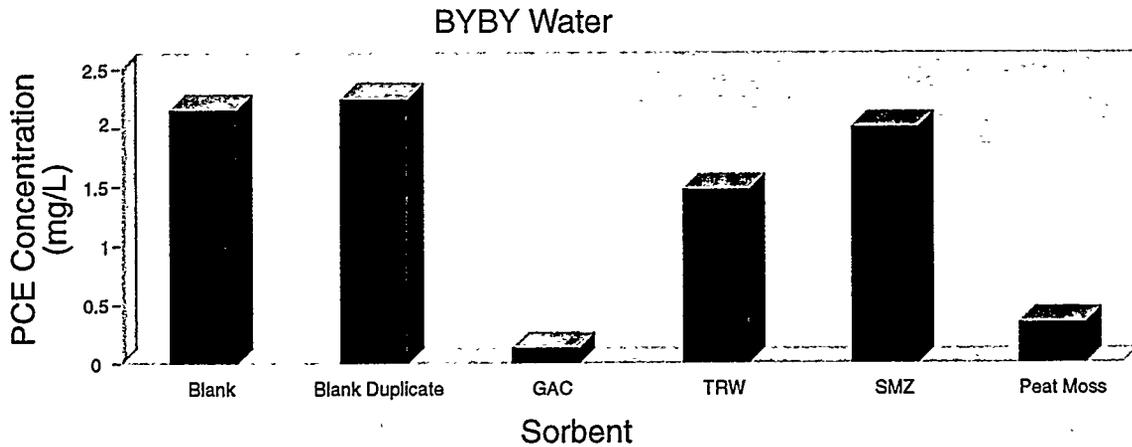


Fig. 3.6. Screening study with various sorbents in BYBY water. In this study, two of the sorbents [granulated activated carbon (GAC) and peat moss] worked well for removing PCE. The duplicate blank provides an indication of error in analysis.

Recent studies have shown that a bimetallic preparation of Fe with a small amount of palladium (Pd, 0.05% by weight) was a superior reductant for TCE (Korte et al. 1995; Liang et al. 1996). The bimetallic system provided dechlorination kinetics that were 1 to 2 orders of magnitude faster than for ZVI alone. Although palladization increases the cost of the iron material, the amount of filings required to achieve the same levels of dechlorination is significantly reduced due to more rapid degradation rates. Furthermore, more complete dechlorination than reduction by iron alone has been observed for the bimetallic system (Liang et al. 1996).

This series of tests examined the relative effect of different ZVI sources and palladium coating on chlorinated solvents in site water.

3.3.2 Approach

Iron Types Tested

The following iron types were tested:

- Fisher Scientific iron, 40 mesh;
- Fisher Scientific iron, 100 mesh;
- Palladium-coated Fisher Scientific iron, 40 mesh;
- Palladium-coated Fisher Scientific iron, 100 mesh;
- Masterbuilder, Inc. (MB) iron, medium grade;
- MB fine grade (average 40 mesh);
- Palladium-coated MB iron, fine grade; and
- Cercona Foams.

Testing Design

Most of the tests were conducted in batch studies with groundwater and filings in a zero headspace atmosphere. Full details are provided in Appendix C. Limited column studies were conducted, using different volumes of filings to determine the impact of exposure time. The disappearance of the parent compound was used to determine a half-life of the solvent in the presence of iron filings. The iron substrates causing the shortest half-lives were chosen for further examination.

A secondary issue was the production of daughter products. The presence of chlorinated daughter products was documented, but their presence and quantity relative to the different agents were not used as a measure of success. The impact of daughter products will be examined further during Phase II.

3.3.3 Results

All of the different types and sizes of iron filings were effective in degrading the chlorinated contaminants present in the different groundwater types; however, degradation efficiency varied. Figures 3.7 and 3.8 show the half-lives of various chlorinated solvents with different types of reactive media. Palladium enhanced the Fisher filings tests, increasing the degradation rate and producing a shorter half-life. The 100 mesh Fisher filings were not as porous as the 40 mesh; this

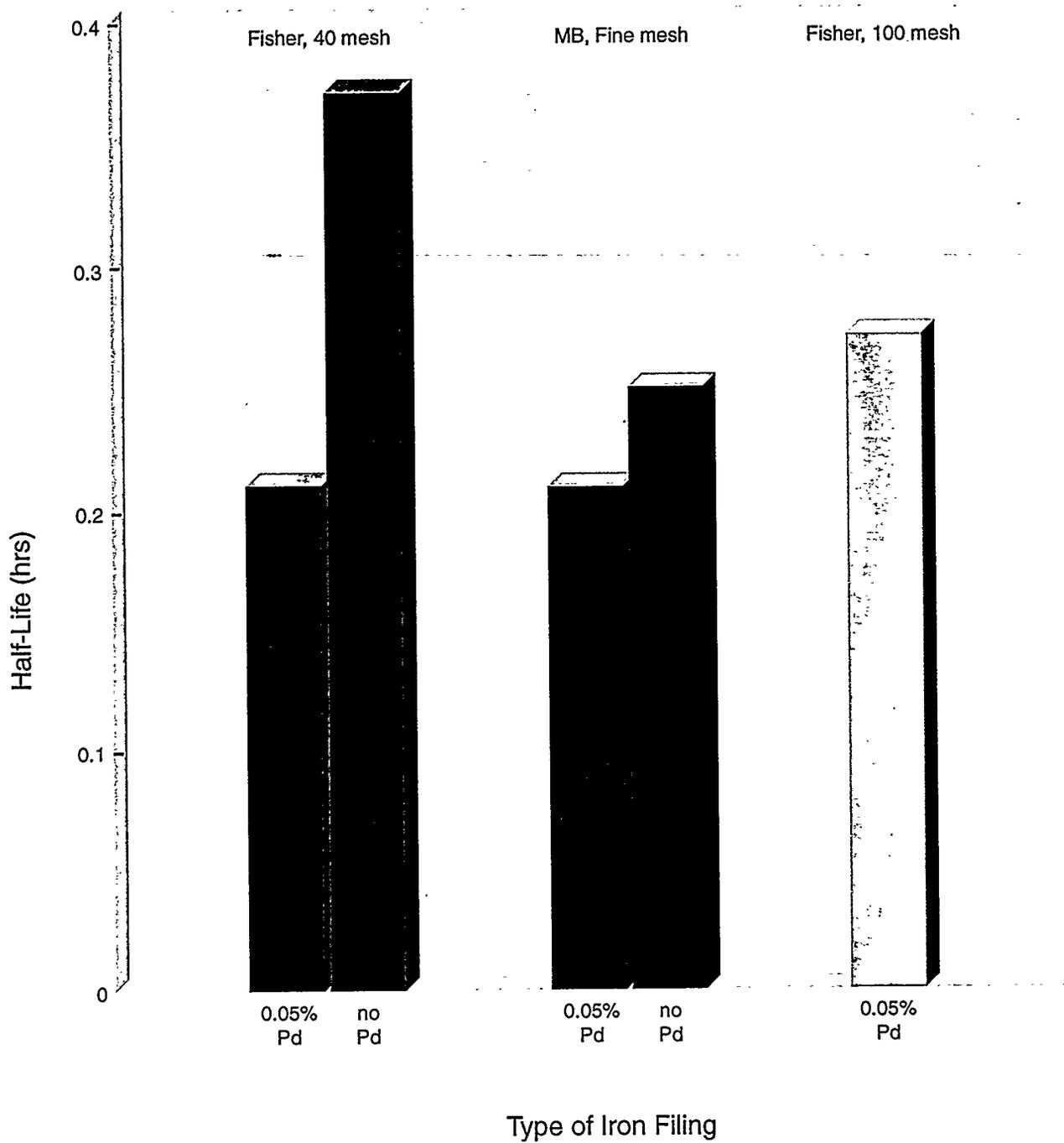


Fig. 3.7. Initial half-lives of carbon tetrachloride in CT water on different types of iron filings. Calculated from batch studies.

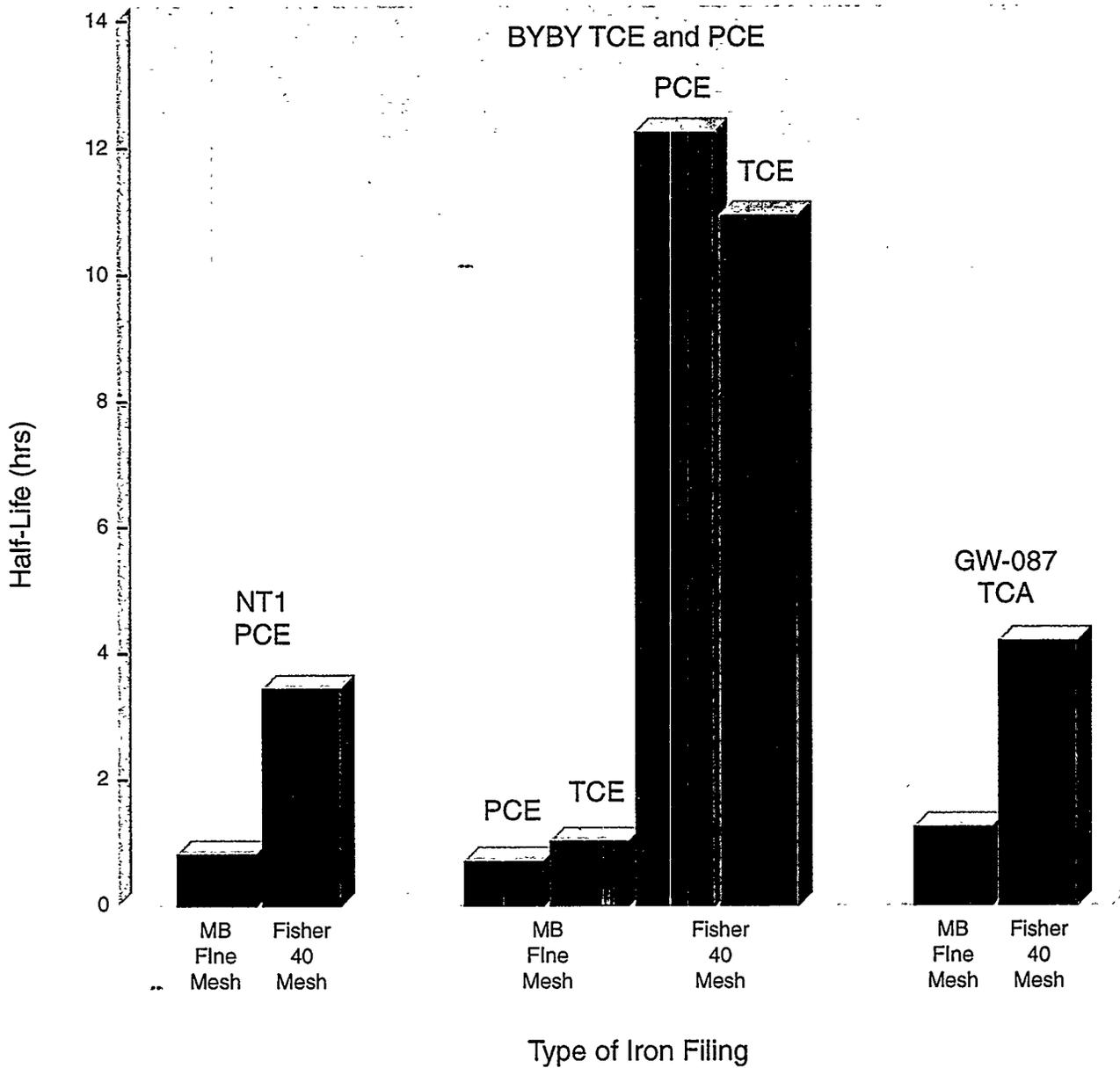


Fig. 3.8. Initial half-lives of chlorinated contaminants on MB and Fisher iron filings not coated with palladium. All groundwater samples were spiked with the chlorinated contaminants.

reduced the dechlorination efficiency of the 100 mesh tests. Palladium provided virtually no enhancement to the MB filings.

Comparing MB filings to Fisher filings, the MB filings are superior. The MB filings have 30% more surface area, providing more sites for dehalogenation and, therefore, better overall performance. Performance cannot be attributed to the fact that MB filings are produced from discarded engine blocks. Previous theories attributed MB performance to sorption of the solvents due to residual oil and grease on the filings. MB technical representatives indicate that is impossible due to the stringent pretreatment of these filings, including burning in a furnace.

3.3.4 Conclusions and Recommendations Regarding ZVI and Organics

MB filings without palladium performed best among the forms of iron tested. Results showed MB produced much shorter half-lives, probably due to greater surface area and the ability to sorb the contaminants. MB also produced smaller amounts of chlorinated byproducts. This presumes that dehalogenation is occurring. On a cost basis, MB (\$0.20/lb) is significantly cheaper than Fisher (\$40/lb). In fact, the cost differential is so extreme that MB can have significant technical shortcomings and still be considered a more viable alternative for the site treatment.

Design Issues

Limited column study data suggest that the mass of reactive media applied greatly influences performance (see Appendix C). A long-term column study focusing on the eventual saturation of sorption sites of MB is needed. It is possible that the half-lives may be extended with time if the sorption sites are not available. Determining the long-term half-life relative to mass will be also be critical in determining the ultimate feasibility of this approach.

3.4 ZVI TESTING — IMPACT ON METALS

3.4.1 Introduction

ZVI and its interactions with groundwater produce redox conditions and particulates that may retain metals identified in BCV CA. The goal of this investigation was to identify candidate types and forms of treatment material that may be suitable for removal of inorganic contaminants at the BCV CA. Since inorganics are accumulated and not destroyed by this technology, a secondary goal was to identify potential pre-design issues that should be considered during the feasibility study. Detailed data regarding this work are provided in Appendix D.

One aspect of the testing was to examine Cercona technology (Dayton, Ohio). This technology utilizes silicates and aluminates to make powder into foam in a reproducible manner. In another approach, powder can be made into aggregates or pellets (up to 2 mm in size). The advantage is that a potentially useful powder can be made "field ready" by producing it in a matrix that is easy to handle. More details on the Cercona technology are provided in Appendix D.

3.4.2 Materials Tested

Test materials and their pertinent characteristics are provided in Table 3.4. All ceramic foam and aggregate materials were provided by Cercona.

3.4.3 Approach

All of the testing was conducted in slurred batches, whereby known amounts of the test sorbent were combined with test water from either NT-1 or BYBY and shaken for 16 to 24 h. The solid and aqueous phases within each sample were separated and analyzed correctly. Experimental details are provided in Appendix D.

In order to compare reagents, a conditional distribution coefficient (K_d) was calculated using the relationship:

$$K_d = S/C, \quad (1)$$

where

S = mass of contaminant 'sorbed' at equilibrium per mass of 'sorbent',
C = equilibrium concentration of soluble contaminant in aqueous phase.

If C is given in g/ml, then K_d has the units ml/g.

3.4.4 Results from Screening of Treatment Media

Many of the ZVI products performed similarly with respect to uranium removal, producing half-lives that are between 0.03 minutes for BYBY and twenty times higher (0.70) for NT-1 water (Figs. 3.9 and 3.10).

Examining uranium removal further, it was concluded that removal is associated with ZVI corrosion. In addition, slightly acidic pH was found to greatly reduce the effectiveness of uranium removal (Fig. 3.11). This is a serious consideration since acidic pH is prevalent in the S-3 area.

Multidosage testing of selected sorbents using uranium-spiked BYBY and NT-1 water was performed using ZVI and sorbents containing iron oxide. Each of the COPCs were amenable to remediation by either ZVI or sorbent, although treatment to target goals required higher dosages for the NT-1 water. In addition to uranium, the metals tested include beryllium, cadmium, manganese, and nickel. All metals were affected by either ZVI or by the sorbent containing iron oxide.

Beta emissions were also analyzed to represent ^{99}Tc . Only those sorbents incorporating ZVI were effective (Fig. 3.12). While literature reports suggest that magnetite and ferrous-iron minerals may remove ^{99}Tc under strictly anaerobic conditions (Haines et al. 1987, Walton et al. 1986), this effect was found to be minimal or at least kinetically slow in nitrogen-purged solutions.

Table 3.4. Select characteristics of Cercona foam aggregate and related materials

Sample code	Description	BET surface area (m ² /g)	Dry bulk density (g/cm ³)	Crystallographic characterization (XRD)	Elemental composition (EDS)
MSD-96-109	Porous synthetic magnetite pellets: ~98% magnetite (from Isaac iron oxide) + Norlig G binder. Fired in Co ₂ @ 800°C.	0.70	1.4	Major: magnetite (Fe ₃ O ₄); minor: quartz (SiO ₂)	Fe; trace Ca, Si, Mn
MSD-96-110	Porous ZVI pellets: ~98% Fe (National Steel) + Norlig G binder. Fired in 7% H ₂ @ 1080°C.	0.92	2.4	Major: iron; minor: fayalite (Fe ₂ SiO ₄), wustite (FeO)	Fe; trace Ca, Si, Mn, Cr
MSD-96-111	Porous ZVI pellets: ~93% Fe (National Steel) + Cercona binder. Fired in 7% H ₂ @ 1080°C.	~0.01	2.1	Major: fayalite, wustite; minor: iron	Fe; trace Ca, Si, Mn, Cr
MSD-96-112	Porous ZVI pellets: ~98% Fe (from Isaac iron oxide) + Norlig G binder. Fired in N ₂ + 50% H ₂ @ 1080°C.	0.05	2.5	Major: iron, wustite	Fe; trace Ca, Si, Al, S
MSD-96-113	Porous ZVI pellets: ~93% mixed oxide (from Isaac iron oxide) + aluminosilicate binder (unfired).	13.3	1.3	Major: magnetite, hematite	Fe; trace Al, Si, Ca, Mn
MSD-96-114	Porous ZVI pellets: ~94% Fe (US Metal) + aluminosilicate binder. Fired in N ₂ + 7% H ₂ + 1080°C.	3.94	2.4	Major: iron; minor: hematite (Fe ₂ O ₃)	Fe; trace Mn, Ca, Al, Si, Ti, S
MSD-96-115	Porous ZVI pellets: ~92% Fe + aluminosilicate binder. Fired in N ₂ + 7% H ₂ @ 1080°C.	0.24	2.5	Major: iron; minor: hematite, magnetite	Fe; Al, Si; trace Mn

Table 3.4 (continued)

Sample code	Description	BET surface area (m ² /g)	Dry bulk density (g/cm ³)	Crystallographic characterization (XRD)	Elemental composition (EDS)
MSD-96-116	Foamed ZVI aggregate: ~92% Fe (US Metal) + Cercona binder. Fired in N ₂ + 50% H ₂ @ 1080°C.	0.8	1.2	Major: iron; minor: magnetite, fayalite, hematite	Fe; Al, Si, trace Mn, Cr, C
MSD-96-118	Porous zeolite (clinoptilolite) + 20 wt % FeOOH, + Cercona binder (unfired).	13.4	0.8-1.0	Major: goethite (FeOOH), clinoptilolite; minor: quartz, biotite	Fe; Al, Si, trace Ca, K
MSD-96-119	Porous zeolite + ~70 wt % Fe (US Metal) + Cercona binder (unfired).		1.6	Major: iron, clinoptilolite; minor: quartz, biotite	Fe; Al, Si, trace Ca, Mn
MSD-96-120	Porous zeolite + ~20 wt % FeS ₂ + Cercona binder (unfired).		1.0	Major: pyrite (FeS ₂), clinoptilolite; minor: quartz, biotite	Fe; S, Si, Al, trace Ca, K
MSD-96-134	Foamed ZVI: ~94% Fe + (US Metal) + Cercona binder. Fired in N ₂ + 50% H ₂ @ 1080°C.	~0.5	~1		
MSD-96-192	Porous zeolite pellets (aluminosilicate bonded clinoptilolite, unfired).		0.6		
MSD-96-193	Foamed bimetallic steel: ~70% Fe (US Metal) + 23% high-silicon steel (Duriron), balance Cercona binder. Fired in N ₂ + 5% H ₂ @ 1080°C.		1.8		

Table 3.4 (continued)

Sample code	Description	BET surface area (m ² /g)	Dry bulk density (g/cm ³)	Crystallographic characterization (XRD)	Elemental composition (EDS)
MSD-96-194	Foamed iron + 2% FeS ₂ , Cercona binder. Fired in N ₂ + 5% H ₂ @ 1080°C.		1.9		
Iron filings	Fisher I-57, ~40 mesh	5.89			
Iron filings	Master Builder's Steel (MBS), ~40 mesh	2.11	2.6		
Activated carbon	Nucon Mersorb-3	767			
Fe ₃ O ₄	Magnetite (Alfa Products)	5.55			
α-FeOOH	Goethite (NOAH Chemicals)	12.7			
Fe ₂ O ₃	Hematite (Alfa Products)	9.39			

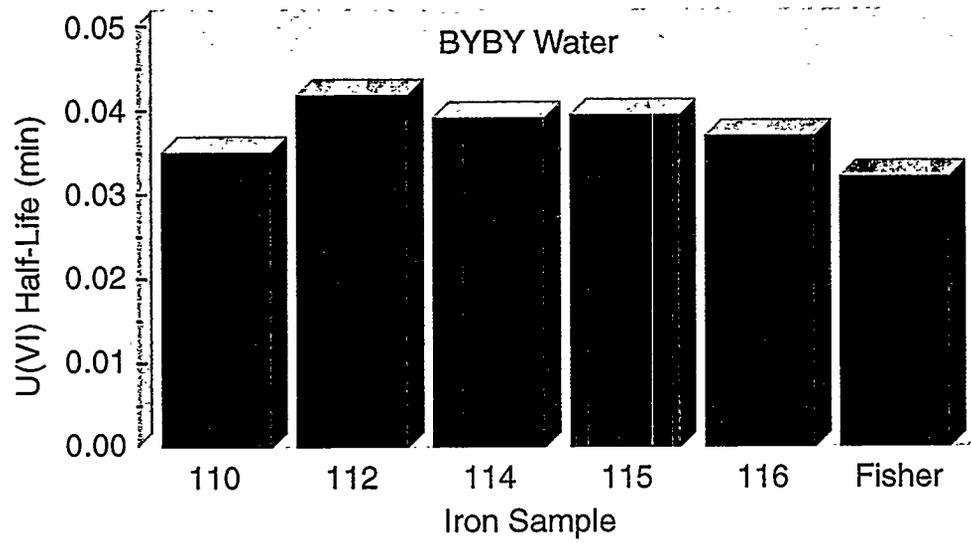


Fig. 3.9. Half-life for uranium removal from solution by ZVI products in BYBY water.

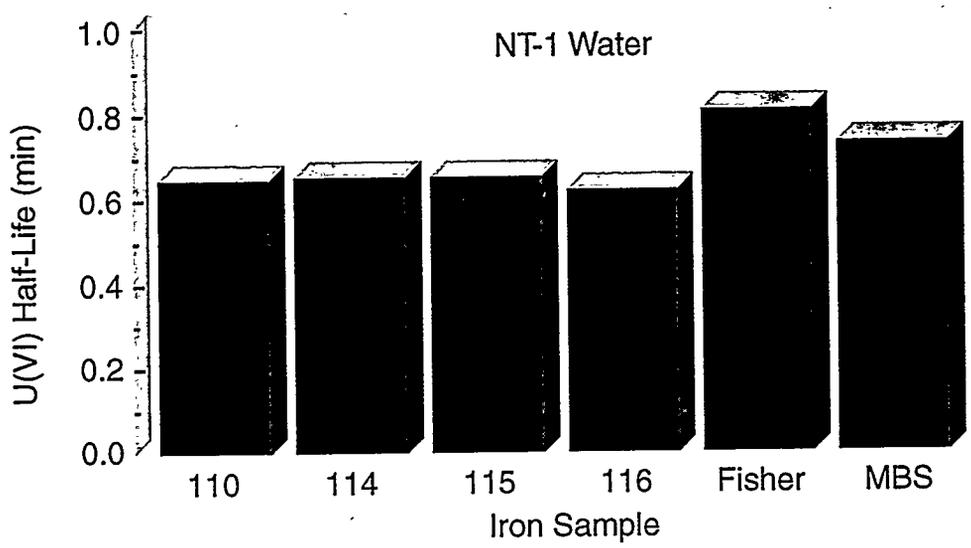


Fig. 3.10. Half-life for uranium removal from solution by ZVI products in NT-1 water.

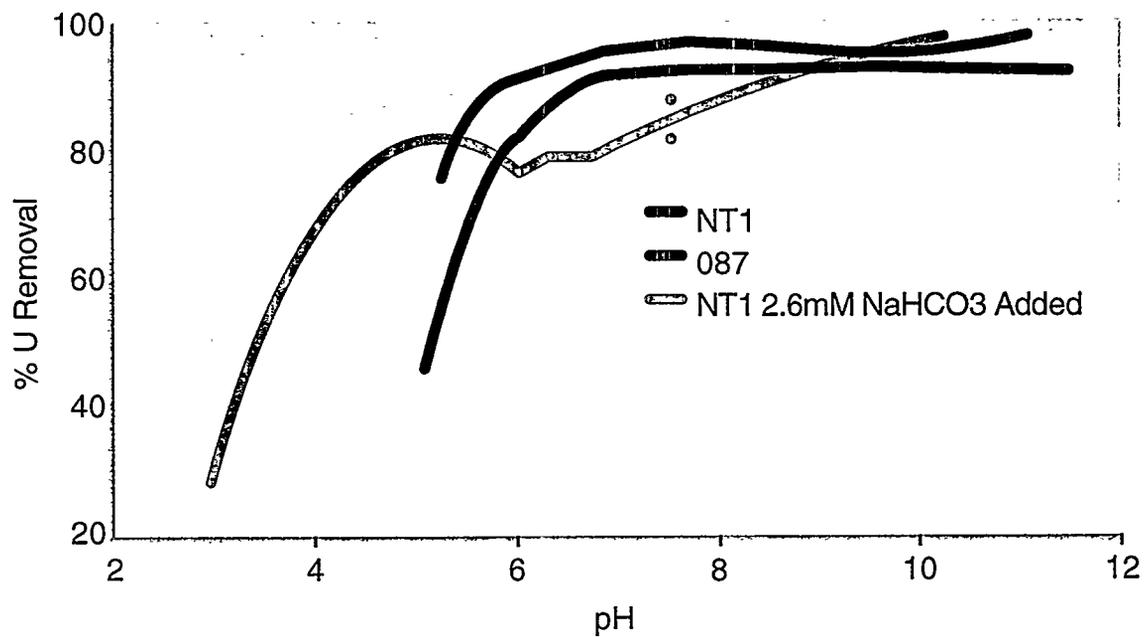
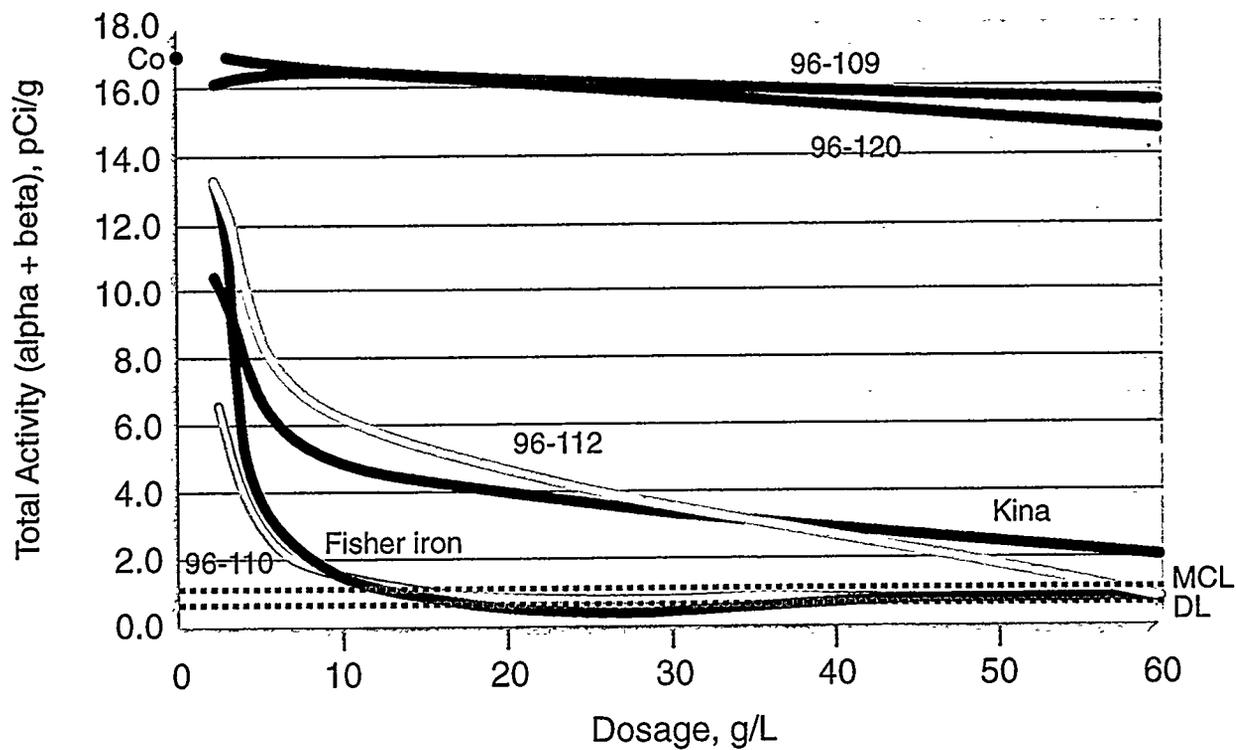


Fig. 3.11. Effect of pH and carbonate on uranium sorption by ferrihydrite.

REMOVAL OF RADIOACTIVITY FROM NT-1 WATER



REMOVAL OF RADIOACTIVITY FROM BYBY WATER

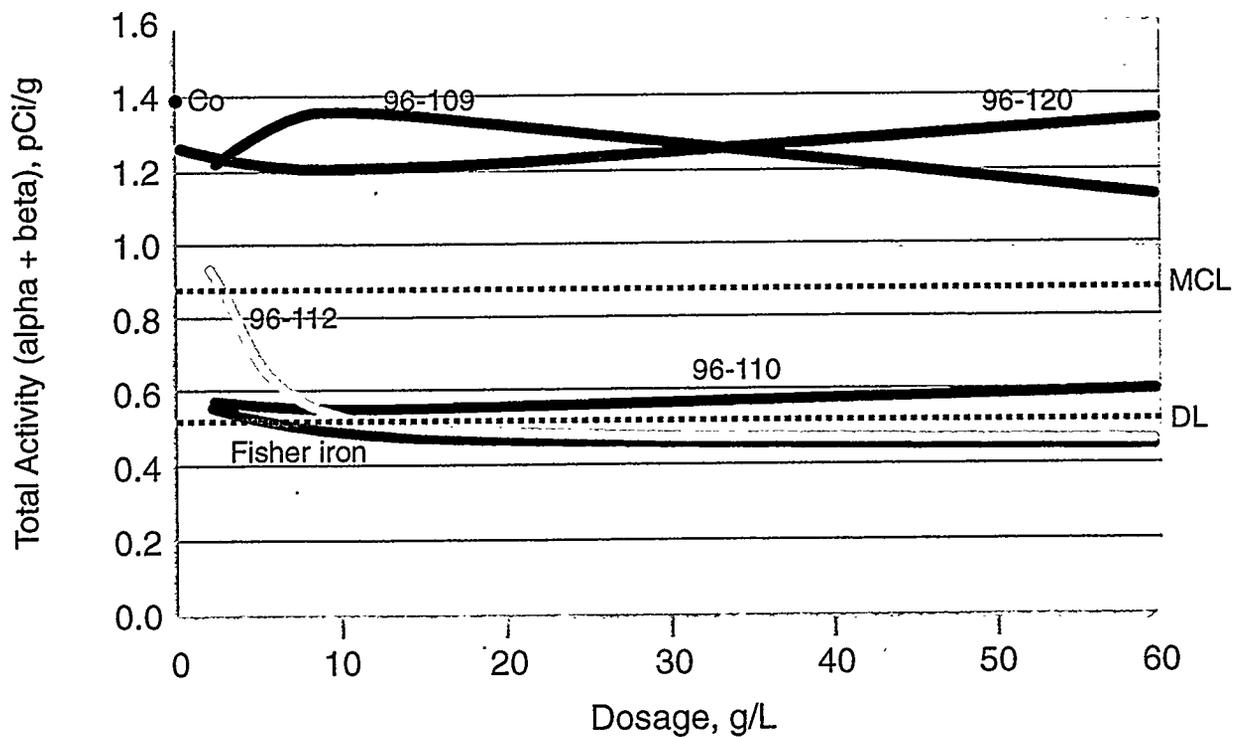


Figure 3.12. Removal of radioactivity from NT-1 and BYBY waters.

3.4.5 Bed Capacities

The packed bed capacity extrapolated K_d data so that effectiveness can be better evaluated. The packed bed capacity is the maximum loading of the adsorbent, expressed in the number of bed volumes which may be treated before the adsorbent is saturated with adsorbate. This is different from the breakthrough capacity since mass transfer kinetics and fluid mechanics dispersion are not considered. Given these limitations, this capacity can be useful in comparing performance.

Assuming uranium is present at 1 mg/L and using the parameters described in Tables 3.5 and 3.6, packed bed capacities were estimated using the equation:

$$R_f = \left[1 + K_d \frac{P_b}{\theta} \right], \quad (2)$$

where

- R_f = maximum number of bed volumes which can be treated,
- P_b = packed bed density (= mass of dry adsorbent per empty bed volume, g/ml),
- θ = total void fraction of the packed bed,
- K_d = slope of the adsorption isotherm.

Estimated bed capacities are shown in Figs. 3.13 and 3.14. Parameters used to evaluate bed capacities are provided in Tables 3.4 and 3.5. Note that although the iron oxides appear to have a high bed capacity in powder form, the capacity is greatly reduced when the same oxide is produced as a more implementable foam. In addition, sorbents exposed to NT-1 water maintained ~1 order of magnitude less capacity compared to those exposed to BYBY water.

3.4.6 Design Issues

ZVI was very effective for the removal of radionuclides and toxic metals from BCV water. Several issues related to the design and operation of a potential treatment system were raised. These issues include:

- The reactivity of iron is coupled to its corrosion. Corrosion will decrease its reactivity, thereby limiting its effective treatment lifetime. Anaerobic conditions could mitigate this effect; however, groundwater in the unconsolidated zone throughout most of BCV is more oxidative, which would support corrosion.
- The predominant removal mechanism for uranium appears to be sorption to iron corrosion products. Figure 3.15 shows the distribution of uranium among three different physical phases present in an iron filing atmosphere. Less than 20% of uranium was located on the solid iron phase. More than 35% was found in the filtrate, indicating this uranium is still dissolved. The remaining 50% of uranium was found in the "slough," particulate matter suspended from the iron coupon. Transport of these sorbed products must be controlled in a full-scale treatment system to avoid liberation of radionuclides downstream of the treatment system.

Table 3.5. Parameters used to evaluate bed capacities for uranium adsorption in BYBY water

Adsorbent	K_d ml/g @ 1×10^{-6} g/ml	Bulk density (g/ml)	$\rho\theta$ (g/ml)	Retardation factor	Intergran porosity
109	29.2	1.36	3.4	100	0.4
175	55	1.36	3.4	188	0.4
Cercofoam	114	1.36	3.4	389	0.4
113	85	1.27	3.2	271	0.4
118	64	0.86	2.2	139	0.4
120	16.7	0.94	2.4	40	0.4
Magnetite	324	1.2	3.0	973	0.4
Goethite	1264	1.0	2.5	3161	0.4
Hematite	953	1.0	2.5	2384	0.4
GAC-Mersorb	303	0.56	1.4	425	0.4
GAC X-10	1400	0.56	1.4	1961	0.4
TRW	2560	0.56	1.4	3585	0.4
Peat moss	5000	0.22	0.3	1501	0.75

Table 3.6. Parameters used to evaluate bed capacities for uranium adsorption in NT-1 water

Adsorbent	K_d ml/g @ 1×10^{-6} g/ml	Bulk density (g/ml)	$\rho\theta$ (g/ml)	Retardation factor	Intergran porosity
113	90	1.9	4.7	420	0.4
Magnetite	221	1.9	4.7	1029	0.4
Goethite	210	1.5	3.9	810	0.4
Hematite	403	1.8	4.6	1851	0.4
GAC-Mersorb	84	0.5	1.2	106	0.4
TRW	600	0.5	1.2	751	0.4
Peat moss	900	0.22	0.3	271	0.75

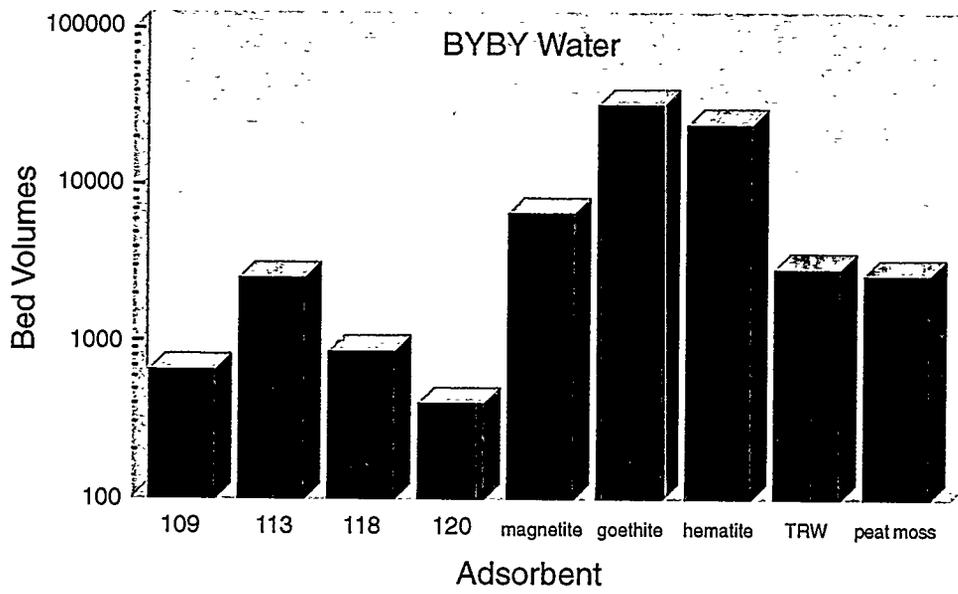


Fig. 3.13. Bed capacities for uranium adsorption in BYBY water.

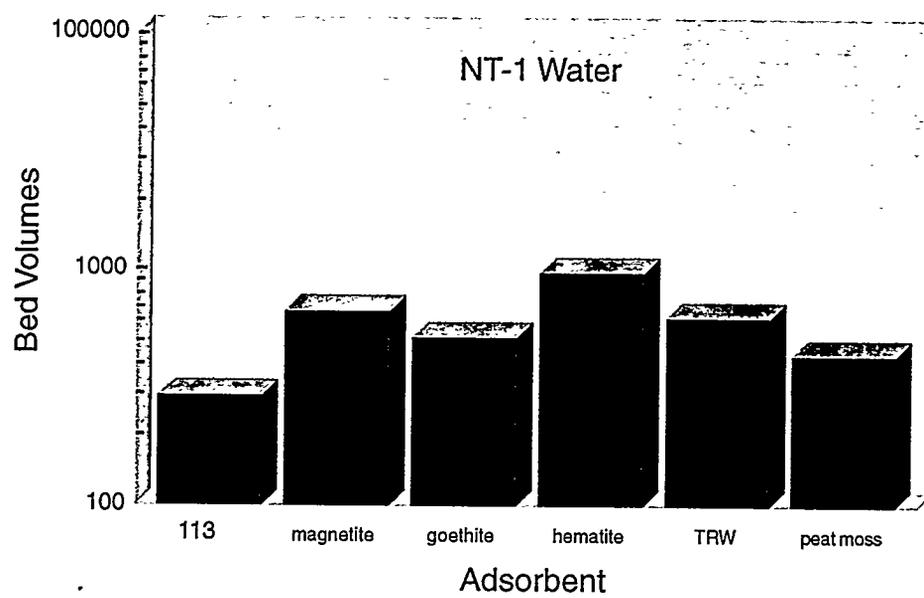


Fig. 3.14. Bed capacities for uranium adsorption in NT-1 water.

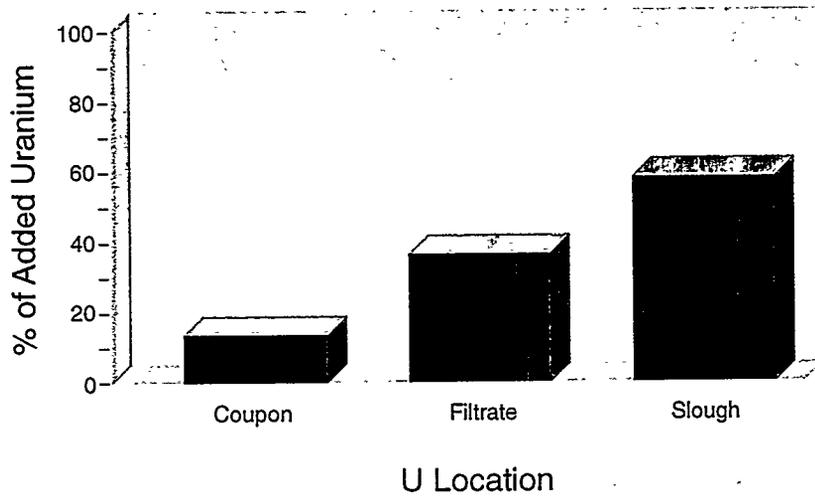


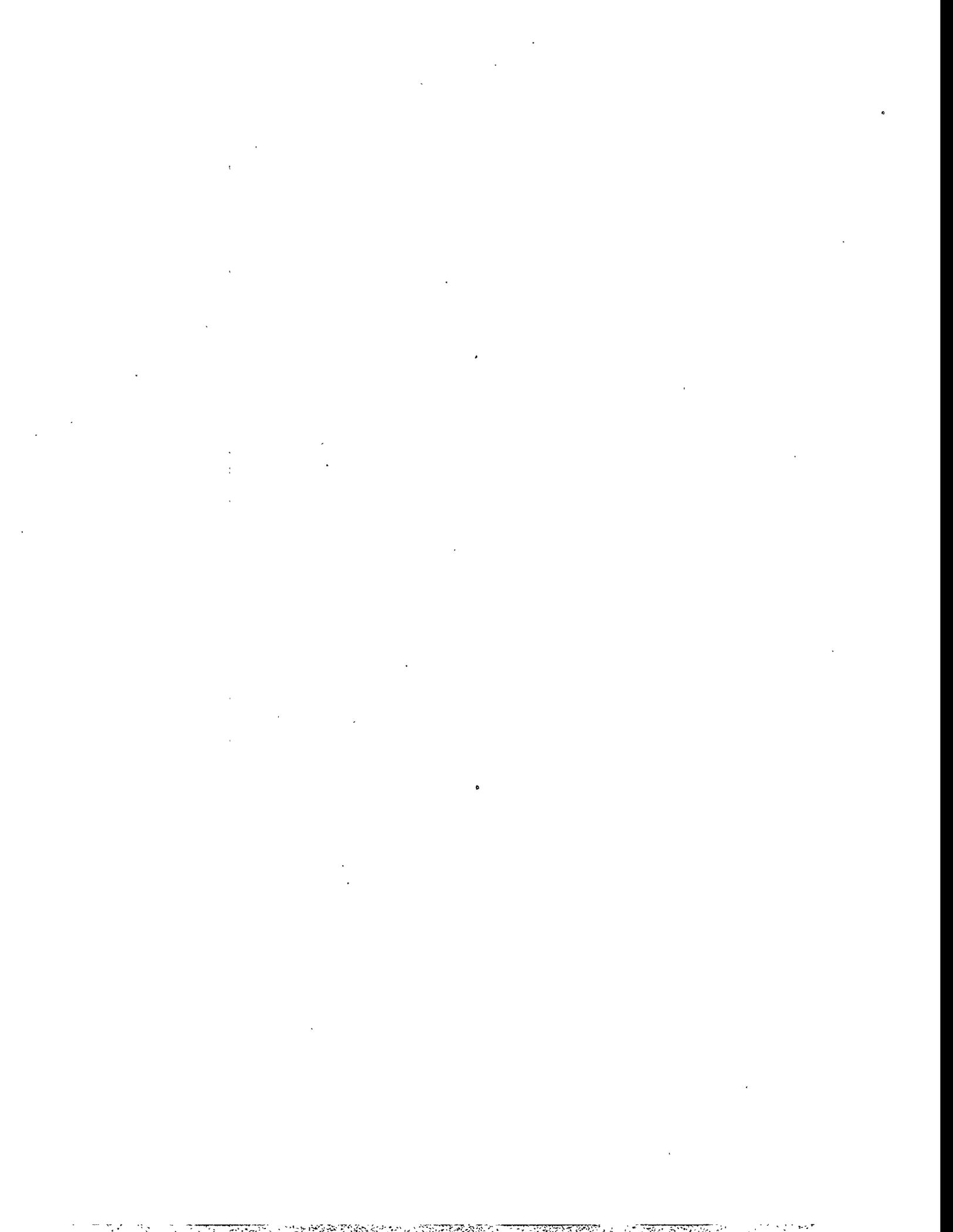
Fig. 3.15. Uranium distribution after one day of reaction with an iron coupon in 1005 mg U/L.

- Iron oxides were effective sorbents for uranium and other metal contaminants such as mercury. For optimal water remediation, the oxide material must be pelletized or foamed to enhance hydraulic conductivity. However, batch experiments showed iron oxides' performances were greatly reduced in a non-powdered form.

3.4.7 Conclusions

Generally, ZVI and iron oxides were effective in removing uranium from both BYBY and NT-1 water. Each product's performance was generally one half to one order of magnitude lower in NT-1 water, presumably due to the increased stringency of this water. Examining the Kd values provided for different ZVI and iron oxide samples, ZVI and iron oxides products had comparable values in BYBY and NT-1 water samples. Iron oxides in powder form produced much higher Kd values due to the increased surface area for reaction. However, it is not feasible to use the powder form in a full-scale application. ZVI and iron oxides Kd values are much lower than the estimated Kd for peat moss, the primary sorption product candidate. Therefore, ZVI and iron oxides are secondary candidates for full-scale application.

The fate of uranium after sorption to iron is not understood. The potential for delayed release of uranium may become a factor that eliminates ZVI and iron oxides from further consideration. The mechanism of uranium removal and its long-term fate in an iron environment must be determined. Some recommendations to address the sloughing issue include mixing ZVI and iron oxide with other products that will enhance the retainment of uranium. This should also be tested in column experiments during Phase 2.



4. BIOLOGICAL TREATMENT TECHNOLOGY

4.1 CONSTRUCTED WETLANDS

4.1.1 Introduction

Constructed wetlands are complex communities of plants, bacteria, and decaying biological material. The physical components of wetlands vary, but all represent a fueled bioreactor that is capable of biodegrading organic matter, transforming inorganic material such as ammonium, nitrate, and phosphorus; and trapping metals from water as it runs through the wetland system. The objective of this study was to apply replicate wetlands test cells to treat seep water as it flows from the groundwater existing site conditions. The primary targets to remove were nitrate and uranium. A full description of this work is provided in Appendix E.

4.1.2 Approach

Three replicate wetland cells containing similar quantities of plants and pea gravel were constructed along the north bank of SS-4 along Bear Creek Road. Each cell received SS-4 water from a dedicated pump at a rate of ~ 200 mls/minute. During the 3-month test period, influent and effluent samples were collected from each cell twice per week. Samples were analyzed for uranium, nitrate, pH, conductivity, and temperature.

4.1.3 Results

4.1.3.1 Uranium removal

Uranium concentrations were consistently lower in the effluent compared to influent concentrations (Fig. 4.1). Influent concentrations ranged between 100 and 200 $\mu\text{g/L}$. Effluent concentrations ranged from 20 to 170 $\mu\text{g/L}$. Calculating the mean removal rates, $\sim 46\%$ removal of uranium was observed. There is some indication that the capacity for uranium removal may have been declining toward the end of the study. This may be explained by the gradual saturation of active sites on the freshly introduced biomass without adequate replenishment. The brevity of the study prevented resolution of this trend, but it can be readily addressed during Phase II.

4.1.3.2 Nitrate removal

During the first half of the test period, nitrate concentrations in effluent samples were slightly lower than the corresponding influent sample, but the difference was marginal. This was attributed to the lack of decaying organic matter that more mature wetlands systems would have to fuel the nitrate removal process. To rectify this deficiency, a simple organic carbon source (corn steeped liquor) was added drip-wise to the influent feed. Nitrate removal data are shown in Fig. 4.2. Approximately 6 to 10 mg/L of nitrate nitrogen were removed prior to carbon addition. After supplementation, the removal rate increased to a peak of > 36 mg/L. The final data set suggested that 36% of the influent nitrate concentration was removed. Furthermore, the record of nitrate concentrations suggests that even though the nitrate influent concentration was increasing, the effluent concentrations were steady or decreasing, suggesting an increased capacity for nitrate removal. These trends suggest that acclimation was occurring throughout the test

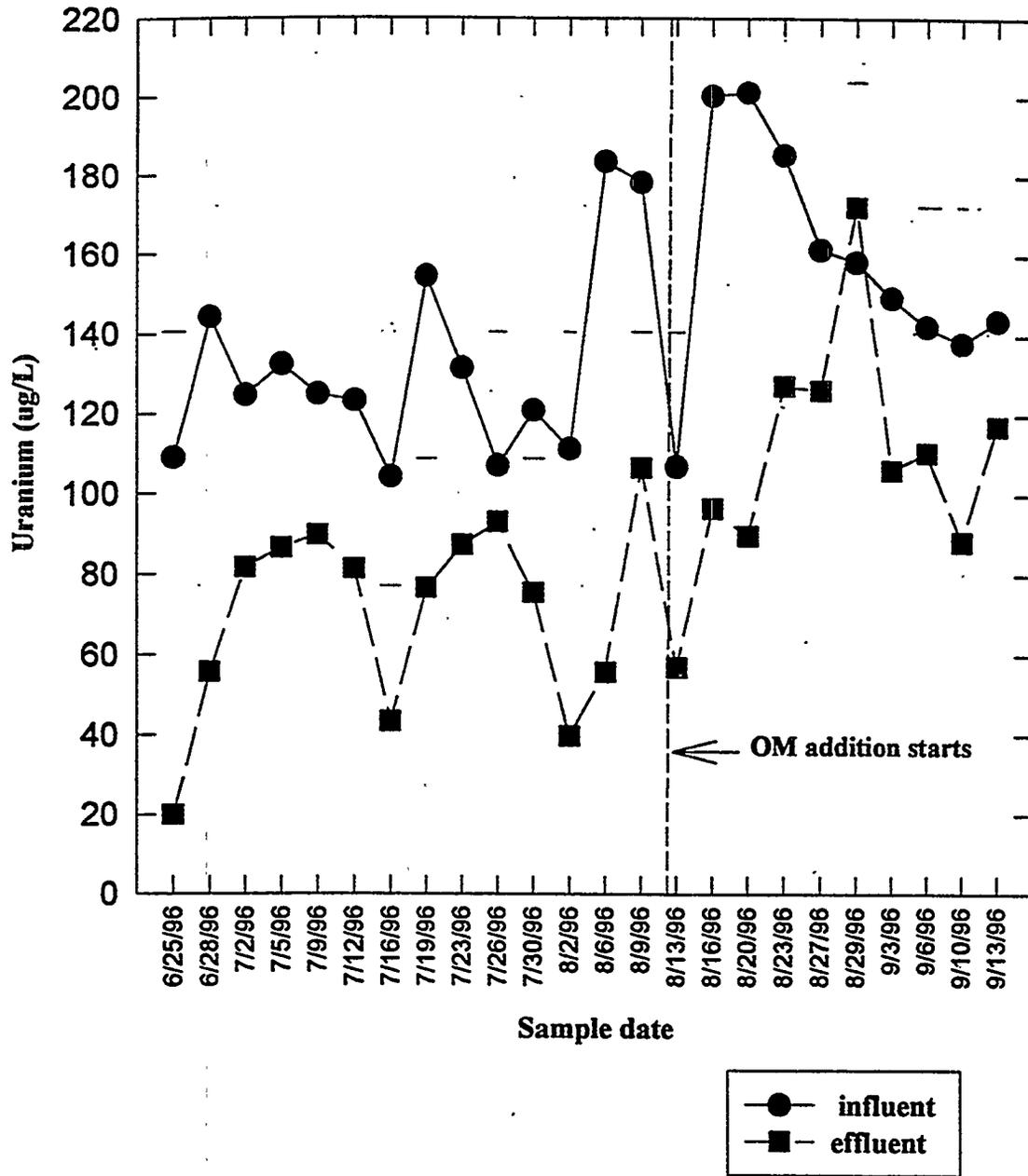


Fig. 4.1. Mean concentrations of total uranium in water entering and exiting Bear Creek wetland cells.

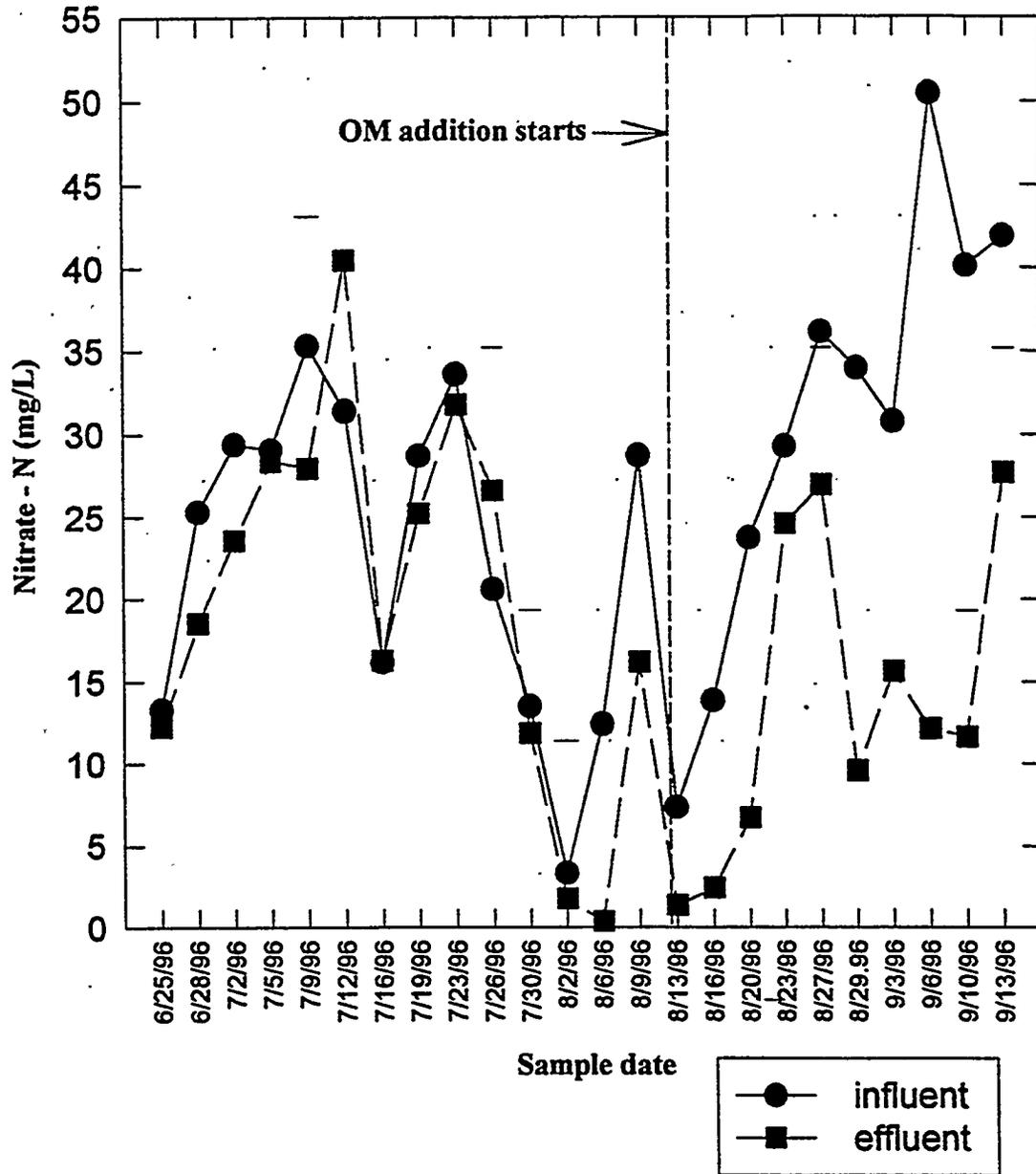


Fig. 4.2. Mean concentrations of $\text{NO}_3\text{-N}$ in water entering and exiting Bear Creek wetland cells.

period; therefore, there was not enough time to reach the potential maximum nitrate removal capacity.

4.2 ALGAL MATS

4.2.1 Introduction

Algal mats are a self-sustaining community of bacteria, protozoa, and blue-green algae. The algae are photosynthetic, producing an oxidative environment and additional carbohydrates (algal mass). Within the mat structure, bacteria colonize in small niches, feeding on the algal biomass and producing anaerobic or reducing conditions. This balance of redox conditions rendered the mats system capable of many different treatment functions. The mats require very little nutrition, generally gaining all requirements from the target water, the sun, and air. The entire system represented a low operations and maintenance alternative for water treatment. However, due to the biotic and photosynthetic nature of the mats, it was not suitable for a subsurface trench configuration. For this reason, it was considered for a surface application.

4.2.2 Approach

The purpose of this study was to demonstrate the general performance of the mats with actual site water. Because the mats are living material, batch systems do not represent the capacity of the system. Therefore, the goal of the tests is to understand the capacity of the mats to remove metals (including uranium), reduce nitrate, and sustain growth in a continuous flow system under site conditions.

Two mats reactors were maintained in the field. Photographic plan and side views are shown in Fig. 4.3. One received NT-1 surface water and the other received SS-4 surface water. Each reactor received water by gravity flow from a storage carboy to the open reactor. Effluent from the reactor was collected and discarded. Field data and samples were collected twice weekly for 4 weeks. Analyses included metals, nitrate, pH, and conductivity.

4.2.3 Results

4.2.3.1 Field parameters

Effluent pH values from both reactors were found to have between 0.5 and 1 standard unit higher pH than influent values. This may be due to the autotrophic nature of the algae, removing carbonate from the system. Conductivity measurements showed an average of 19% reduction after treatment with the mats. The maximum single change in conductivity within corresponding influent/effluent samples was 36%. Temperature increased after treatment by 5°C; however, this is due to the increased exposure to the summer heat and not a direct result of biological activity.

4.2.3.2 Uranium removal

The SS-4 water contained the highest concentration of uranium, with a maximum observed concentration of 165 µg/L (Fig. 4.4). Effluent concentrations ranged between 0 and 30 µg/L, suggesting effective removal. Removal was confirmed by the presence of uranium in mats solids used for treatment (Fig. 4.5).

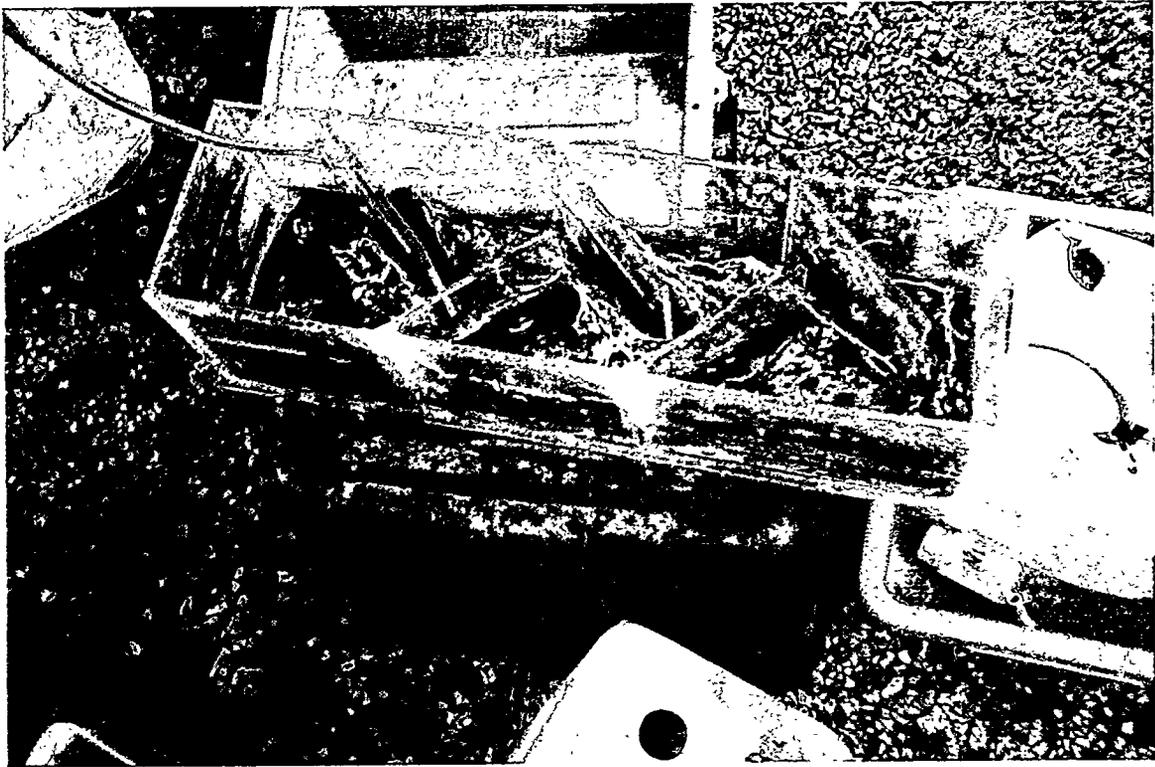


Fig. 4.3. Algal mat reactor. Plan view (a) and side view(b).

Uranium

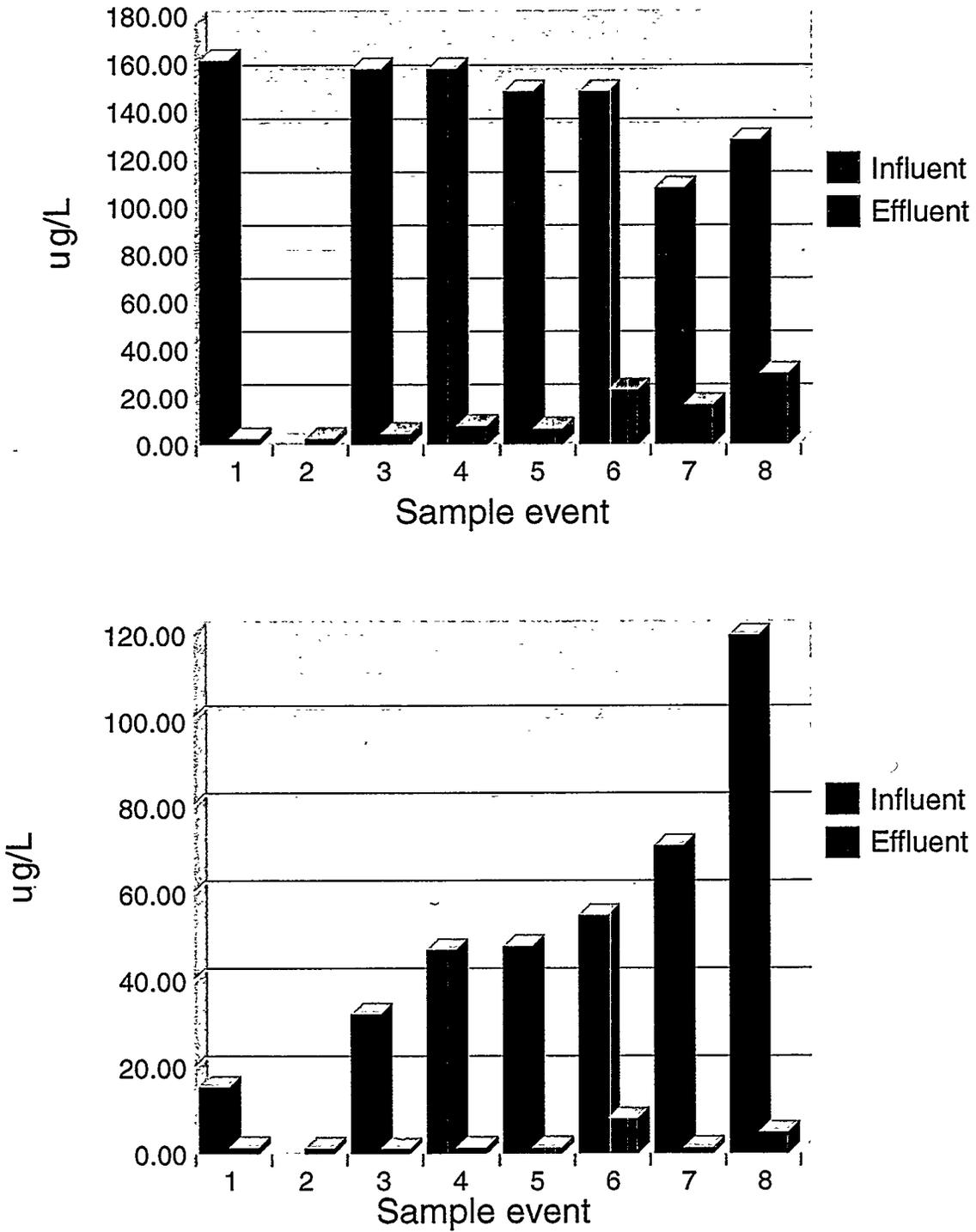


Fig. 4.4. Algal mat treatment of NT-1 (top) and SS-4 (bottom).

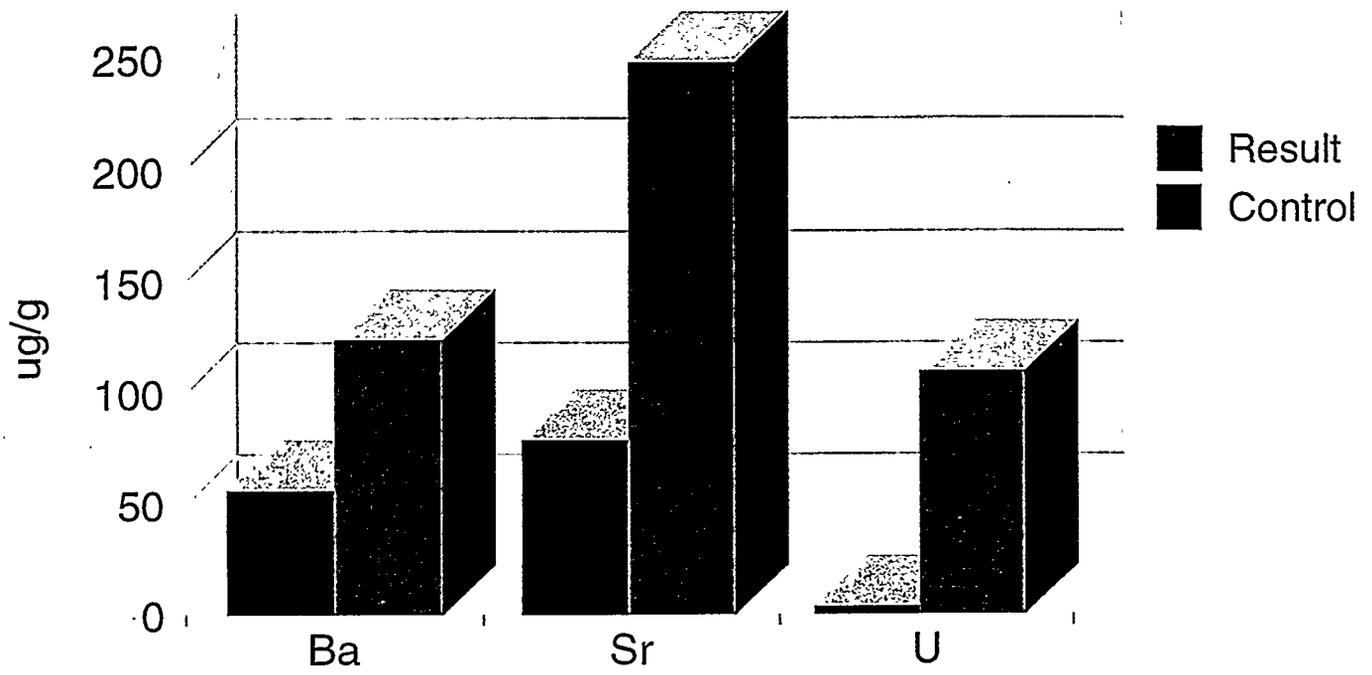


Fig. 4.5. Results of metal analysis on algal mats used to remediate SS-4 water: barium, strontium, and uranium.

4.2.3.3 Other Metals

In addition to uranium, many metals were removed from both NT-1 and SS-4. In NT-1, aluminum, barium, calcium, cadmium, manganese, nickel, and strontium were reduced by more than 30% and as high as 98% (Table 4.1). The reactor treating SS-4 water removed barium, calcium, magnesium, manganese, and strontium between 25 and 46% (Table 4.2).

4.3 PHYTOREMEDIATION

4.3.1 Introduction

Phytoremediation is a new approach to remediating metals in soil and groundwater. The technology places plants known to hyperaccumulate metals into the contaminated medium. The plants roots system either sorb or take up the target metals, removing them from the medium. Plants can be harvested, dried, and disposed of at a fraction of the mass of the original medium. Reports of field tests are limited, and certain plants can be adversely affected by stringent conditions. Therefore, a field screening of the suggested plant system was needed to determine the feasibility of using phytoremediation as a surface water treatment system.

4.3.2 Approach

The objective of the treatment system was primarily to remove uranium. Other metals were also examined; their removal was considered a secondary advantage. The sunflower-based treatment system was supplied by Phytotech (Monmouth Junction, New Jersey) (see Fig. 4.6) A series of batch tests were completed using water from NT-1 surface water, NT-1 piezometer water, and SS-4 surface water. Each test consisted of placing a tray of six plants into approximately 30 gallons of water such that the clean roots were submerged. The plants were left in the water for 48 h. Triplicate trays were tested for each water type, and a single sample was collected from each bucket of water prior and after completion of the test. Plant roots were tested with each batch. Plant shoots (upper plant mass) were analyzed once. Untreated roots and shoots were also submitted for analysis.

4.3.3 Results

Each batch of plant suffered stress during transportation to the test site, and during the test itself. Air temperatures reached daily highs in excess of 90°F, with even more intensity within the greenhouse. Due to these factors, it was not possible to determine if exposure to the test water caused stress or wilting. One exception was batch 3, which tested subsurface water. Plants exposed to this batch wilted more severely than any other batch, and remained that way for the duration of the test. This extensive wilting was attributed to a lack of oxygen in the water. All other batches tested either aerated subsurface water or surface water, which is naturally aerated. Even severe wilting did not completely hinder the plants metal removing capacity.

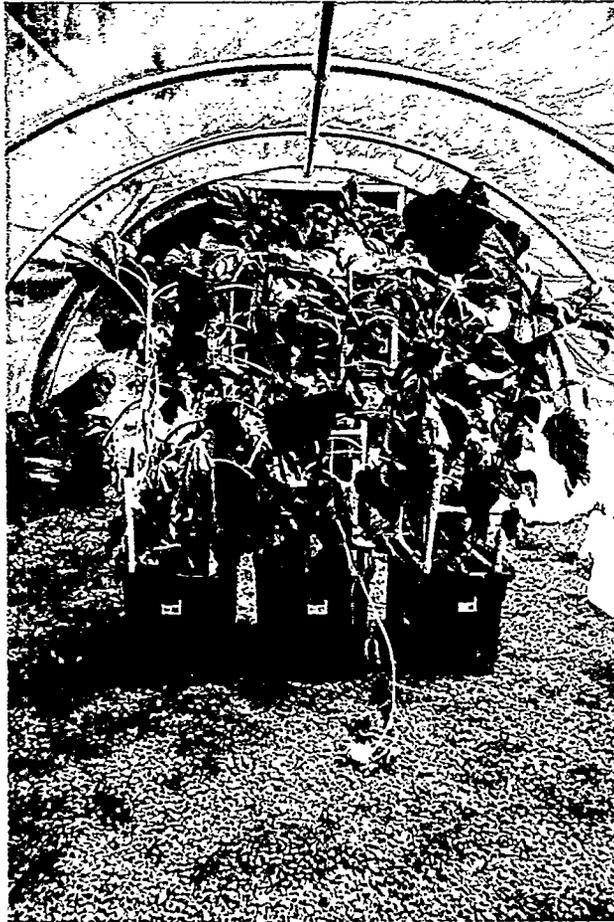
Results of the different batches were highly variable (see Tables 4.3 and 4.4). Uranium was removed from NT-1 water in four of the six tests, with a maximum removal of 50%. Uranium removal from SS-4 water was less, with 8% and 16% removed. Removal of aluminum, cadmium,

Table 4.1. Mean influent and effluent concentrations of metals removed by mats treatment of NT-1 surface water

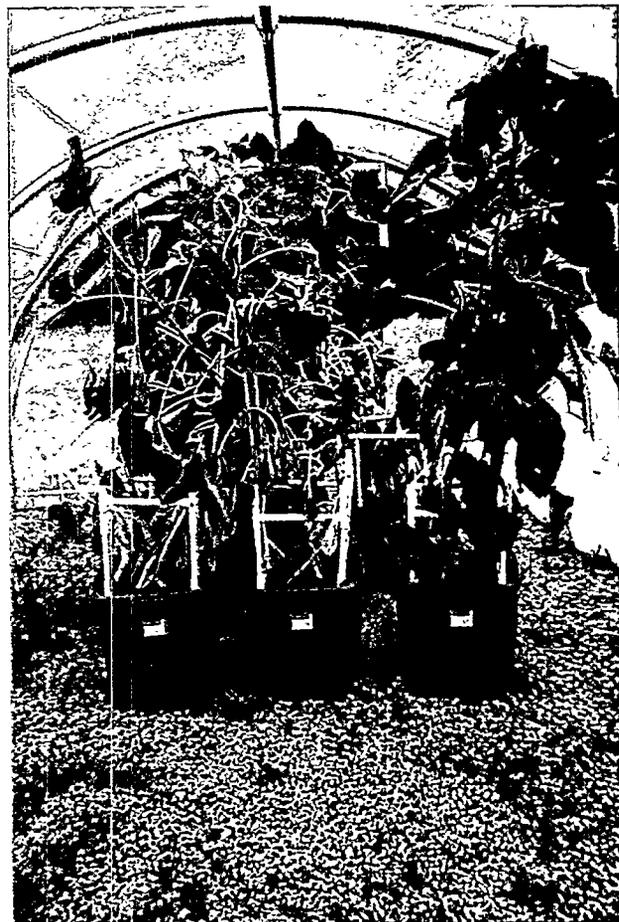
Metal	Mean influent concentration (ppb)	Mean effluent concentration (ppb)	Percent removal
Aluminum	163	72	56
Barium	547	167	68
Cadmium	38	1.5	96
Calcium	227	156	31
Magnesium	32,670	27,960	14
Manganese	5,870	130	98
Nickel	168	15	91
Strontium	698	473	32
Thallium	1.66	1.58	5
Uranium	55.4	2.5	96

Table 4.2. Mean influent and effluent concentrations of metals removed by mats treatment of SS-4 water

Metal	Mean influent concentration (ppb)	Mean effluent concentration (ppb)	Percent removal
Barium	186	111	40
Calcium	105	58	45
Magnesium	21,620	16,170	25
Manganese	9.5	5.1	46
Strontium	322	189	41
Uranium	146	11	93



Batch 1



Batch 2

Fig. 4.6. Phytoremediation batch tests: Batch 1(a), Batch 2(b). Batches 1 and 2 used NT-1 surface water and SS-4 water.

Table 4.3. Pretreatment values in test water from NT-1

Analyte	Batch 1	Batch 2	Batch 3	Batch 4
Aluminum	0.19	0.035	16.3	17.3
Barium	0.073	0.38	11.3	14
Beryllium			0.0123	0.0117
Boron	0.027	0.028	0.0663	
Cadmium		0.022	0.78	0.88
Calcium	40.7	140	2333	2533
Cobalt			0.51	0.58
Copper	0.0044	0.0058		
Iron	0.083	0.0056	0.19	0.21
Magnesium	0.083	21.3		380
Manganese	0.049	3.37	143	160
Nickel	0.0113	0.097	3.63	4
Phosphorous	0.22	0.22		
Potassium	3.9	4.4	40	51.7
Sodium	6.13	21	403	440
Strontium	0.15	0.43	6	6.53
Thallium			6	0.0014
Titanium	0.0038	0.0038	0.049	0.052
Uranium	0.00763	0.0176	0.006	0.006
Zinc	0.003	0.037	0.07	0.022

Table 4.4. Pretreatment values in test water from SS-4

Analyte	Batch 1	Batch 2
Aluminum	0.053	0.0397
Barium	0.087	0.137
Boron	0.044	0.045
Calcium	57.7	73
Lithium	0.015	0.0187
Magnesium	13	18
Manganese	0.0032	0.00157
Potassium	2.97	2.4
Sodium	11	11.7
Strontium	0.15	0.2
Uranium	0.0757	0.16

iron, manganese, nickel, potassium, and silver was observed, but the frequency and extent of removal was variable. Examining metal content in roots and shoots showed higher concentrations than control samples, but it was not possible to match the mass removed from water with the mass found in the plant.

4.4 CONCLUSION OF BIOLOGICAL TREATMENT TESTING

Table 4.5 describes the overall performance of the biotreatment systems. All three biological treatment systems were effective in removing uranium from test water. The wetlands system also removed nitrate to a significant degree. Its capacity to remove other metals is unknown since analysis included only uranium. Other metals were removed in both the phytoremediation and the algal mats systems. These results prove that although BCV water has harsh characteristics, biological systems can work effectively under these conditions.

Table 4.5. Overall summary of biological treatment testing

Approach	Passive	Uranium removal	Nitrate removal	Other metals
Wetlands	+	+	+	NA
Mats	+/-	+	+/-	+
Phytoremediation	-	+	NA	+

NA = Data not available.

The issues that distinguish these systems among themselves and among all of the BCV test technologies is the manner in which each would be implemented. The wetlands system is the only true passive system, but land area requirements and flow control will be key success factors. The algal mats can be considered semi-passive due to their regenerative nature and their capacity to handle varying flow rates. The phytoremediation system is not passive, requiring labor to propagate and harvest plants on a daily basis. Therefore, the wetlands and algal mats are viable options that should be tested further in Phase II.

5. PHASE I CONCLUSIONS

Field Characterization

Field screening activity identified three migration pathways within the eastern BCV area. One of these pathways stems from the S-3 Site and extends toward NT-1 and NT-2. The other two lead directly from the S-3 Site to Bear Creek in a southerly and southwesterly direction. Each of these pathways contains a distinct combination of uranium, nitrate, TDS, ⁹⁹Tc, and other nonradioactive metals. Therefore an individual system may be required specifically for each individual pathway.

Uranium Removal

Eight of the twelve test treatments performed well with BYBY water. The best performers were Dowex 21K resin, peat moss, algal mats, ZVI, iron oxides, and wetlands. Other treatment agents that were tested and did not perform well include zeolites, cercon zeolites, and biobeads. Capacity estimates based on equilibrium conditions suggested Dowex and peat moss have the highest potential capacity (> 5 mg U/g resin), with other media providing capacities in the range of 1 to 2 mg U/g medium.

Only five of the twelve media tested were able to perform under the high TDS conditions provided by NT-1 water. The principal interference in NT-1 appears to be nitrate, although high calcium and aluminum also contributed to low scoring of several sorbents. A leading performer, peat moss had lower removal efficiencies in this water, but still has potential for application with a capacity of 0.9 mg uranium removed per gram of peat moss used. ZVI is also a candidate for treatment in this area. The mechanism for removal appears to be the rapid corrosion of the iron, producing a colloid that binds uranium. Reduction of uranium to insoluble forms and uranium precipitation were also removal factors. Other media that performed well include iron oxides, algal mats, and TRW (a coal-based solvent).

Metals Removal

Several metals are present at relatively high levels within BCV CA. It is a secondary goal to remove these metals during treatment to reduce their impact on surface water ecology. Testing showed that sorbents were relatively ineffective in removing metals other than uranium from the test water from either source. Algal mats showed promising results with aluminum, barium, calcium, cadmium, magnesium, manganese, nickel, and strontium.

ZVI removed metals during batch experiments, but not during preliminary column experiments. This is attributed to more rapid corrosion of ZVI in batch tests and the longer residence time for metals to be exposed to the iron (compared to the column).

Nitrate Removal

Nitrate removal is an important consideration based on nitrate's negative impact on surface water ecology and its interference with treatment of NT-1 water. Nitrate reduction was observed in the wetlands and algal mats systems, although more testing is required to establish the

maximum potential rate of removal. In addition, the effect of biomass grown in a peat moss/ZVI environment should also be considered for further investigation. This combination of components provides the reducing environment, a support matrix, and a small amount of degradable carbon to support accelerated nitrate removal. This assembly of treatment media is the only treatment option identified at this time for nitrate removal in a trench configuration.

VOC Destruction

VOCs are present at most sites within BCV CA; therefore, their fate in a given treatment system is an important consideration. In batch experiments, both Fisher iron and MB iron removed VOCs from test water. MB iron performed with a shorter half-life than Fisher iron. Byproducts typical of reactive treatment were observed, indicating that sorption was not the sole mechanism for removal. Carbon tetrachloride daughter product half-lives were longer than the carbon tetrachloride half-life. This is potentially a serious issue because daughter products such as dichloromethane and chloroform can present adverse ecological and health effects. Palladium enhanced both iron forms, but the gain was too small to compensate for the added cost of palladium treatment.

Treatment Media Ranking

All media were ranked based on treatment performance, tolerance of TDS, and implementability (Table 5.1). The following list shows the ranking with the best candidates first. No single medium can satisfy all BCV requirements, so the ranking should be considered subjective and amenable to change based on site-specific needs.

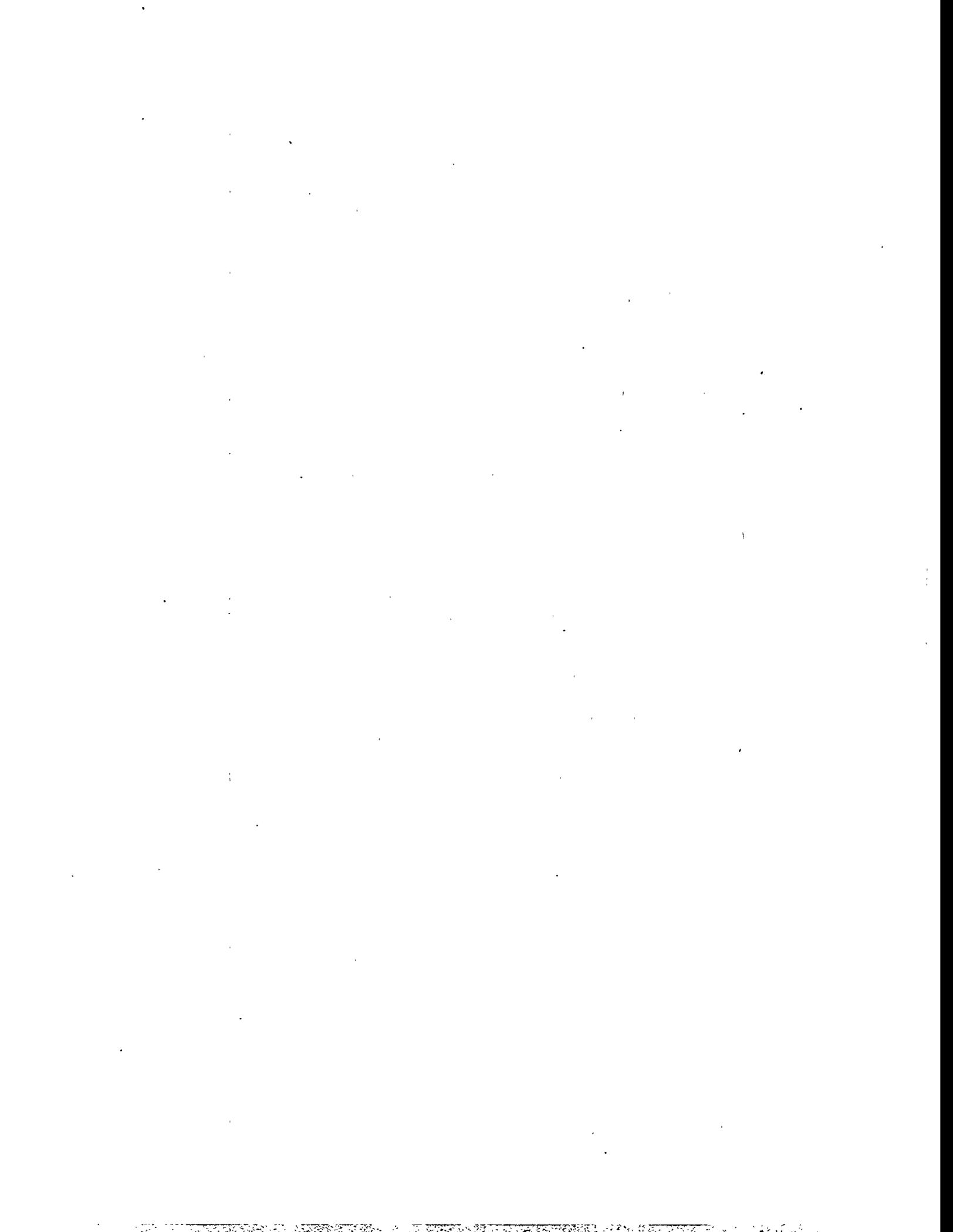
Table 5.1. Treatment media ranking

Medium	Target	Concerns
1. Peat moss	U, metals, VOC, nitrate	Unsure of long-term efficiency
2. ZVI	U, metals, VOC	Colloid release of U, VOC byproduct release
3. Iron oxides	U, VOC	Colloid release of U
4. Dowex	U	Little tolerance for TDS, effective only for U
5. Algal mats	U, metals, nitrate (surface water)	Needs sunlight, unsure of nitrate reduction capacity, full-scale engineering needed
6. Wetlands	U, nitrate	Fate of accumulated uranium, winter effects, long-term disposal of accumulated U in biomass
7. TRW	U	Not commercially available

6. RECOMMENDATIONS FOR PHASE II

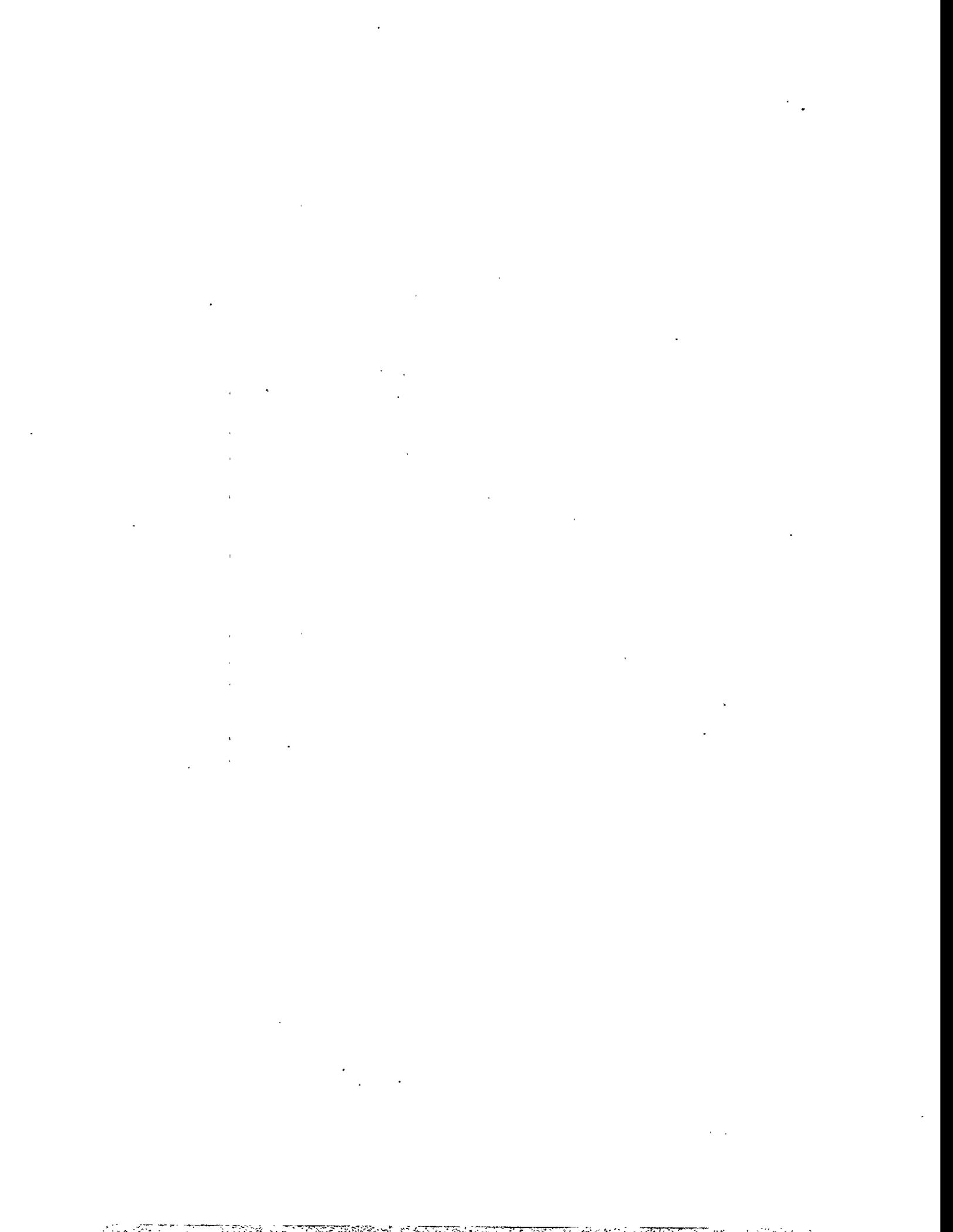
The objective of Phase II is to define those issues that impact treatment efficiency in a continual flow mode under actual site conditions. The goal of Phase II is to produce the guidance that is required to design an early action.

- (1) Conduct long-term column tests on field panels at S-3 Site to obtain a better understanding of uranium breakthrough and fate of VOCs, nitrate, and other metals using peat moss, ZVI, Dowex resin, and algal mats.
- (2) Identify and develop solutions for engineering issues related to implementation. Issues include pH buffering capacity, clogging, contaminant remobilization, undesirable endproducts, and medium configuration. Determine site-specific impact of native soil interaction.
- (3) Determine effectiveness of hydraulic and contaminant capture in trenches. Conduct pumping/slug tests on 4-in. piezometers. Install trenches and, possibly, additional piezometers to conduct pumping tests at the two types of flowpaths shallow to Bear Creek and deep to tributaries. Determine possible flow rates and treatment efficiency to size treatment trench. Evaluate changes during winter versus summer as well as baseflow versus storm events.
- (4) Determine treatment system configurations (e.g., above or below ground, backfilling trench, or removable configurations). Conduct paper study of existing systems that have been installed. Assess innovative deployment options and test during trench installation.
- (5) Conduct in-stream testing to determine long-term effectiveness and removal rates, and obtain sizing information for algal mats reduction of nitrate, uranium, and other metals at high nitrate and dissolved solids sites (NT-1, Bear Creek at S-3 Site). Define design strategy such as mat anchoring, precipitate capture, and storm flow control.
- (6) Define and address construction and waste water discharge issues, including permitting, reinjection, health and safety, waste generation, and radiological considerations.



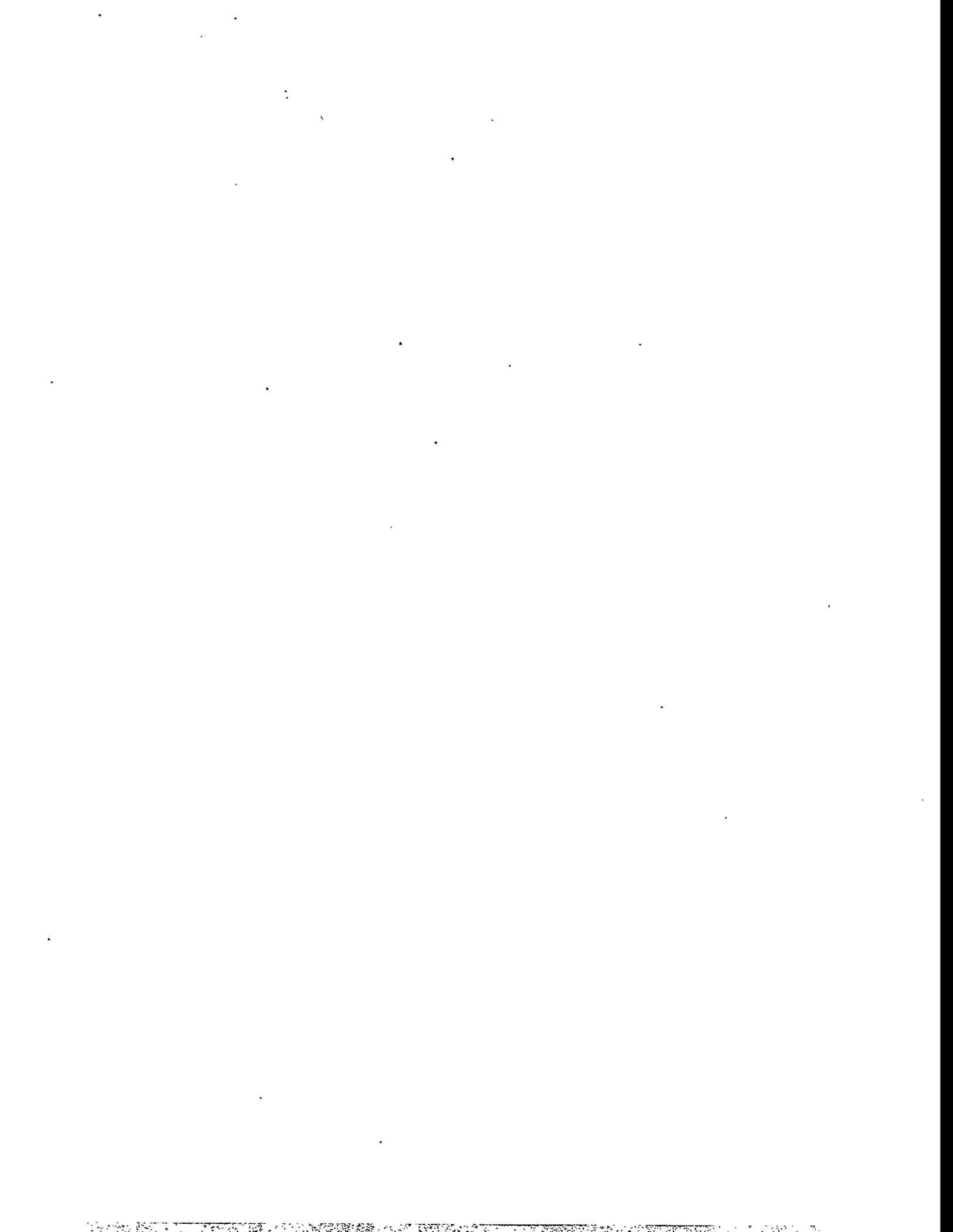
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APPENDIX A

**BEAR CREEK VALLEY TREATABILITY STUDY
PHASE I FIELD CHARACTERIZATION**



1. INTRODUCTION

This appendix describes the current results of site characterization activities outlined in Phase I of the *Bear Creek Valley Characterization Area Technology Demonstration Action Plan* (SAIC 1996a). Detailed direction regarding the Sampling and Analysis Plan, the Quality Assurance Project Plan, the Health and Safety Plan, and the Waste Management Plan for the site characterization is presented in the *Bear Creek Valley Passive Surface Water Treatment Technology Demonstrations, Phase I, Site Characterization* (SAIC 1996b). The areas of investigation are shown on Fig. 1 (all figures appear at end of appendix).

The scope of the site characterization at Bear Creek, NT-1, and NT-2 includes six tasks: (1) surface water field screenings, (2) surface water and seep sampling, (3) temporary piezometer installation and groundwater sampling, (4) hydraulic testing, (5) data evaluation, and (6) project support and technical report preparation. The detailed activities for each task are defined in the Sampling and Analysis Plan (Sect. 2) of the *Bear Creek Valley Passive Surface Water Treatment Technology Demonstrations, Phase I, Site Characterization* (SAIC 1996b).

The information presented and discussed in this appendix is preliminary and reflects Event 1 (summer) activities. A final report will be issued after results from Event 2 (winter) field activities are received.

2. OBJECTIVES

The field characterization activity was designed to provide site-specific data related to the migration pathways of contaminants in the unconsolidated zone and to determine the impact of these flowpaths on the tributaries.

The objectives of the field activities included the following:

- determine the discrete locations where contaminants are entering Bear Creek main stem, NT-1, and NT-2; the surface water quality at these locations; and the temporal changes in surface water flow and water quality;
- determine subsurface geologic, hydraulic, and geochemical conditions where contaminants are entering Bear Creek, NT-1, and NT-2, such as determining depth to bedrock, hydraulic conductivity, hydraulic gradients, porosity, changes in groundwater inflow rates to the tributaries, spatial and temporal groundwater quality variations, and impact of storm events and seasons on groundwater flow and quality (i.e., evaluate shallow stormflow impact); and
- obtain representative groundwater samples from BYBY, S-3 Site, and NT-1 for the principal investigators to test during Phase I laboratory work.

3. APPROACH

The investigation approach for the site characterization was designed to determine the following (SAIC 1996b):

- locate the discrete points of groundwater discharge in tributaries NT-1, NT-2, and Bear Creek adjacent to the S-3 Site through surface water sample collection and in-field screening (Task 1);
- determine contaminant geochemistry of surface water and selected seeps along these reaches (Task 2);
- analyze groundwater field parameters near discharge points, and identify locations of groundwater contaminant pathways (Task 3);
- provide site-specific groundwater and geotechnical data for the Phase I laboratory testing of potential treatment media (Task 3); and
- obtain sufficient data on site hydrogeology to support Phase I laboratory testing and location of the groundwater capture and treatment systems in Phases II and III (Task 4).

4. SITE CHARACTERIZATION FIELD ACTIVITIES

The site characterization field activities include Tasks 1 through 4. There are two major sampling efforts in the site characterization: a summer (current) event and a winter event. The winter event has not been completed at this time. Accomplishments and progress of each task during the summer sampling event are summarized in this section.

4.1 TASK 1: SURFACE WATER FIELD SCREENINGS

Surface water grab samples were collected at 73 locations to find discrete points of groundwater discharge along reaches of Bear Creek, NT-1, and NT-2 (Figs. 2 through 4). Sample collection in NT-1 and NT-2 was upstream from each confluence with Bear Creek. Sample collection in Bear Creek was conducted upstream of pooled water caused by a large beaver dam at BCK 12.46.

Samples were collected from the main channel of each stream and from identifiable seeps adjacent to the main channel. Recognition of seepage areas was done visually (by noting obvious wet areas) and by observing trends in field measurements in the main stream. At each sampling location, conductivity, pH, and temperature were measured. Field analysis of nitrate concentration was also performed. Trends in the field parameter measurements are shown in Figs. 2 through 4. Selected locations were analyzed for uranium by the Y-12 Analytical Services Organization (ASO) (Figs. 5 through 7). These data are also summarized in Tables 1 through 3 (all tables appear at the end of appendix).

Significant field observations: Bear Creek was initially sampled during a dry (summer low-flow) period (June 6, 1996). Except for a small pool located at Station BC 135, the creek was dry upstream of Station BC 1030. Initiation of flow coincided with the locations of two seeps adjacent to the stream channel. Data from the previously dry reach were collected at a later date following a rain event (summer high-flow period, June 14, 1996) (Fig. 4).

Outstanding task activities: A second round of surface water screenings is scheduled during the upcoming winter sampling event. The objective will be to determine whether locations of seepage areas change in response to seasonal changes and to identify any additional high-flow period seepage areas.

4.2 TASK 2: SURFACE WATER (SEEP) SAMPLING

Surface water (seep) samples were collected from five locations (Figs. 2 through 4): Stations NT2 970, NT1 200, NT1 390, BC 1030, and BC 1280. The purpose was to determine surface water contaminant geochemistry at these locations. The sample locations were at the most active or significant seeps based on the results of Task 1 field screening. These samples were submitted to the Y-12 ASO for the following analyses: volatile organics, inductively coupled plasma (ICP) metals, radiochemistry (including fluorimetric uranium and tritium), anions, alkalinity, mercury, bicarbonate, and total dissolved solids/total suspended solids (TDS/TSS) (Table 4). Field parameters were measured at time of collection (Table 5).

Significant field observations: Conductivity measured while collecting a surface water sample at Station NT1 390 on September 19, 1996 was significantly higher (17.4 mS/cm) than measured during the Task 1 field screenings on June 4, 1996 (1.07 mS/cm). The only other surface water sample location with higher measured conductivity was Station NT1 075 (22.3 mS/cm). Since the initial Task 1 field screenings, additional activity by a beaver population has flooded the lower reach of NT-1 and currently prevents collection of a sample at Station NT1 075 (Fig. 3).

Outstanding task activities: A second round of surface water (seep) sampling is scheduled during the upcoming winter sampling event. The objective will be to determine whether the chemistry of the surface water and seeps change in response to seasonal changes.

4.3 TASK 3: PIEZOMETER INSTALLATION AND GROUNDWATER SAMPLING

To identify groundwater contaminant pathways, temporary piezometers were installed adjacent to locations of groundwater discharge recognized in the previous tasks. The piezometers were installed in two phases. The first phase involved installation of 25 temporary piezometers (TPB-01, -02, -04 through -06, and -08 through -27) using push probe (geoprobe) drilling methods (Fig. 8). All borings were pushed to refusal (bedrock) and piezometers constructed using 1-in. diameter PVC casing with 2-ft screened intervals at total depth (Fig. 9). Groundwater grab samples were collected from each piezometer during the sampling event (summer baseflow period) and field screened for specific conductivity, pH, temperature, and nitrate concentration. Nearly all piezometers were sampled for uranium screening by the Y-12 ASO. During this phase, a staged approach was employed to use the results from the initial piezometer screenings to

determine the locations of the later ones. Boring information for each push probe temporary piezometer, including depth to water measured in each on June 24, 1996, is in Table 6.

In the second phase, four temporary piezometers (GW-834 through -837) were installed using hollow stem auger drilling methods (Fig. 10). These temporary piezometers were located to intercept contaminated groundwater flow identified from results of the first phase. All borings were augered to refusal (bedrock) and piezometers constructed using 4-in. diameter PVC casing with 2-ft screened intervals at total depth (Fig. 9). Attempts were unsuccessful to collect shelly tube samples for geotechnical analysis from these borings. The shelly tubes could not be pushed through the sample interval without crushing and, therefore, were not collecting sufficient sample volume for analysis. Piezometers were developed by Y-12 Groundwater Protection Program personnel (Kimbrough et al 1994). One piezometer (GW-836) was not completely developed due to slow recharge rate. Boring information for each augered temporary piezometer is in Table 7.

Groundwater samples were collected from three of the piezometers (GW-834, -835, and -837) and submitted to the Y-12 ASO for the following analyses: volatile organics, ICP metals, radiochemistry (including fluorimetric uranium and tritium), anions, alkalinity, mercury, bicarbonate, and TDS/TSS (Table 8). Field measurements were also recorded at the time of sample collection (Table 9).

To better delineate groundwater contaminant pathways, five additional temporary piezometers (TPB-28 through -32) were installed at the end of the second phase using push probe (air hammer) techniques (Fig. 8). All borings were pushed to refusal (bedrock) and piezometers constructed using 1-in. diameter PVC with 2.1-ft screened intervals at total depth (Fig. 9). Groundwater grab samples were collected from these piezometers for field screening of conductivity, pH, temperature, and nitrate concentration and uranium screening by the Y-12 ASO.

Significant field observations: Each of the push probe temporary piezometers had groundwater grab samples collected between June 14 through 26, 1996. Following a heavy rainstorm, the piezometers at NT-1 were sampled on August 2, 1996 for field screening (conductivity, pH, and temperature). TPB-02 had the highest conductivity reading for groundwater (30.3 mS/cm) observed to date (Fig. 8).

Elevated beta/gamma readings were encountered during the boring of GW-836 (~400 cpm). These readings were from soil below the water table brought to the surface on the augers. Elevated mercury vapor concentration was measured in the soil cuttings from GW-837 (maximum 0.777 mg/ml). Cuttings were left uncovered overnight and mercury vapor concentration dropped below an acceptable value, allowing work to continue.

Outstanding task activities: Groundwater grab samples from piezometers TPB-28 through -32 will be collected for field screening of conductivity, pH, and temperature and uranium screening by the Y-12 ASO. These activities will be coordinated with Y-12 Health Physics due to recent radiological control requirements.

Groundwater grab samples from the push probe piezometers will be collected and field screened at base- and high-flow periods during the upcoming winter sampling event. Groundwater samples will also be collected during these periods from the augered piezometers for chemical

analysis by the Y-12 ASO. The objective will be to determine how chemistry of groundwater changes in response to seasonal changes and also to variations in flow during the winter event.

4.4 TASK 4: WATER TABLE LEVEL MONITORING AND HYDRAULIC TESTING

Continuous monitoring of water level, specific conductivity, and temperature in GW-834, -835, 836, and -837 began on August 28, 1996 and continued through September 30, 1996 (one month duration). The purpose of this task was to obtain sufficient data on site hydrogeology to support Phase I laboratory testing and Phase III location selection of the groundwater capture and treatment trench (SAIC 1996a). The results of the monitoring are shown on Figs. 11 through 14.

Outstanding task activities: A pump test will also be conducted in piezometer(s) to attempt to characterize the aquifer and to estimate the pumping flow rates the piezometer(s) can sustain with time.

Continuous monitoring of water level, specific conductivity, and temperature will be conducted for one month during the winter sampling event. This equipment will then be removed and decontaminated. Water levels in the push probe piezometers will be measured periodically to record any changes in depth. The objective will be to determine whether groundwater levels change in response to seasonal variations.

4.5 SAMPLING AND MEASUREMENT METHODS

Surface and groundwater field screen parameters are measured using a Horiba U-10 instrument (specific conductivity, pH, and temperature). Nitrate concentrations are determined in the field using a HACH AccuVac Nitraver 5 Nitrate Test Kit with a measurement range of 0 to 50 ppm.

Surface water for analysis by the Y-12 ASO has been collected as grab samples using a dipper (for VOA collection) and a peristaltic pump. Use of the pump allowed filtering of samples in the field with disposable in-line filters.

The push probe piezometers were purged dry with a peristaltic pump and allowed to recover before sampling groundwater for field screen parameters. The augered piezometers were developed as per approved Lockheed Martin Energy Systems, Inc. procedures (Kimbrough et al. 1994) prior to sampling. Groundwater grab samples for analysis by the Y-12 ASO were then collected from the temporary piezometers using a peristaltic pump and a check ball apparatus (for VOA collection). Use of the peristaltic pump allowed the filtering of samples in the field with disposable in-line filters.

Depth to water in the push probe piezometers was measured using an electronic water level indicator. Continuous monitoring of water level, conductivity, and temperature in each augered piezometer was recorded using an Omnidata® EasyLogger™ 900 Series datalogger, a Druck® pressure transducer (water level), and a Hydrolab® H20® Multiprobe (specific conductivity and temperature).

All locations requiring horizontal and vertical control have been established. A civil survey has been conducted as specified in the Quality Assurance Project Plan (SAIC 1996b).

5. PRELIMINARY DATA EVALUATION (TASK 5)

A preliminary data evaluation for each site investigation task conducted during the summer sampling event is presented in this section.

5.1 SURFACE WATER FIELD SCREENINGS

Conductivity, pH, temperature, and nitrate concentration observed during the screening of surface water and seeps can be used to recognize discrete points of groundwater discharge at Bear Creek, NT-1, and NT-2. At each stream, seep discharge has characteristic measurement responses. The trends of values observed in the stream are shown to be influenced by these discharges. Observations at each location are summarized below.

Bear Creek

- Eight seeps were identified along Bear Creek: BC 600, BC 900, BC 1030, BC 1150, BC 1215, BC 1280, BC 1300, and BC 1330. During summer baseflow (June 6, 1996), stream flow began at Station 1030 (Fig. 2). Following a period of rain prior to June 14, 1996, water was present in the previously dry reach of Bear Creek upstream of Station BC 1030 (summer high flow) and allowed identification of seeps at BC 600 and BC 900.
- In-stream values for pH (7.0 to 7.4) and temperature (16 to 19° C) were similar along the reaches of upper Bear Creek sampled during high- and low-flow periods. A short reach with significantly higher conductivity water was observed between Stations BC 500 and 750 during the high-flow period measured on June 14, 1996 (Fig. 2). In-stream values for specific conductance outside this short reach were similar during high- and low-flow periods (~ 1.0 mS/cmM).
- In-stream nitrate concentrations were 2 to 3 times higher in the low-flow period compared to the high-flow period.
- Identified seeps up-stream of BC 1030 (high-flow period only) generally had screening values similar to adjacent in-stream values for specific conductance, pH, and temperature. Identified seeps down-stream of and including BC 1030 (low-flow period only) fit two patterns compared with adjacent in-stream values: (1) similar nitrate concentrations and lower temperature (BC 1030, 1150, and 1330); and (2) non-detectable nitrate concentrations and slightly higher temperature (BC 1215, 1280, and 1300). For seeps below BC 1030, pH values were generally lower than in-stream values.
- Uranium concentrations in seeps up-stream of BC 1030 (high-flow period) were 2 to 3 times higher than those seeps down-stream of and including BC 1030 (low-flow period).

No single seep can account for uranium contamination in upper Bear Creek. Contamination is likely derived from more diffuse seepage of groundwater into the channel of Bear Creek above BCK 12.46. Identifiable seeps located at sites with higher groundwater discharge likely define a preferential groundwater flow path(s). The occurrence of a groundwater discharge point adjacent to the location where dry weather flow starts in Bear Creek may indicate that this seep (BC 1030) is connected to this pathway(s).

NT-1

- Three active seeps were identified in NT-1: NT1 075, NT1 200, and NT1 390.
- Seeps at NT-1 are characterized by higher conductivity and nitrate concentrations and lower pH compared to adjacent in-stream values (Fig. 3).
- The in-stream concentration of nitrate increases down-stream from approximately 10 ppm at NT1 500 to > 50 ppm at NT1 250 where the concentration exceeded the upper limit of the in-field analytical method (50 ppm). Concentrations of nitrate at seeps NT1 200 and NT1 390 were 1800 and 720 ppm, respectively (September 19, 1996). The concentration of nitrate and the specific conductance at seep NT1 390 varied between sampling events (June 4 and September 19, 1996): nitrate concentration increased from 20 ppm to 720 ppm and specific conductance increased from 1.07 mS/cm to 17.4 mS/cm.
- Coincident with the increase of nitrate concentration, pH of in-stream flow decreases down-stream from NT1 390. This is consistent with the additive discharge of groundwater with lower pH from the seeps to NT-1 compared to the in-stream values along this reach.

No single seep can account for contamination observed in NT-1. However, NT-1 is contaminated by discharge from a zone extending from approximately NT1 500 to NT1 50. Within this zone, identifiable seeps are located at sites with higher groundwater discharge (NT1 75, 200, and 390) and may indicate discharge from preferential groundwater flow paths. These seeps probably account for a large proportion of the total contaminant influx into NT-1.

NT-2

- Two active seeps were identified in NT2: NT2 645 and NT2 970.
- Seeps at NT2 are characterized by higher conductivity and nitrate concentrations and lower pH compared to values measured in the adjacent stream (Fig. 4).
- The in-stream nitrate concentration increases from less than 20 ppm to > 50 ppm between NT-2 1000 and NT-2 950. This is coincident with the seep at NT2 970, which had a nitrate concentration of 1000 ppm on September 12, 1996.

No single seep can account for contamination observed in NT-2. However, this stream is contaminated by discharge from a zone extending from approximately NT2 645 to NT2 970. Within this zone, two identifiable seeps are located at sites with higher groundwater discharge (NT2 645 and 970) and indicate discharge from preferential groundwater flow paths. Of these

two seeps, NT2 970 appears to account for the largest proportion of the total contaminant influx into NT-2.

5.2 GROUNDWATER SAMPLING

Screening results of groundwater from the temporary push probe piezometers are consistent with the screening results from the active seeps (groundwater discharge points) recognized during the surface water screenings. By using a staged approach in installing these piezometers, locations of groundwater contaminant pathways during the summer baseflow period have been delineated. Three migration pathways have been identified and are shown in Fig. 15. The screening results from push probe piezometers characterizing these pathways are summarized below:

- Migration pathway 1:** to Bear Creek south of the S-3 site;
shown in Piezometers TPB-09 and TPB-19 by elevated conductivity, nitrate concentrations, uranium concentrations, and gross alpha and beta activity, and by a decrease in pH.
- Migration pathway 2:** to Bear Creek through the area Piezometers TPB-07, -08, -15, and -16 are located;
shown by elevated uranium concentrations and gross alpha and beta activity in these piezometers. Nitrate concentrations in these piezometers were not elevated.
- Migration pathway 3:** along NT-1 and extending to NT-2;
shown by elevated conductivity, nitrate concentrations, and gross alpha and beta activity in Piezometers TPB-01, -02, -04, and -24. Uranium concentrations are relatively low overall. This pathway also discharges to NT-2 further along stratigraphic strike. At NT-2, it is characterized by elevated conductivity in Piezometer TPB-12 and elevated gross alpha and beta activity in Piezometers TPB-13 and -20.

Augered piezometers are located within one of the three contaminant pathways recognized along NT-1 and Bear Creek (Fig. 15). A preliminary evaluation of the analytical results of groundwater collected from the augered piezometers GW-834, -835, and -837 shows the values to be consistent with the push probe piezometers field screening results. The analytical results are summarized in Table 10.

The analytical results from the groundwater seep at Station NT1 200 along NT-1 (Fig. 3) may show a significant exception to the characterization of these contaminant pathways. At this single location, uranium concentration is similar to that seen in the temporary piezometers within migration pathways 1 and 2 along Bear Creek. Confirmation of this result will be made during Event 2 (winter) sampling of the site characterization. The analytical results from the groundwater seep at NT1 200 are summarized below:

- NT1 200 (in migration pathway 3): nitrate concentrations (1800 mg/L);
uranium concentrations (2.1 µg/g);
gross alpha (56 pCi/L);
gross beta (740 pCi/L);
⁹⁹Tc (15,000 pCi/L).

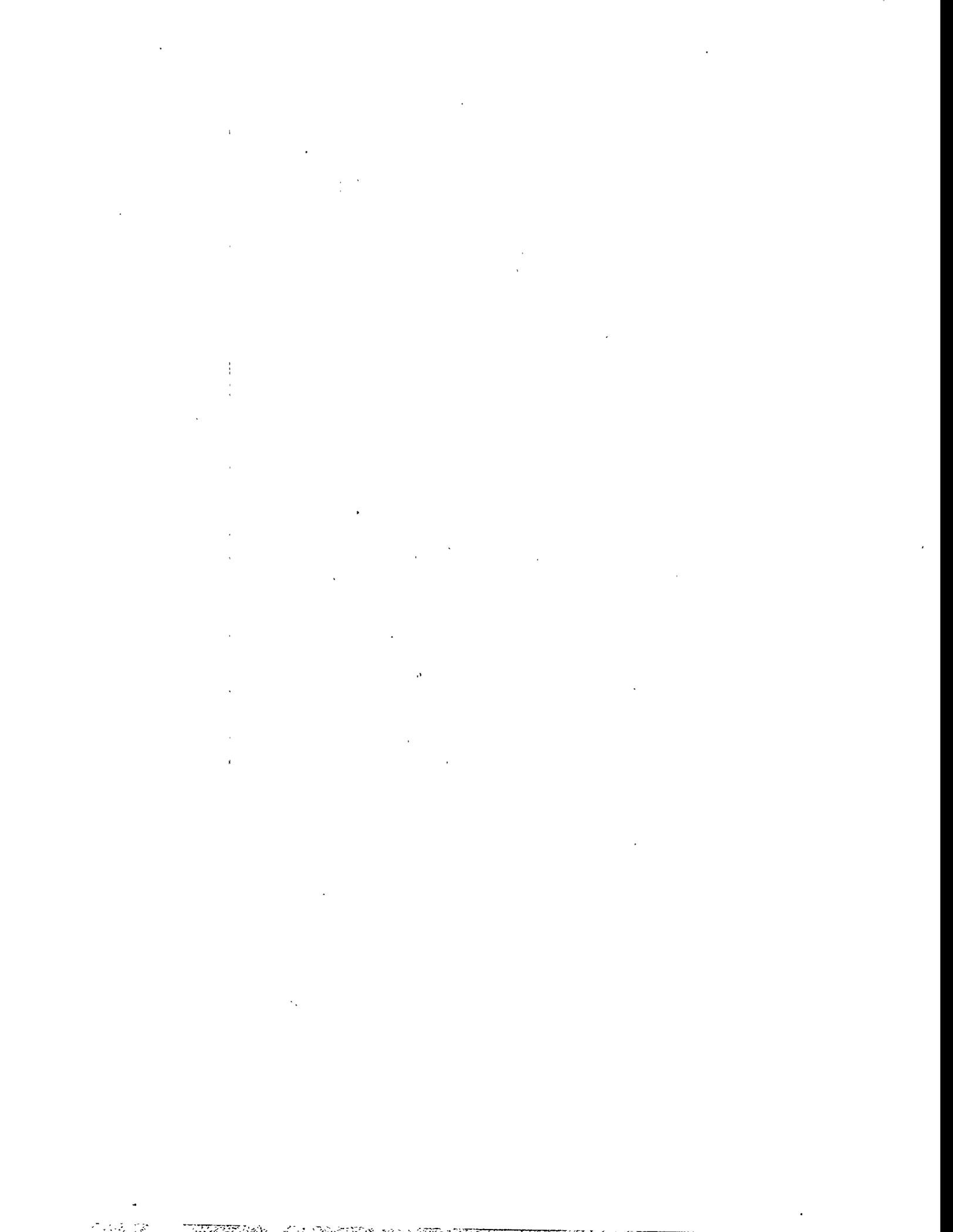
A complete evaluation of the analytical results will be presented in the final report of the site characterization activities following completion of all field and analytical activities.

5.3 WATER TABLE LEVEL, CONDUCTIVITY, AND TEMPERATURE MONITORING

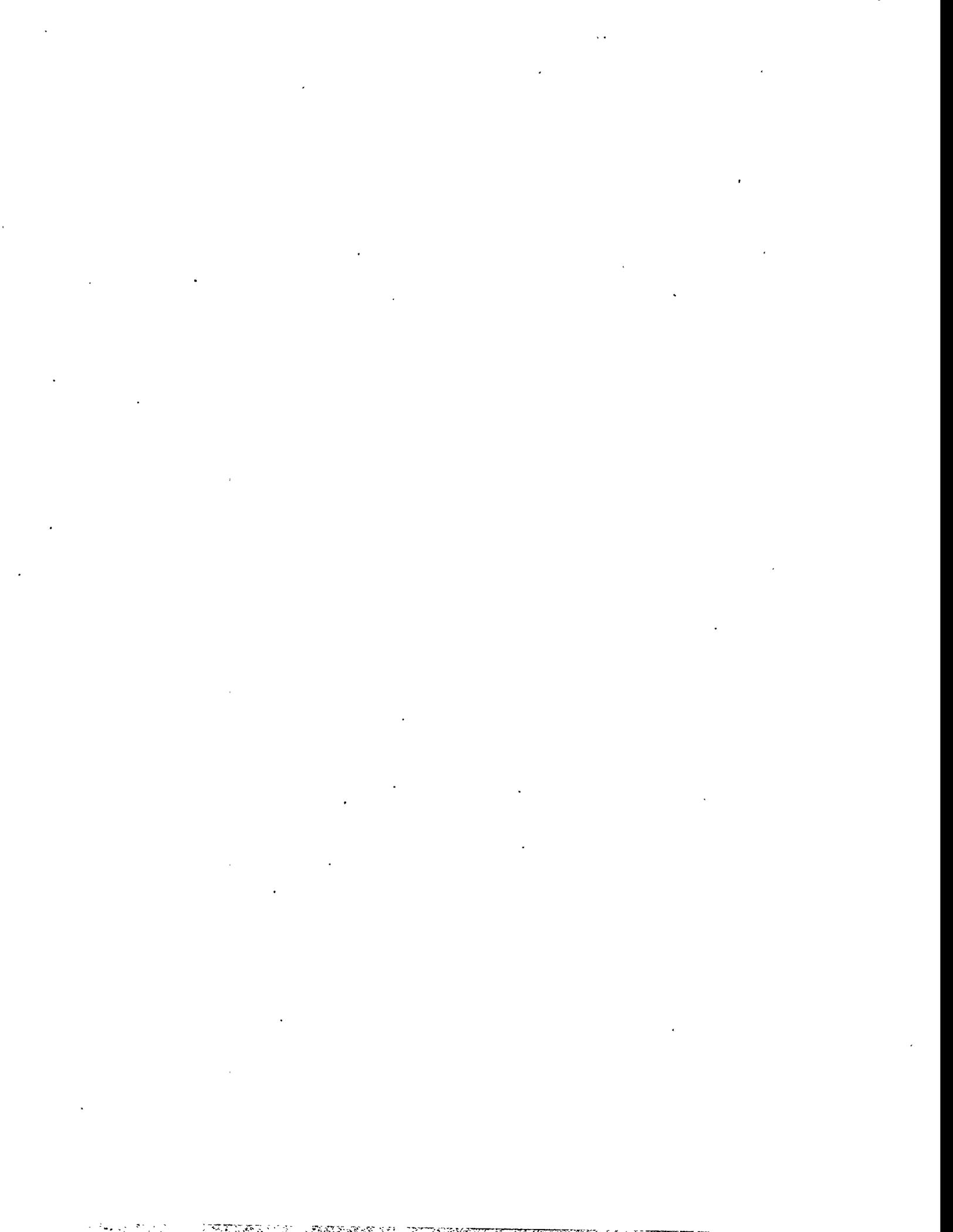
Water table levels, conductivity, and temperature have varied little during the monitoring in GW-834, -835, -836, and -837. A slight water level increase was noted in BPA-02 on September 4, 1996. Weather data have not been incorporated in the interpretation at this time.

6. REFERENCES

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- SAIC (Science Applications International Corporation). 1996a. *Bear Creek Valley Characterization Area Technology Demonstration Action Plan*, Draft, Y/EN-5479, prepared for Lockheed Martin Energy Systems, Inc., Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, April.
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FIGURES



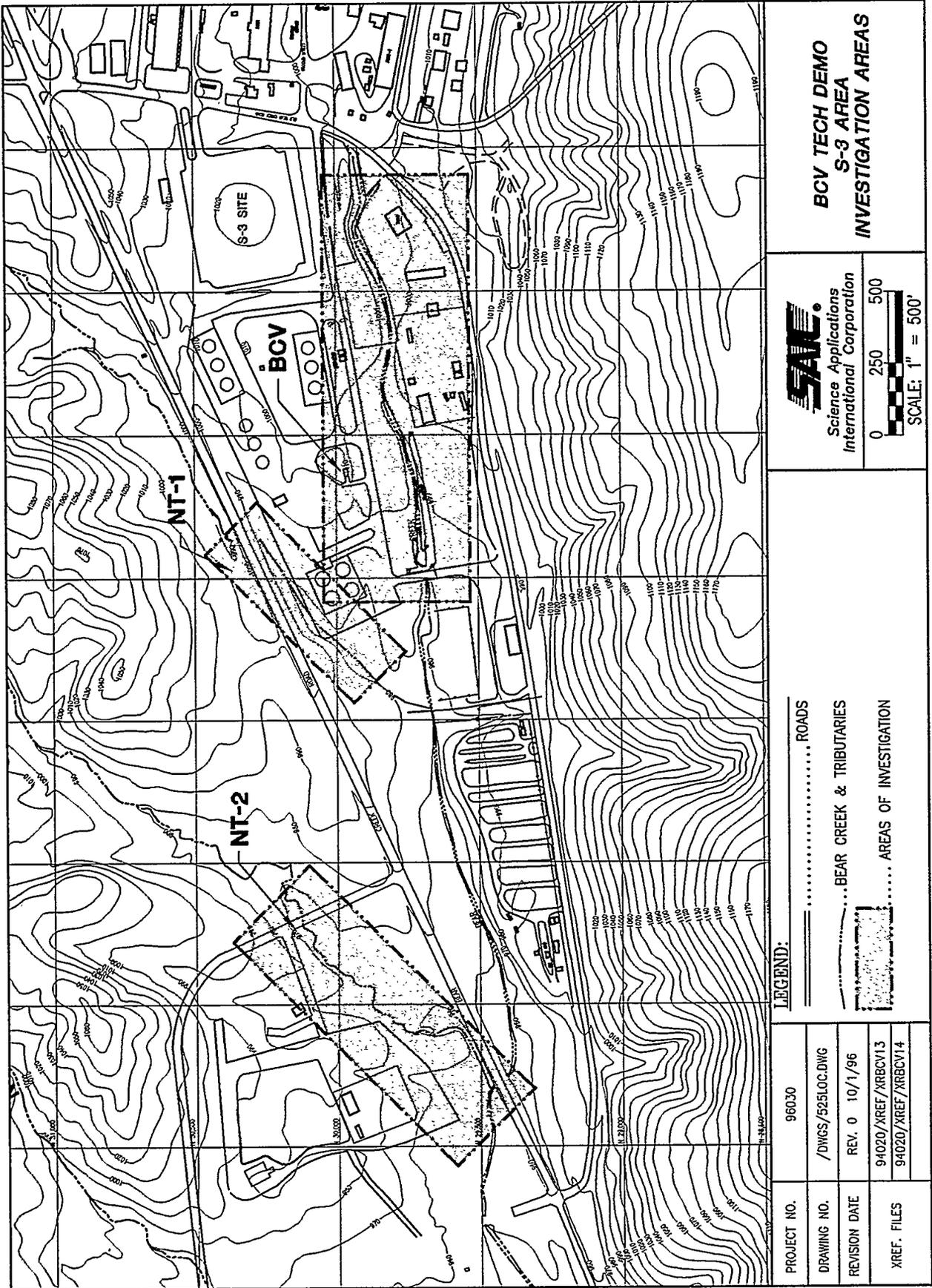
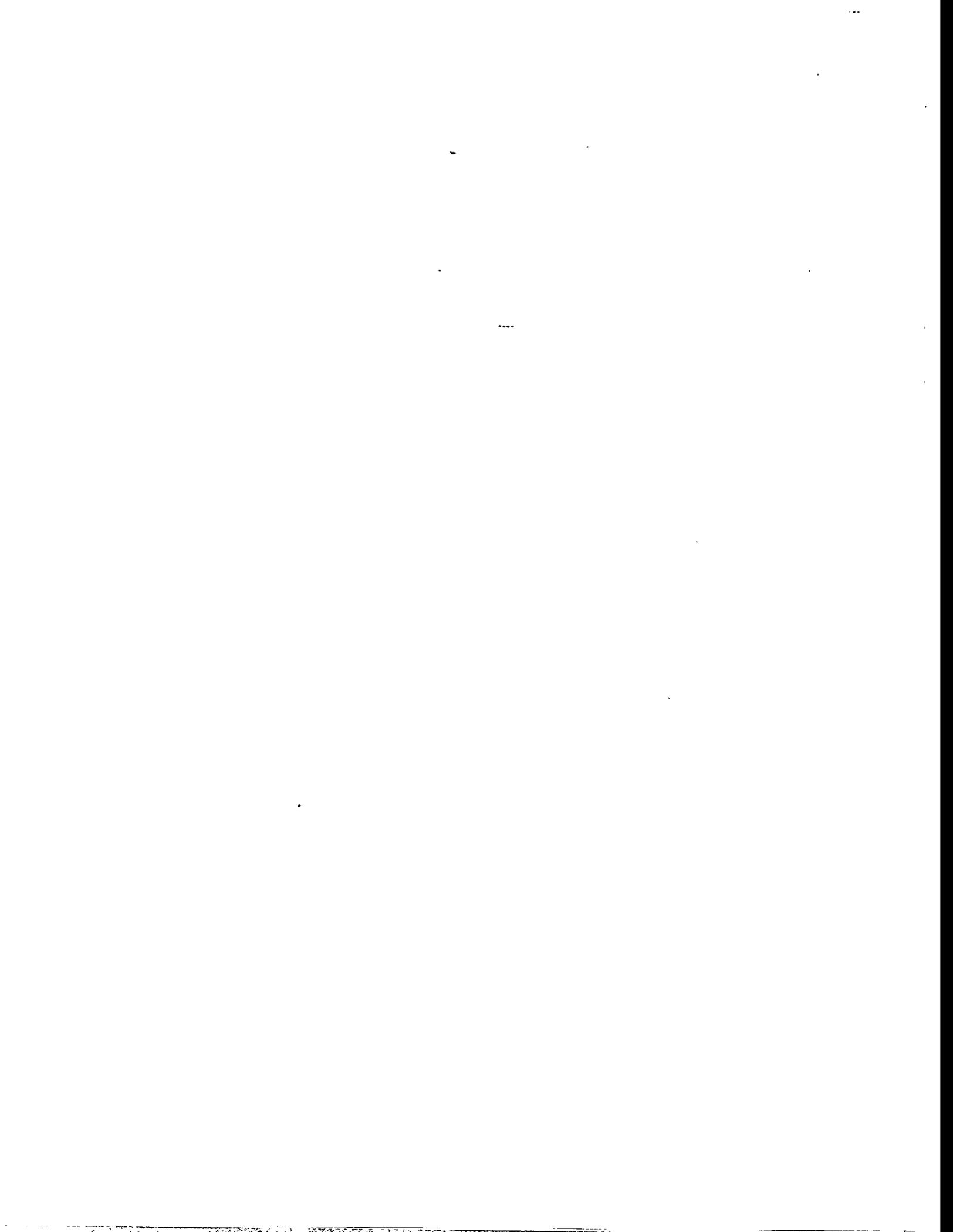
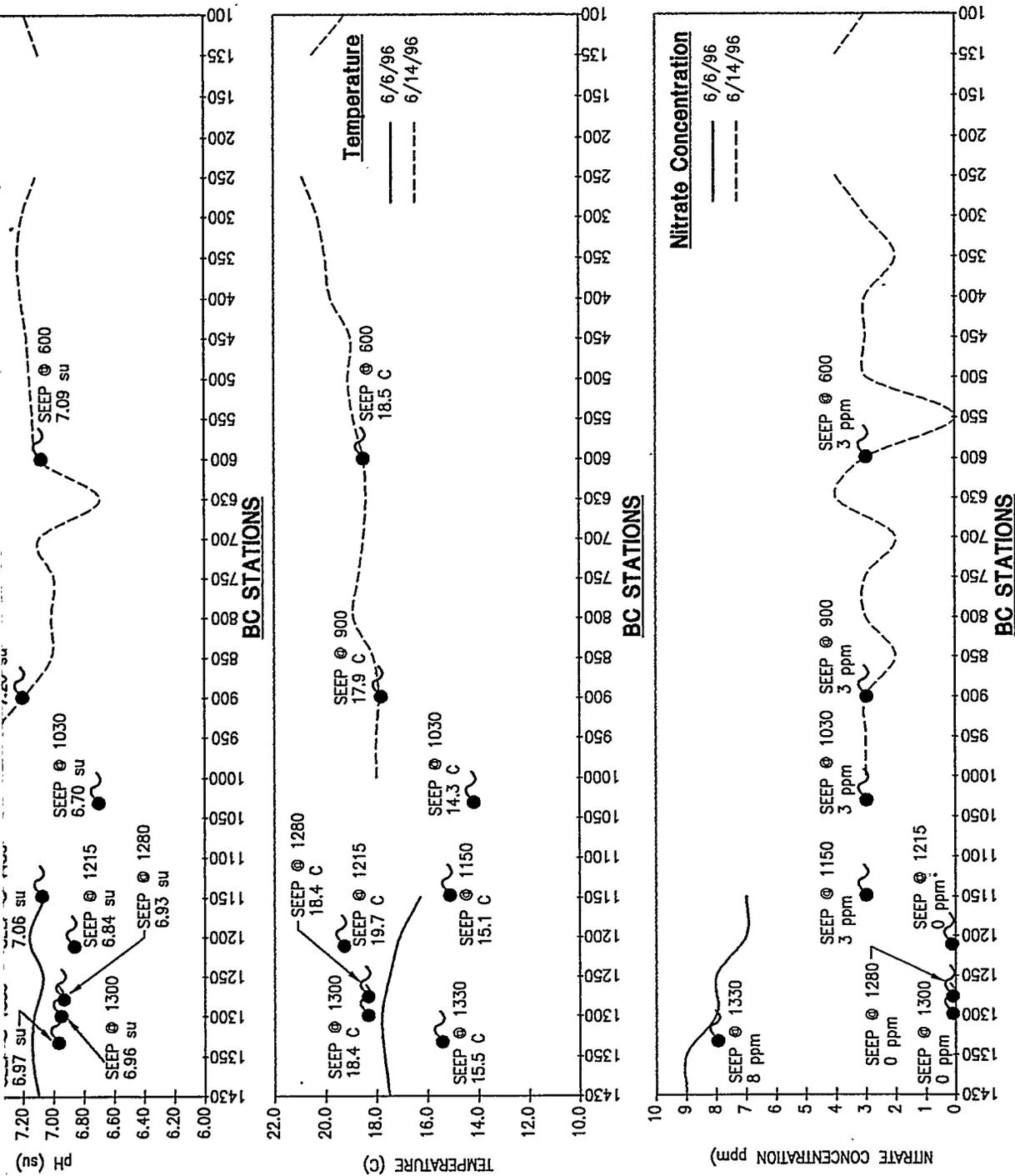


Fig. 1. Areas of investigation.





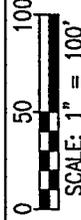
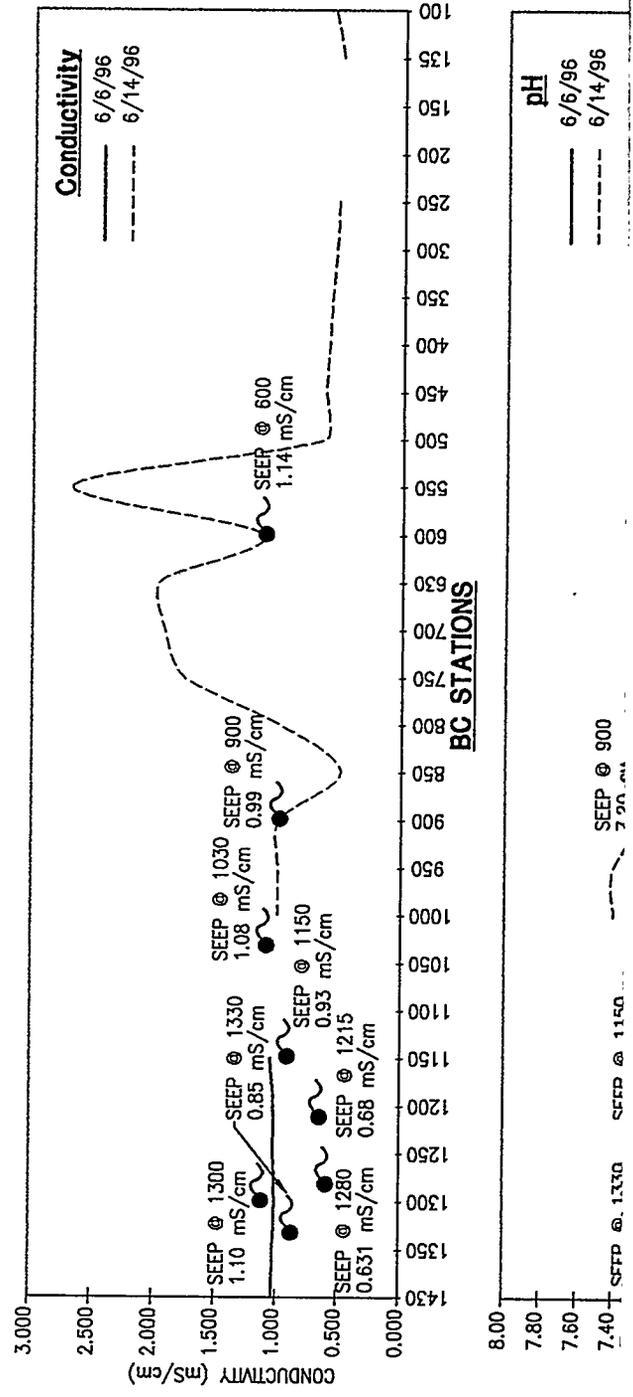
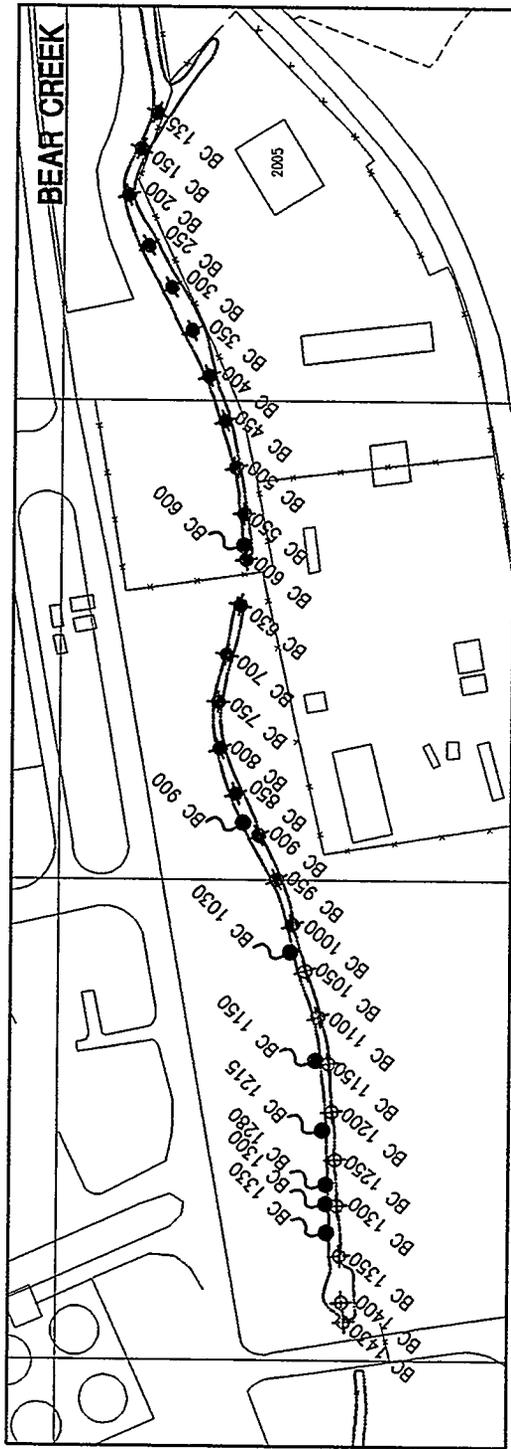
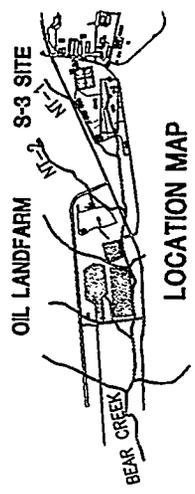
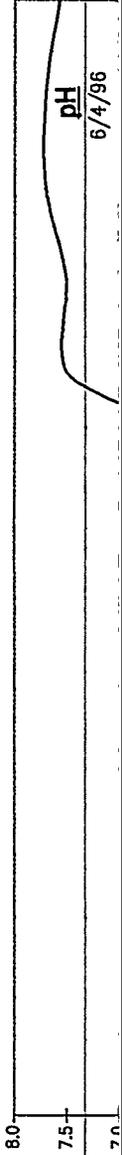
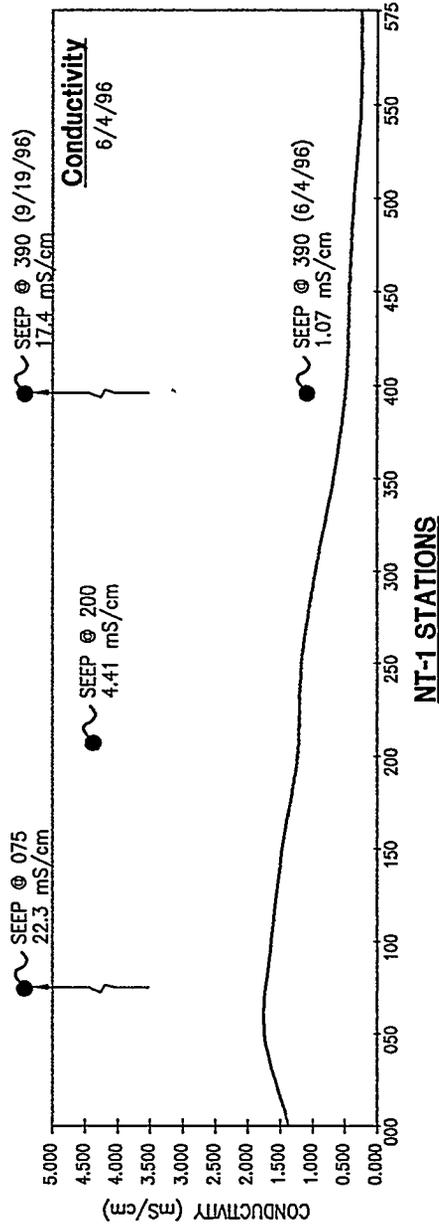
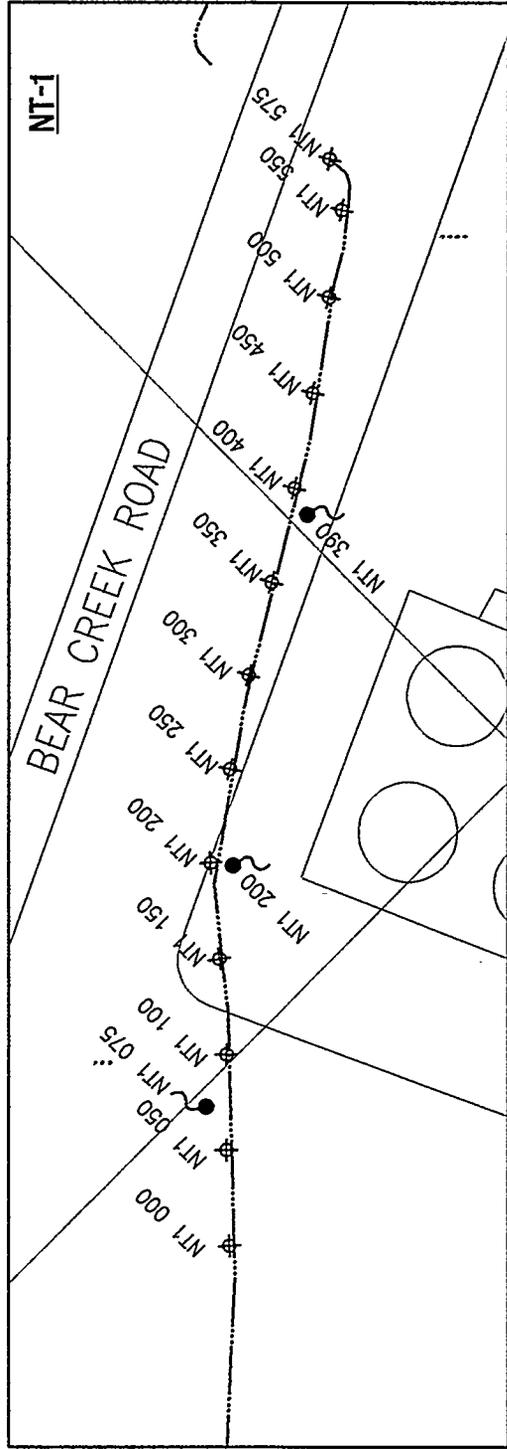
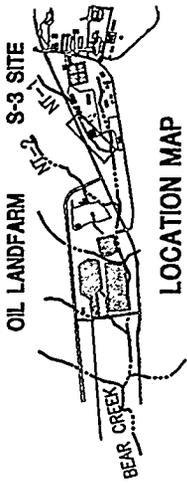
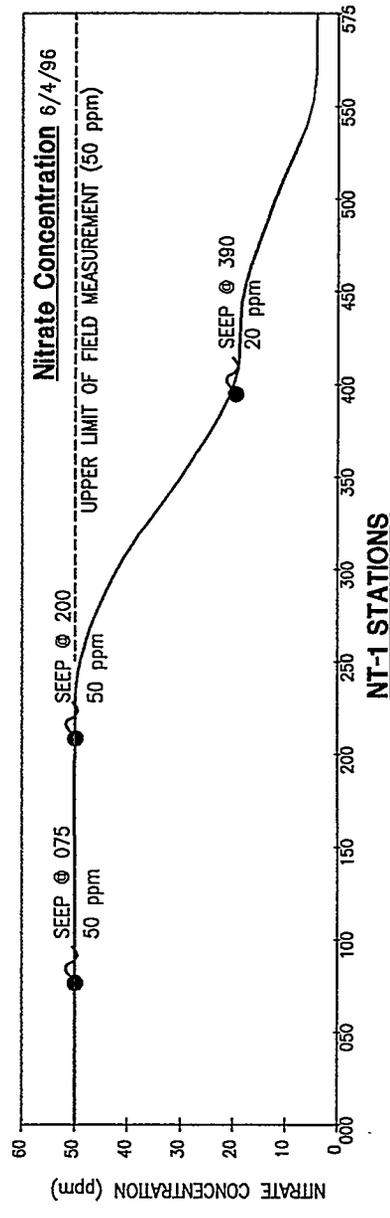
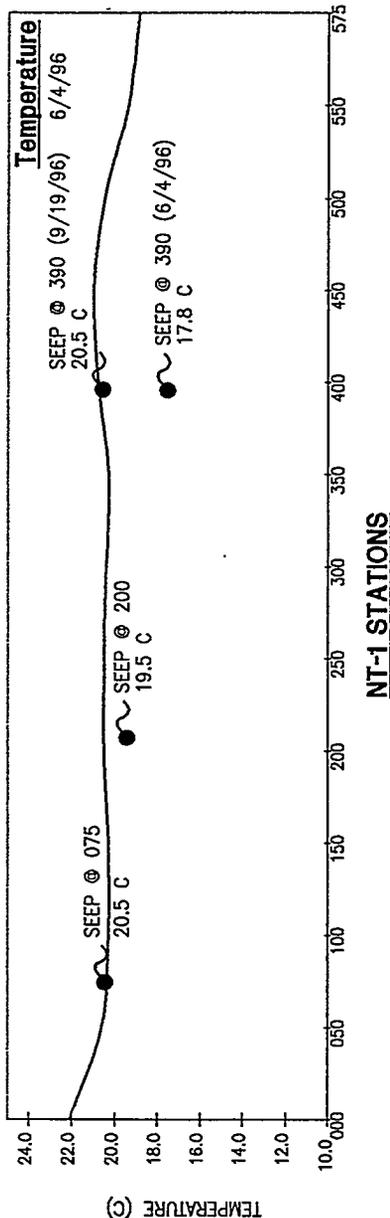
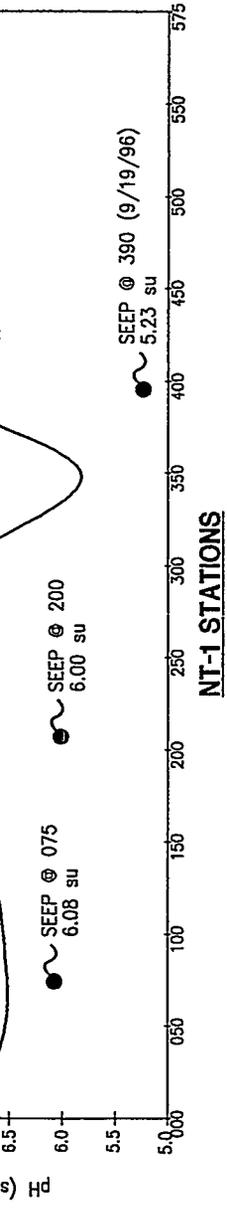
PROJECT NO.	96030	BEAR CREEK VALLEY S-3 AREA
DRAWING NO.	/DWGS/525BCV.DWG	 Science Applications International Corporation
REVISION DATE	REV. 1 / 11-18-96	
XREF. FILES	94020/XREF/XRBCV14	 SCALE: 1" = 100'
LEGEND: ROADS BEAR CREEK & TRIBUTARIES TRIBUTARIES SAMPLE STATIONS STREAM (6/6/96) STREAM (6/14/96) SEEP		

Fig. 2. Bear Creek surface water sample locations and field screening results.

Y-12 PLANT NORTH

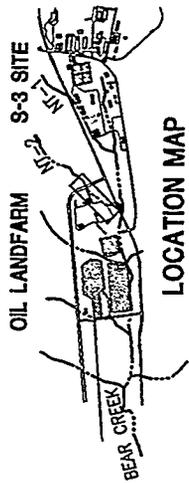




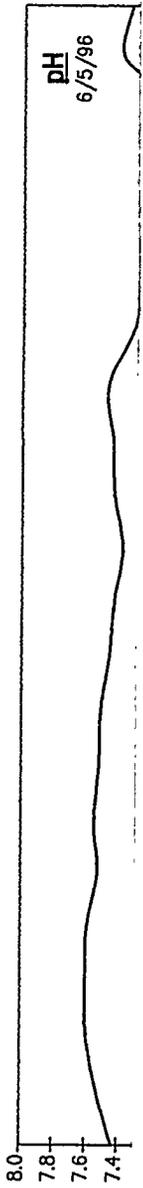
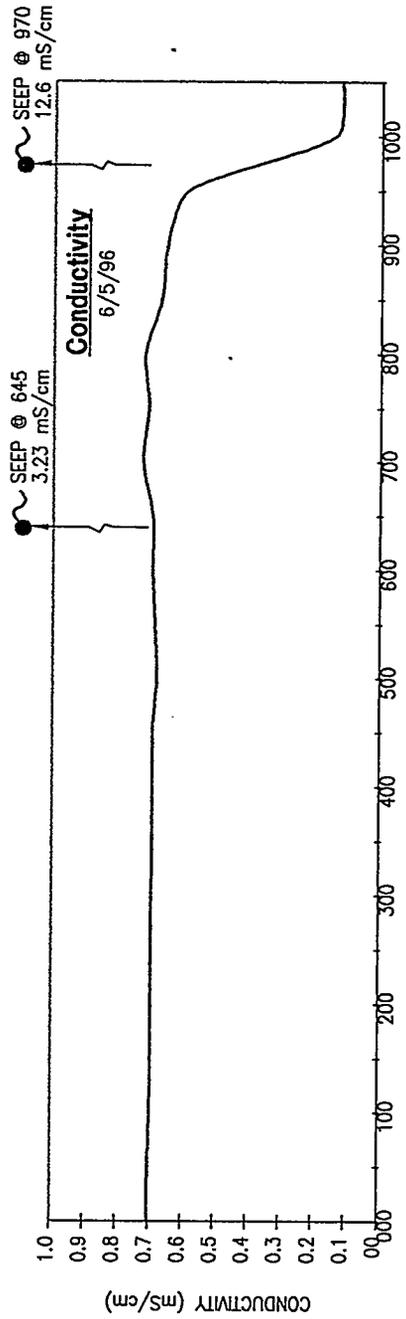
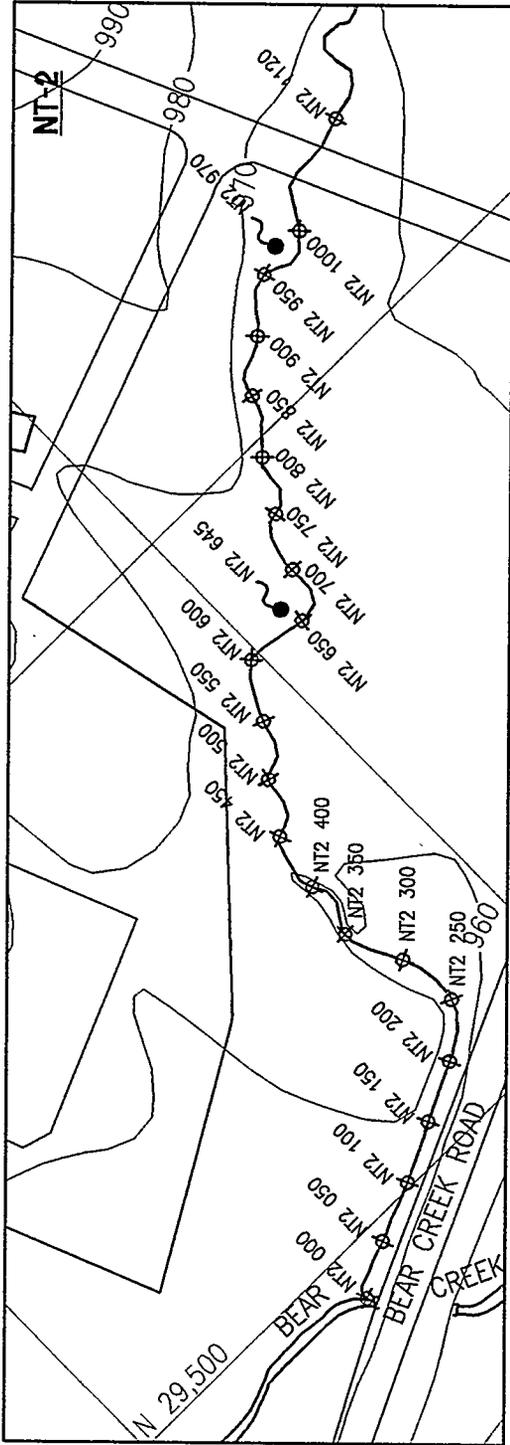


PROJECT NO.	96030	SAE	NORTH TRIBUTARY 1 BEAR CREEK VALLEY
DRAWING NO.	/DWGS/525NT1.DWG	Science Applications International Corporation	
REVISION DATE	REV. 0 09/24/96		
XREF. FILES	94020/XREF/XRBCV14	LEGEND: ROADS BEAR CREEK & TRIBUTARIES SAMPLE STATIONS ⊕ NT1 150 STREAM ● NT1 075 SEEP	

Fig. 3. North Tributary 1 (NT-1) surface water sample locations and field screening results.



Y-12 PLANT NORTH



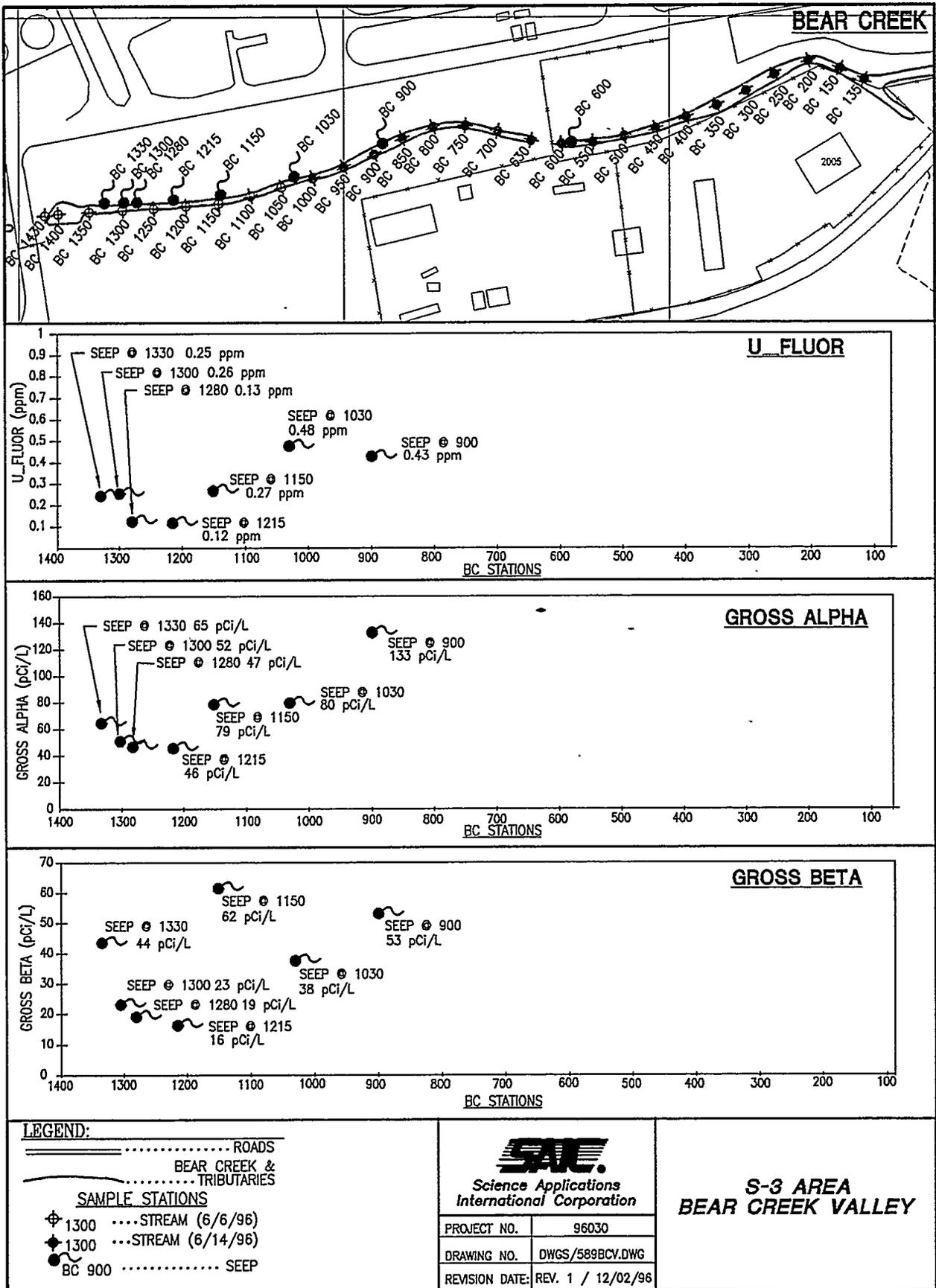


Fig. 5. Bear Creek surface water uranium screening results.

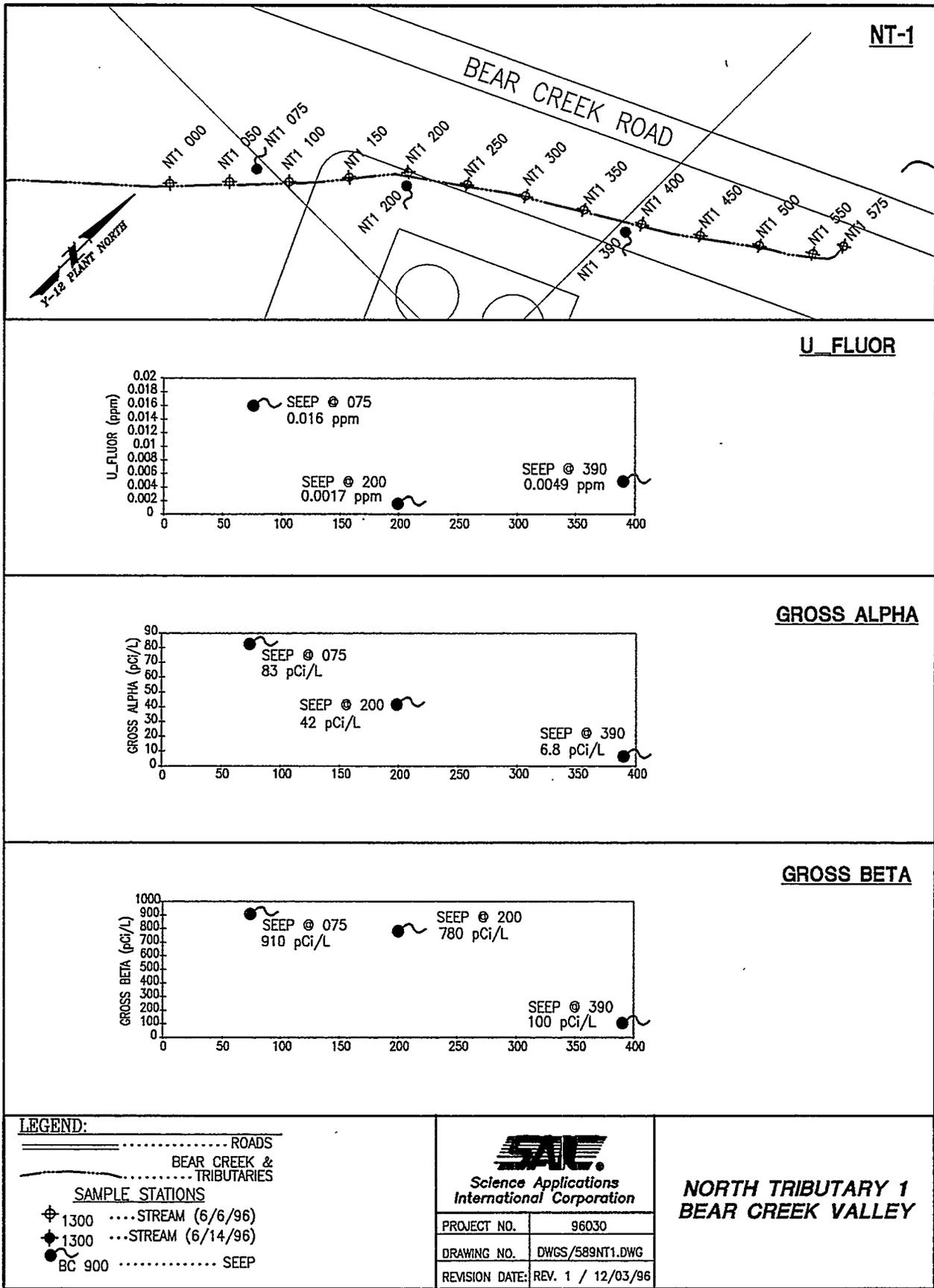


Fig. 6. North Tributary 1 (NT-1) surface water uranium screening results.

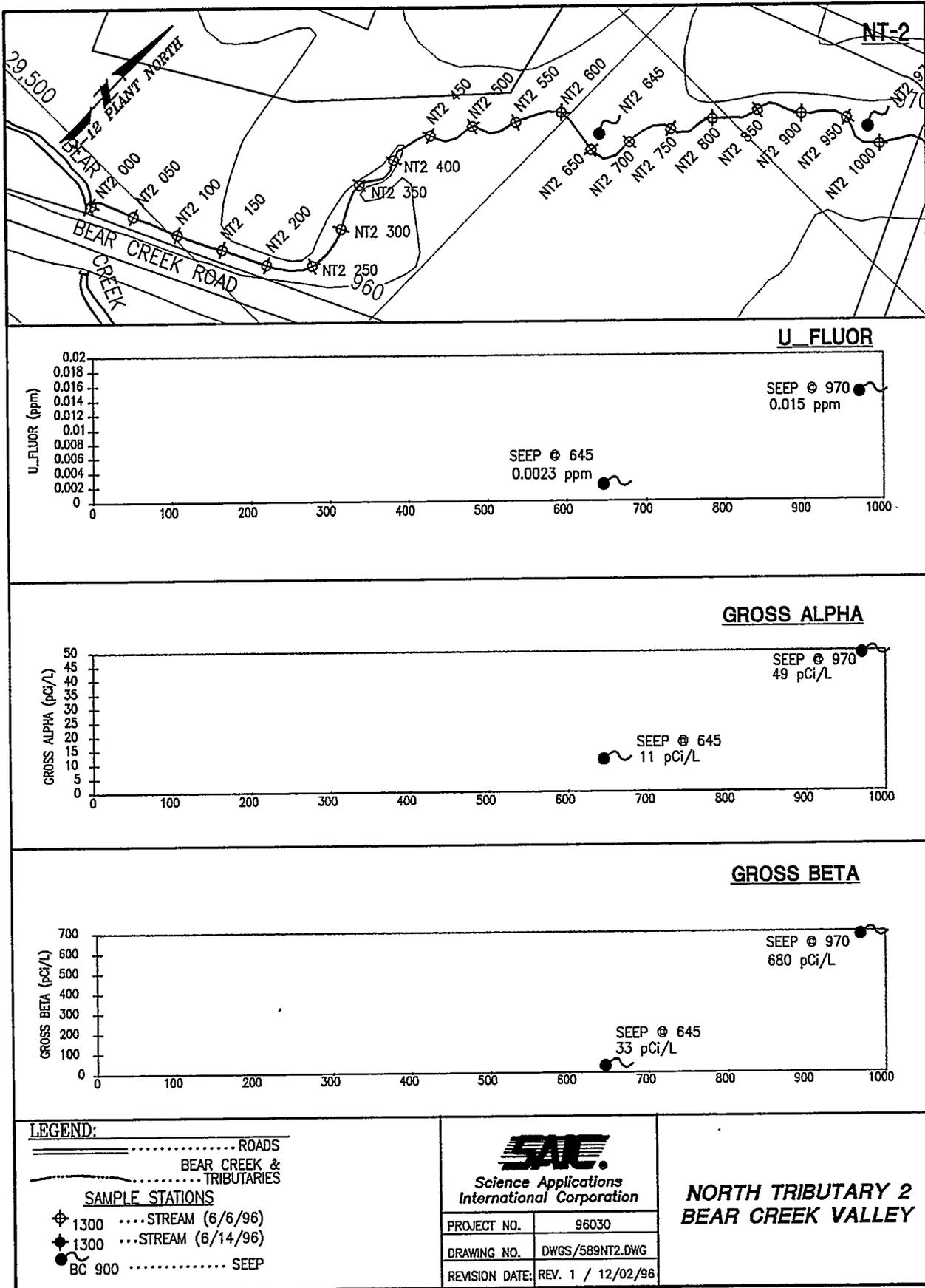
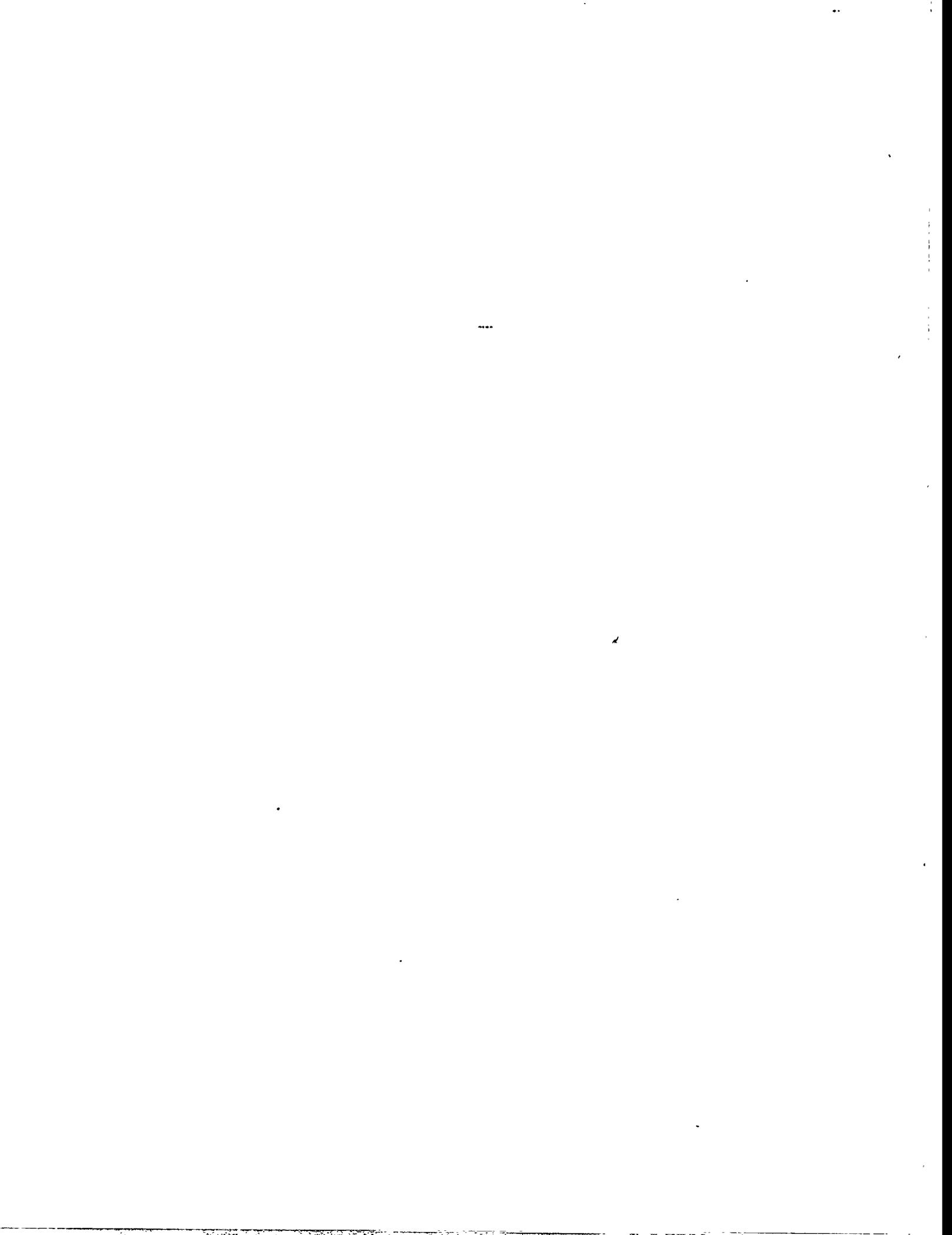
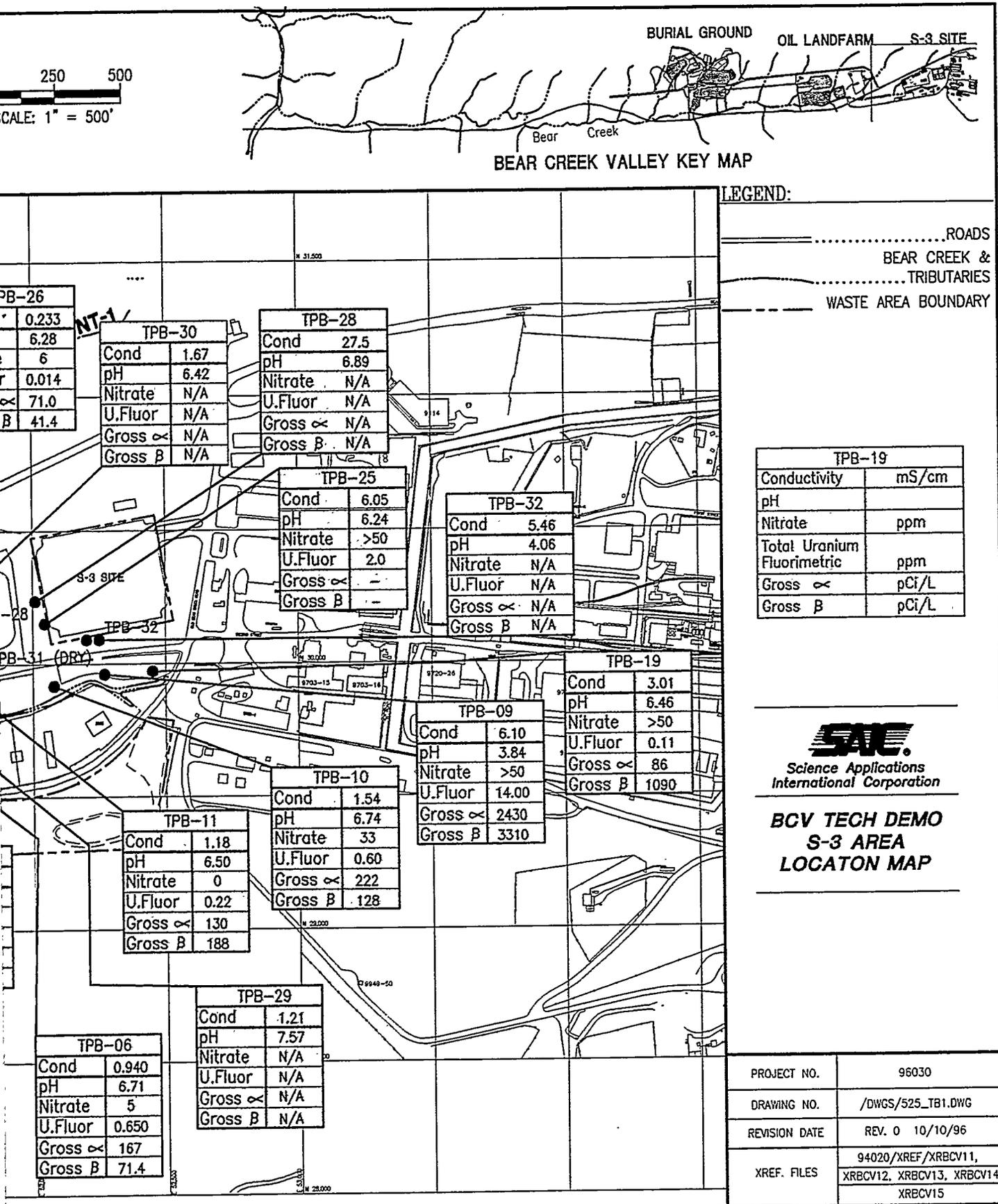


Fig. 7. North Tributary 2 (NT-2) surface water uranium screening results.





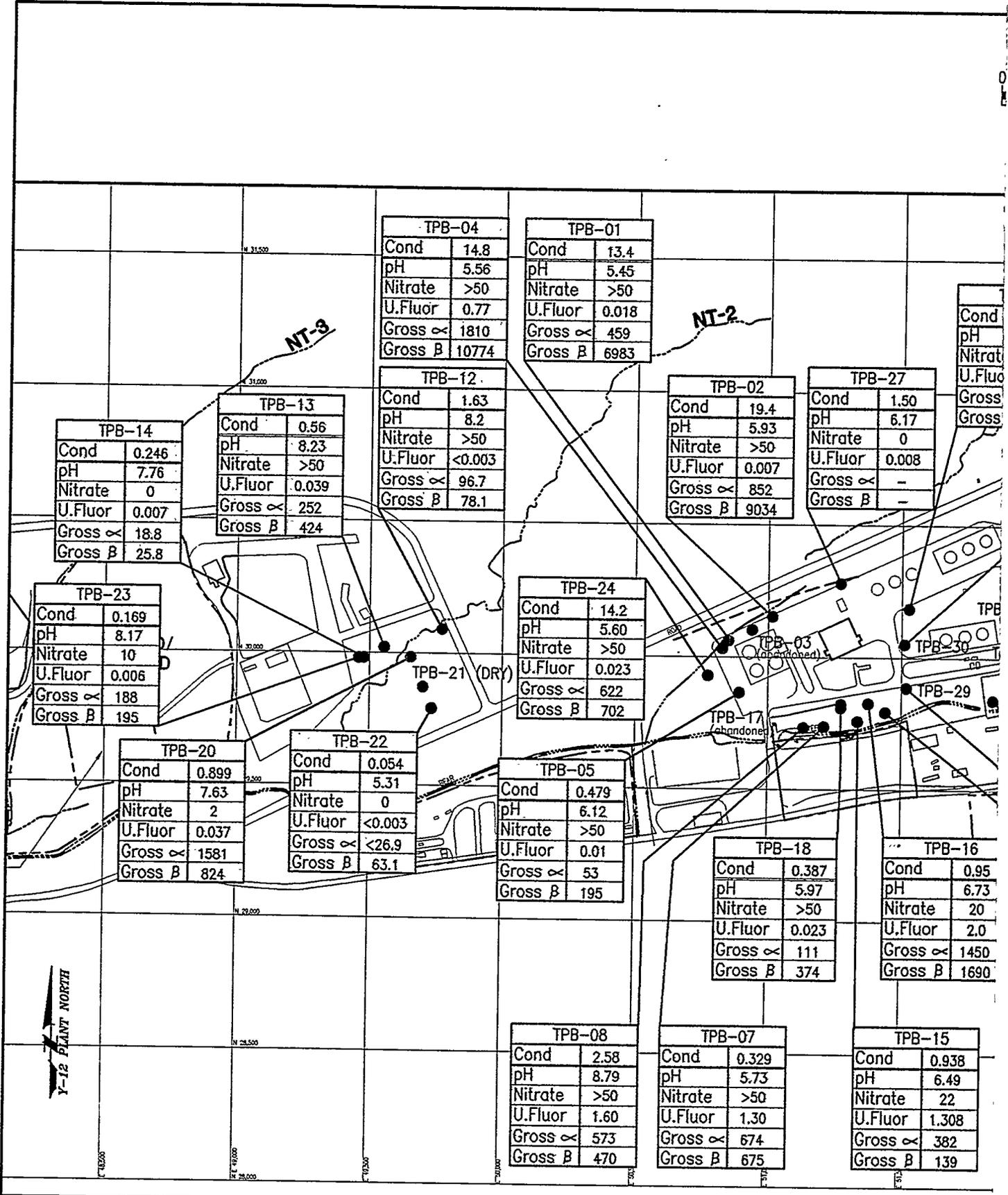
TPB-19	
Conductivity	mS/cm
pH	
Nitrate	ppm
Total Uranium Fluorimetric	ppm
Gross α	pCi/L
Gross β	pCi/L



**BCV TECH DEMO
S-3 AREA
LOCATON MAP**

PROJECT NO.	96030
DRAWING NO.	/DWGS/525_TB1.DWG
REVISION DATE	REV. 0 10/10/96
XREF. FILES	94020/XREF/XRBCV11, XRBCV12, XRBCV13, XRBCV14 XRBCV15

Fig. 8. Push probe temporary piezometer locations and groundwater screening results.



TPB-04	
Cond	14.8
pH	5.56
Nitrate	>50
U.Fluor	0.77
Gross ∞	1810
Gross β	10774

TPB-01	
Cond	13.4
pH	5.45
Nitrate	>50
U.Fluor	0.018
Gross ∞	459
Gross β	6983

TPB-12	
Cond	1.63
pH	8.2
Nitrate	>50
U.Fluor	<0.003
Gross ∞	96.7
Gross β	78.1

TPB-02	
Cond	19.4
pH	5.93
Nitrate	>50
U.Fluor	0.007
Gross ∞	852
Gross β	9034

TPB-27	
Cond	1.50
pH	6.17
Nitrate	0
U.Fluor	0.008
Gross ∞	-
Gross β	-

TPB-14	
Cond	0.246
pH	7.76
Nitrate	0
U.Fluor	0.007
Gross ∞	18.8
Gross β	25.8

TPB-13	
Cond	0.56
pH	8.23
Nitrate	>50
U.Fluor	0.039
Gross ∞	252
Gross β	424

TPB-23	
Cond	0.169
pH	8.17
Nitrate	10
U.Fluor	0.006
Gross ∞	188
Gross β	195

TPB-24	
Cond	14.2
pH	5.60
Nitrate	>50
U.Fluor	0.023
Gross ∞	622
Gross β	702

TPB-20	
Cond	0.899
pH	7.63
Nitrate	2
U.Fluor	0.037
Gross ∞	1581
Gross β	824

TPB-22	
Cond	0.054
pH	5.31
Nitrate	0
U.Fluor	<0.003
Gross ∞	<26.9
Gross β	63.1

TPB-05	
Cond	0.479
pH	6.12
Nitrate	>50
U.Fluor	0.01
Gross ∞	53
Gross β	195

TPB-18	
Cond	0.387
pH	5.97
Nitrate	>50
U.Fluor	0.023
Gross ∞	111
Gross β	374

TPB-16	
Cond	0.95
pH	6.73
Nitrate	20
U.Fluor	2.0
Gross ∞	1450
Gross β	1690

TPB-08	
Cond	2.58
pH	8.79
Nitrate	>50
U.Fluor	1.60
Gross ∞	573
Gross β	470

TPB-07	
Cond	0.329
pH	5.73
Nitrate	>50
U.Fluor	1.30
Gross ∞	674
Gross β	675

TPB-15	
Cond	0.938
pH	6.49
Nitrate	22
U.Fluor	1.308
Gross ∞	382
Gross β	139

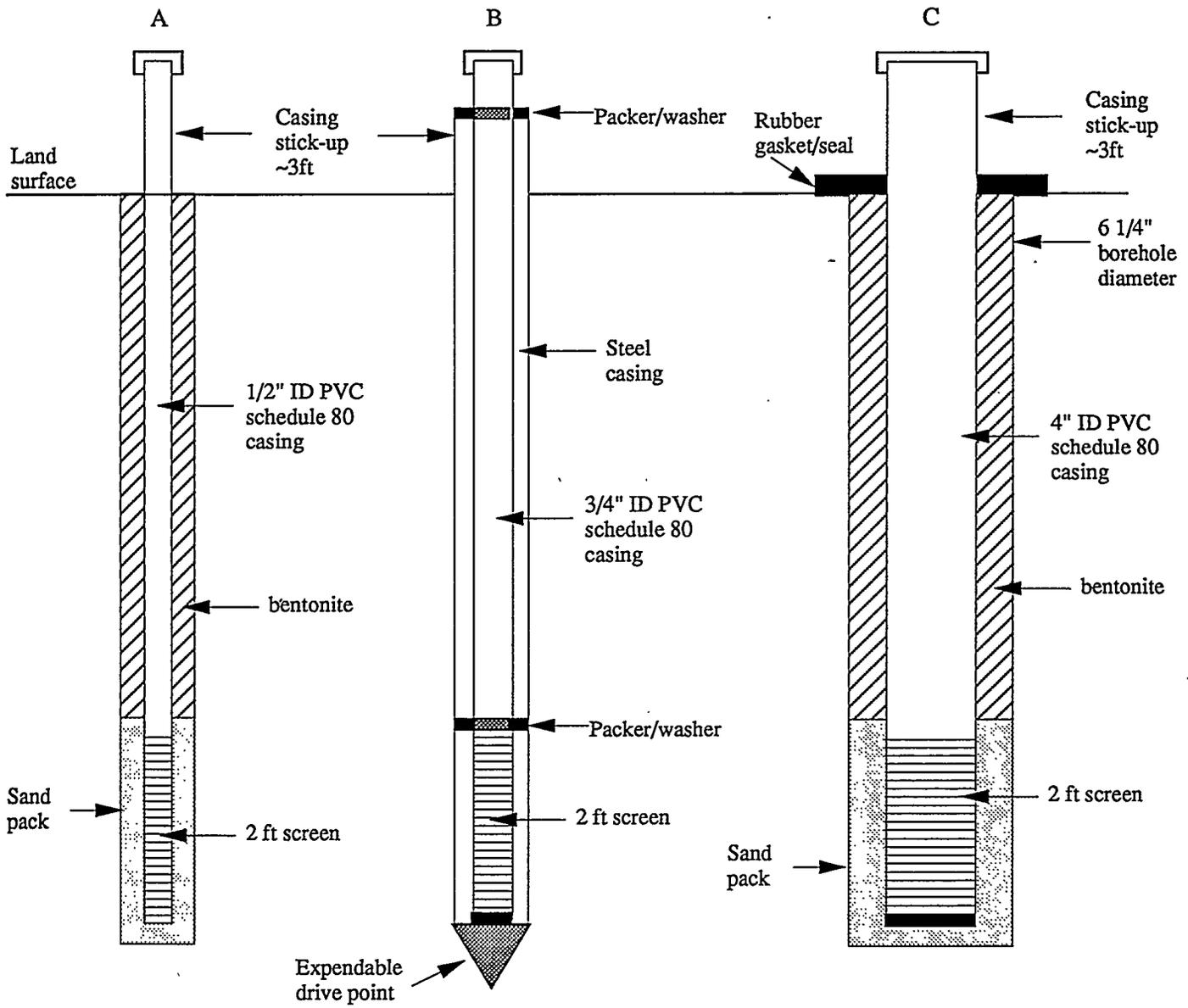
TPB-30	
Cond	
pH	
Nitrate	
U.Fluor	
Gross ∞	
Gross β	

TPB-29	
Cond	
pH	
Nitrate	
U.Fluor	
Gross ∞	
Gross β	

TPB-03 (abandoned)

TPB-17 (abandoned)

TPB-21 (DRY)



Construction A - TPB-01 through -27

Construction B - TPB-28 through -32

Construction C - BPA-01 through -04

Fig. 9. Generalized piezometer construction logs.

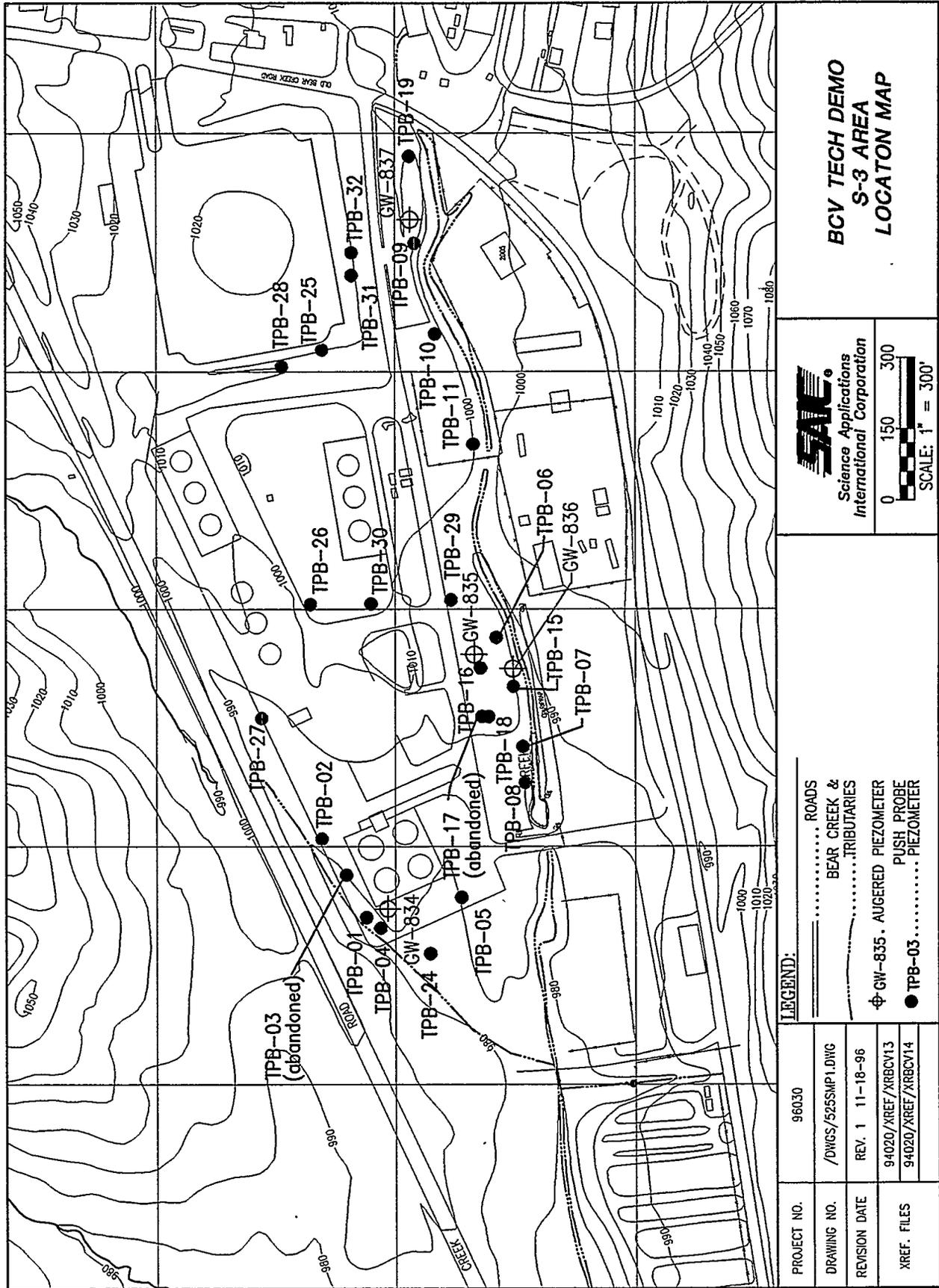
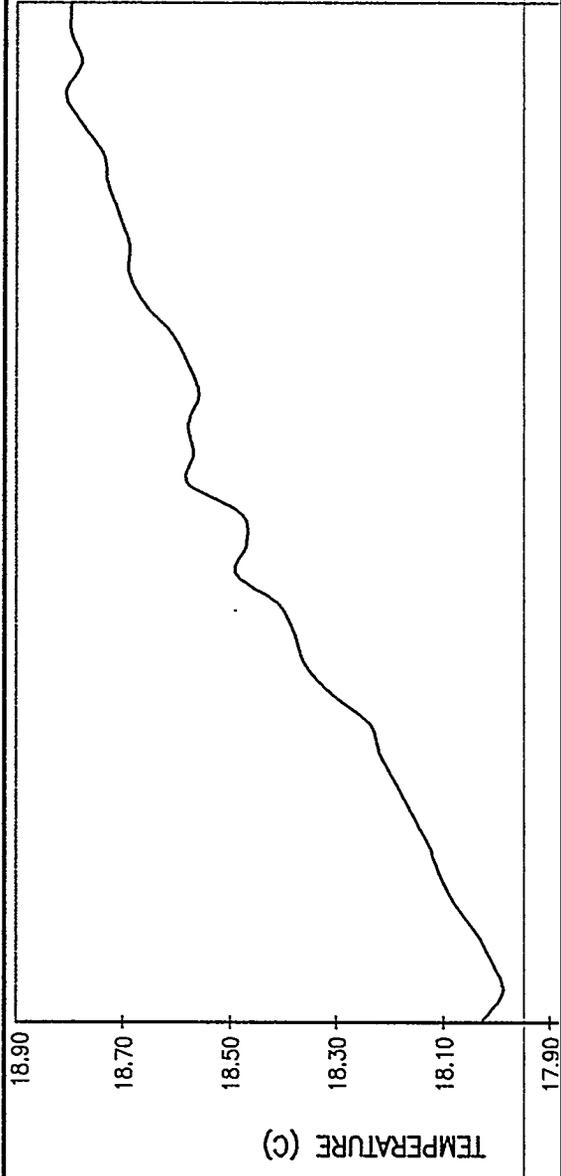
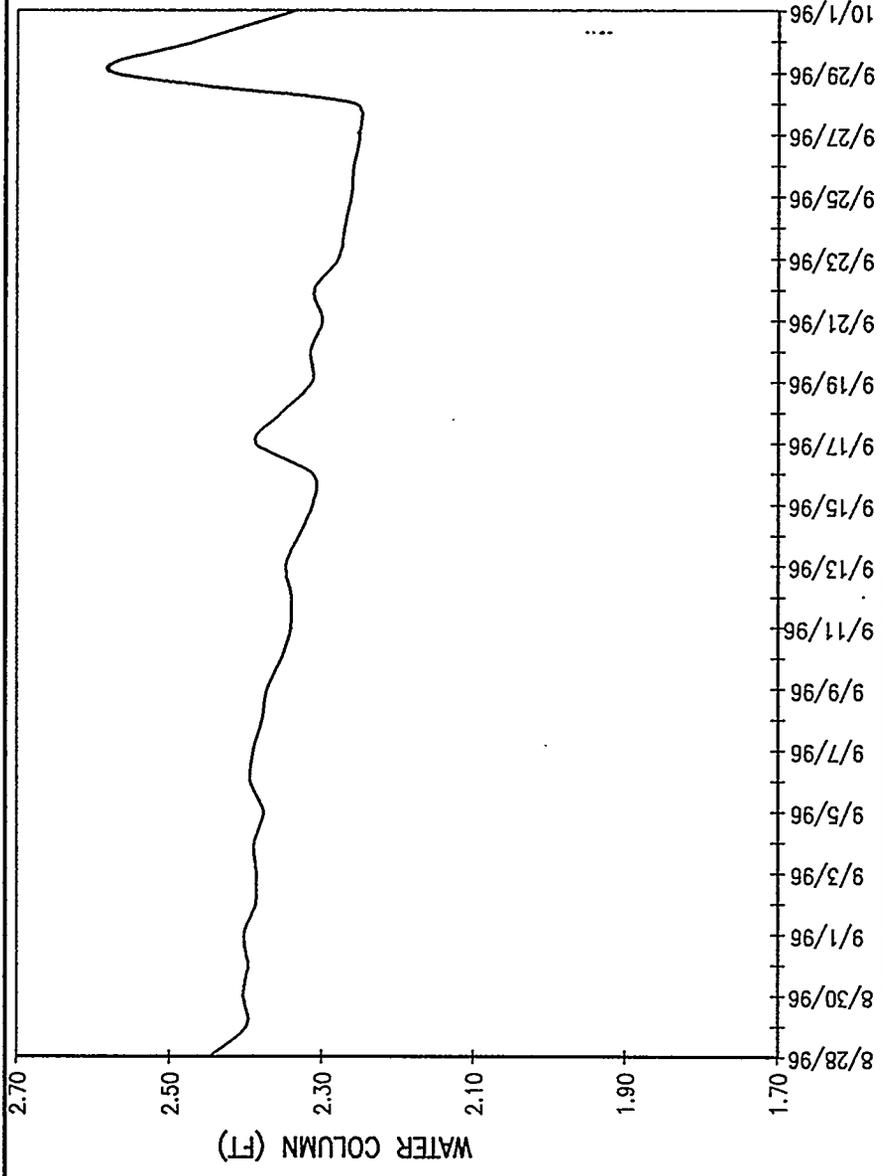
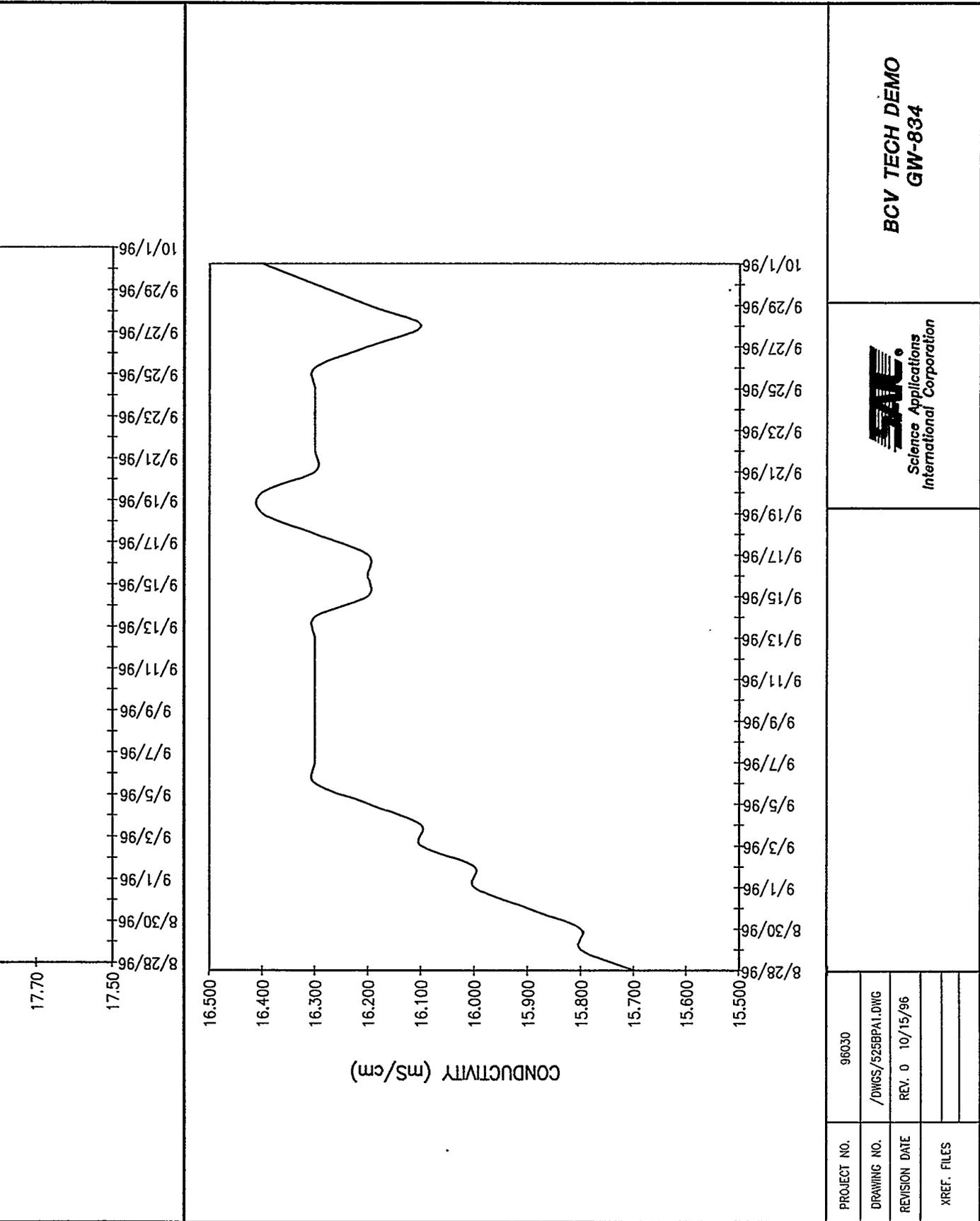


Fig. 10. Augered temporary piezometer locations.



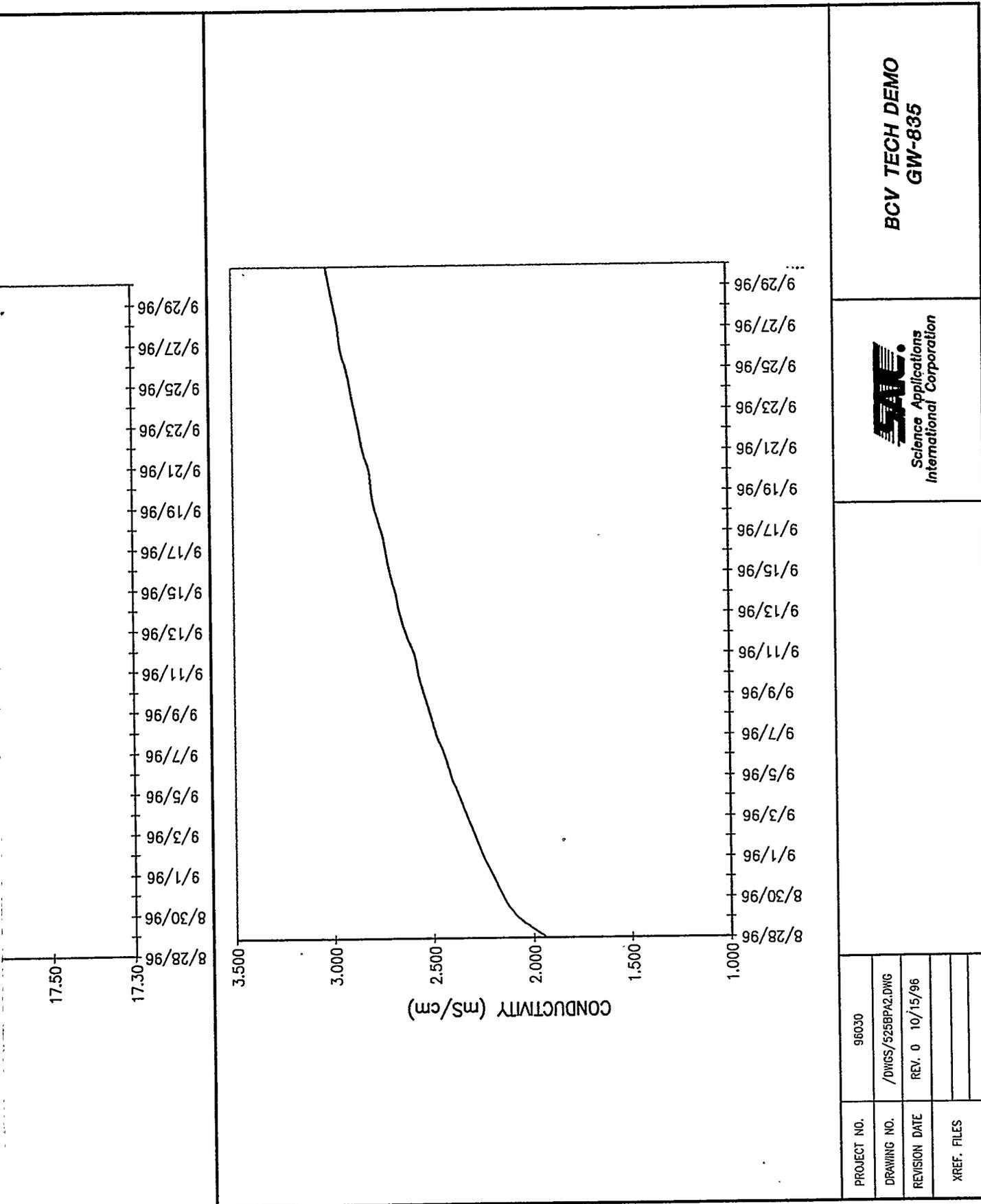


BCV TECH DEMO
GW-834



PROJECT NO.	96030
DRAWING NO.	/DWGS/525BPA1.DWG
REVISION DATE	REV. 0 10/15/96
XREF. FILES	

Fig. 11. GW-834 continuous water level, temperature, and conductivity monitoring.

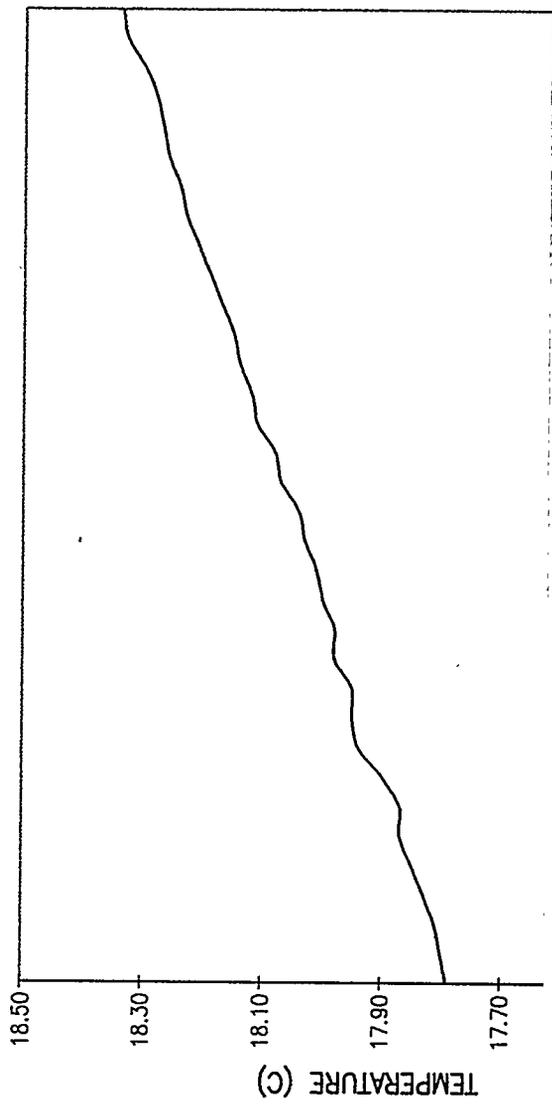
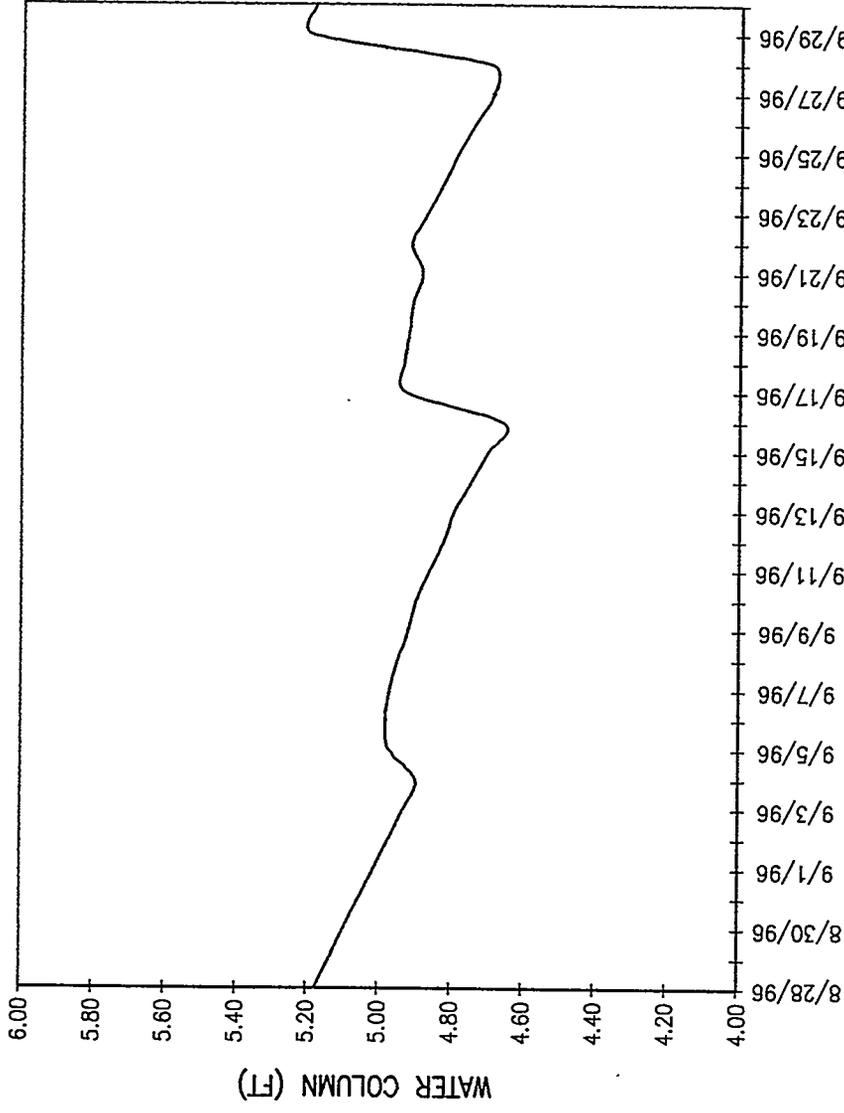


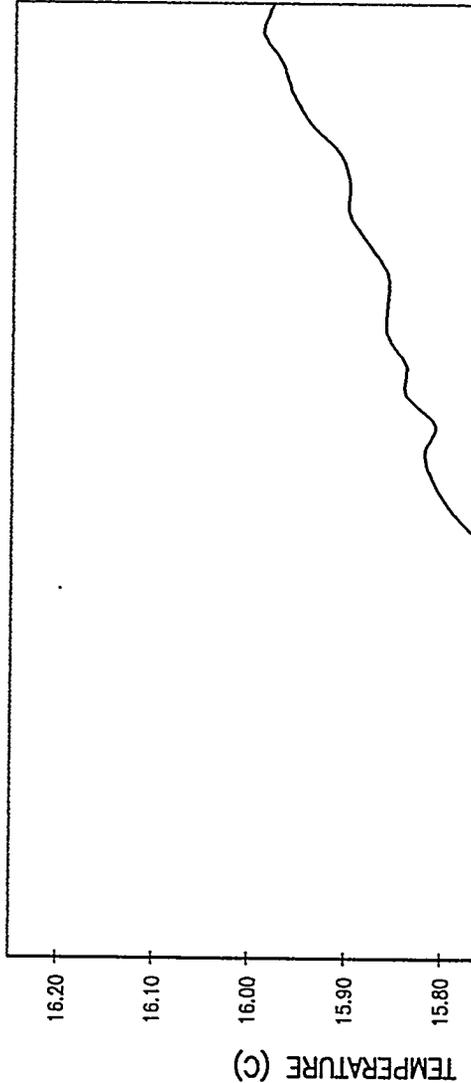
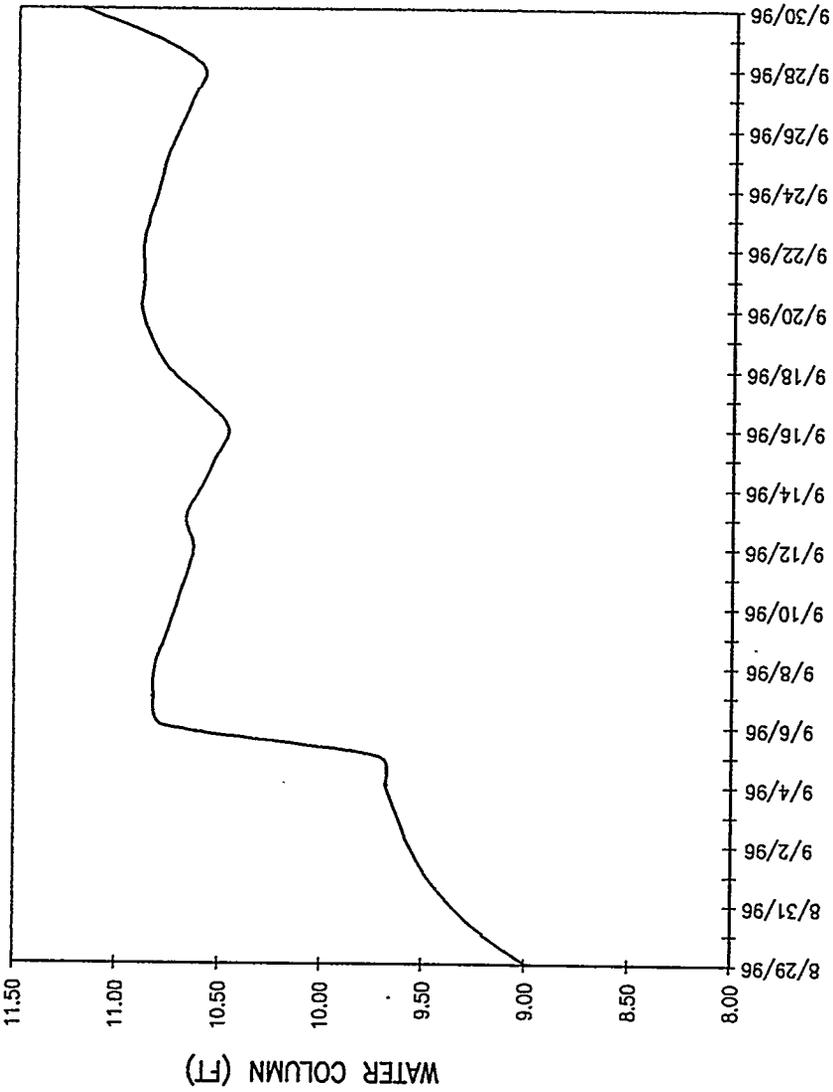
BCV TECH DEMO
GW-835

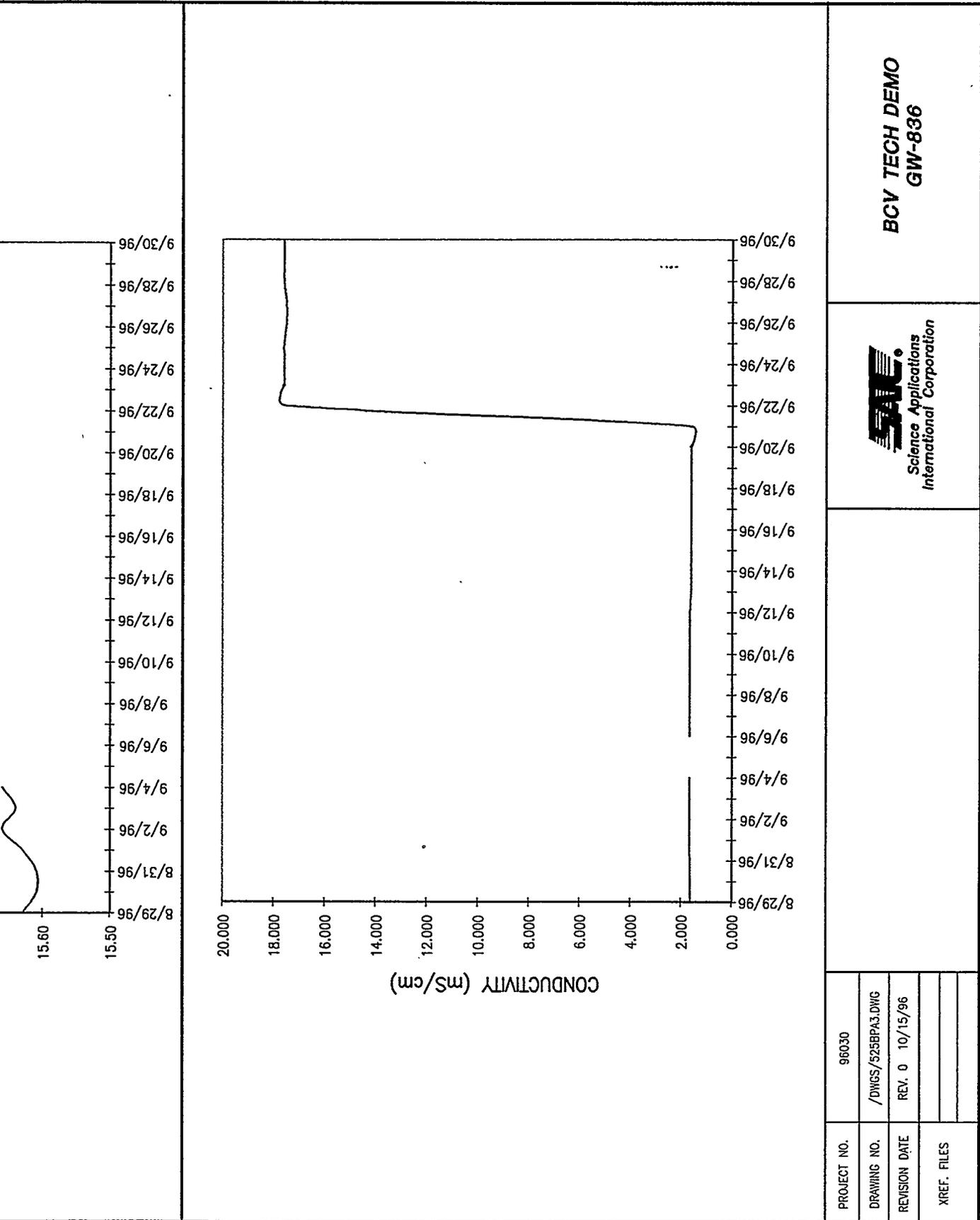


PROJECT NO.	96030
DRAWING NO.	/DWGS/S25BP2.DWG
REVISION DATE	REV. 0 10/15/96
XREF. FILES	

Fig. 12. GW-835 continuous water level, temperature, and conductivity monitoring.







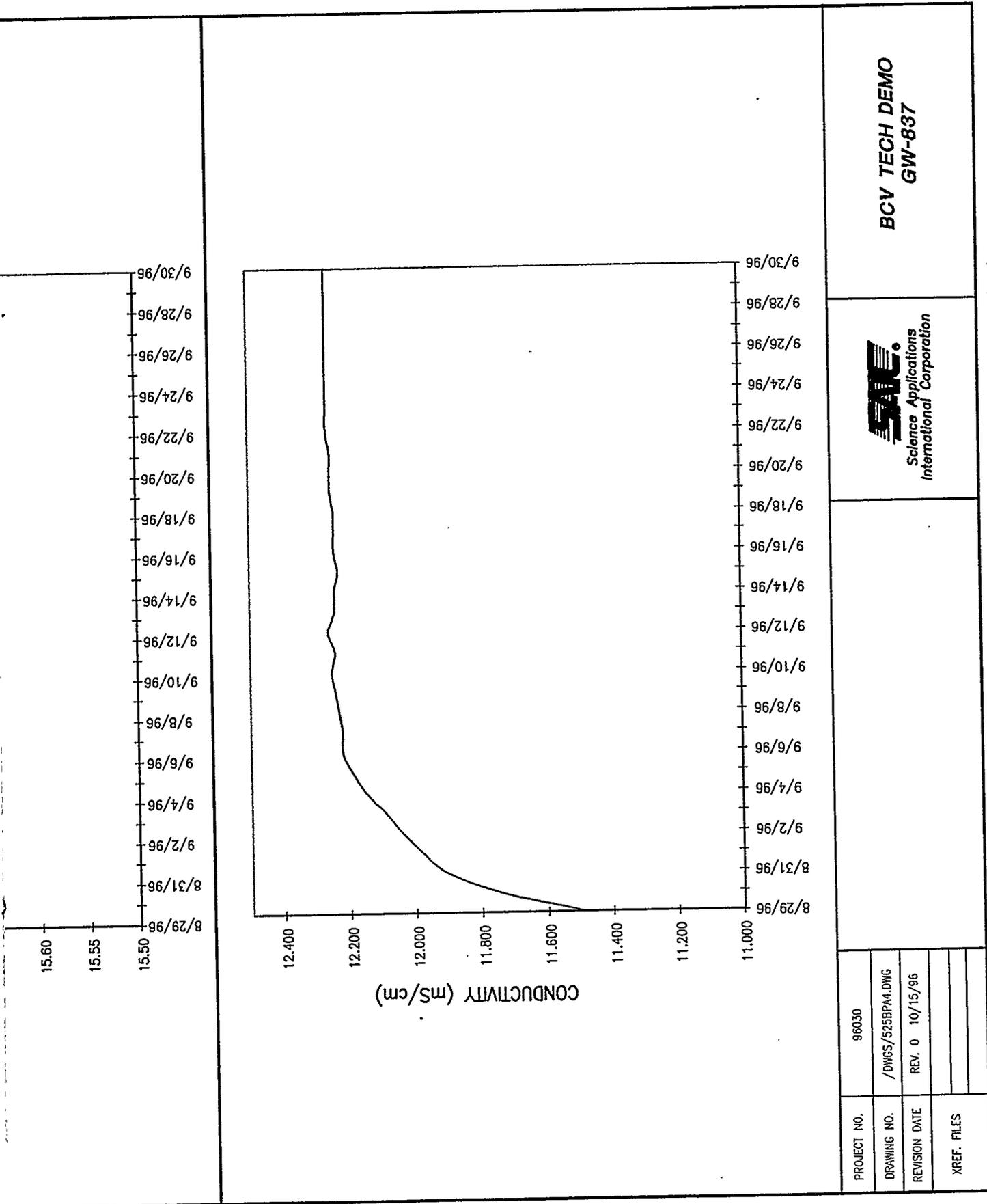
BCV TECH DEMO
GW-836



Science Applications
International Corporation

PROJECT NO.	96030
DRAWING NO.	/DWGS/525BP3A3.DWG
REVISION DATE	REV. 0 10/15/96
XREF. FILES	

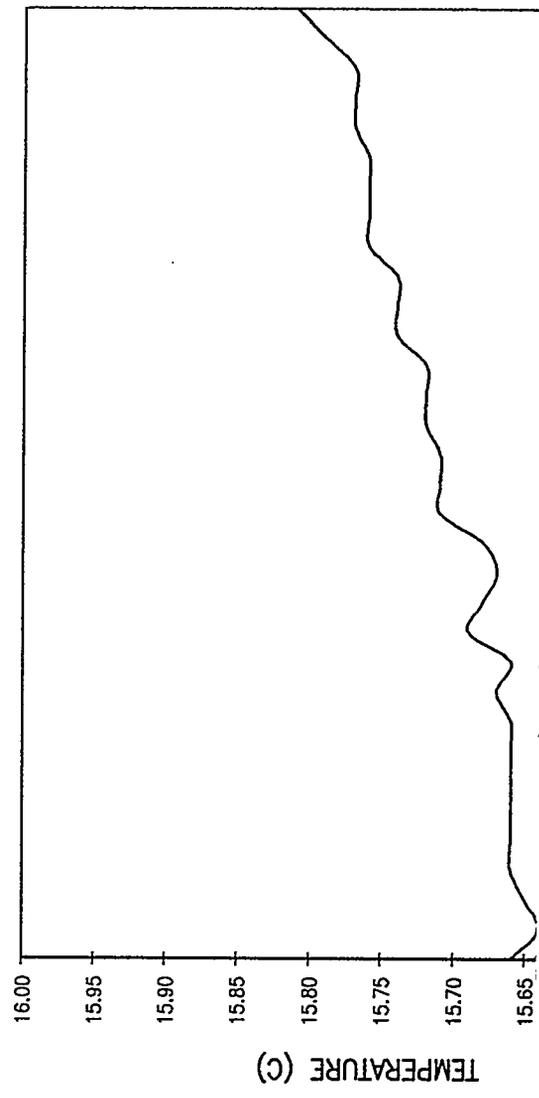
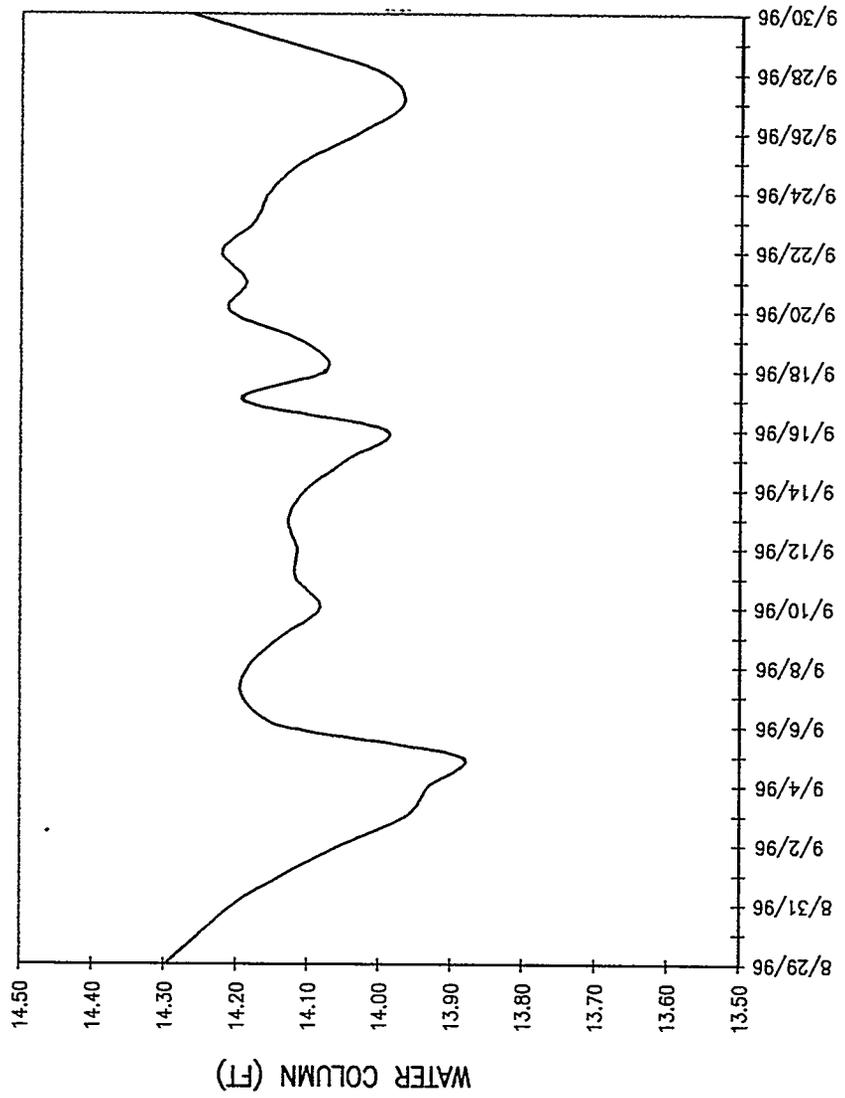
Fig. 13. GW-836 continuous water level, temperature, and conductivity monitoring.

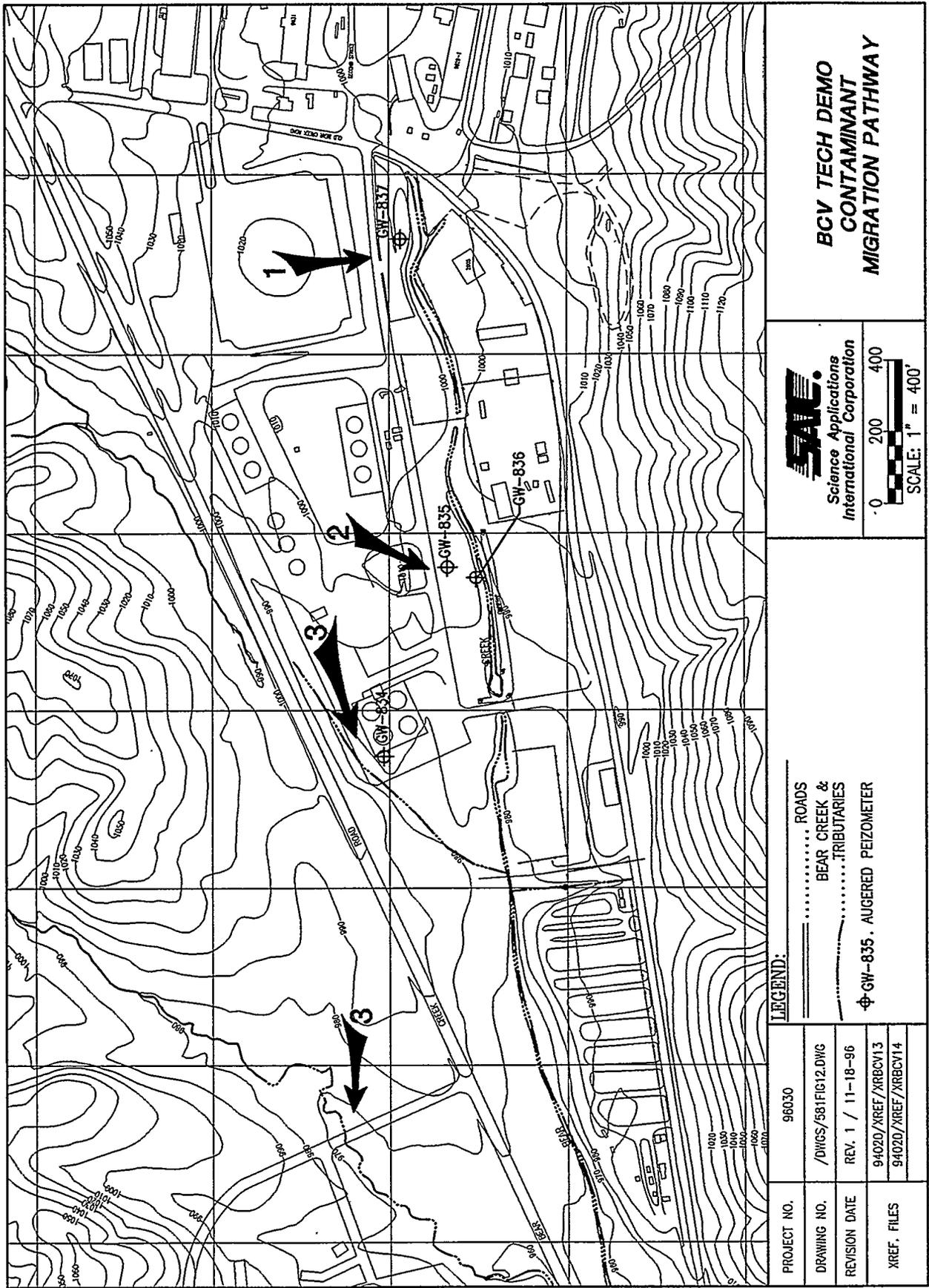


BCV TECH DEMO
GW-837



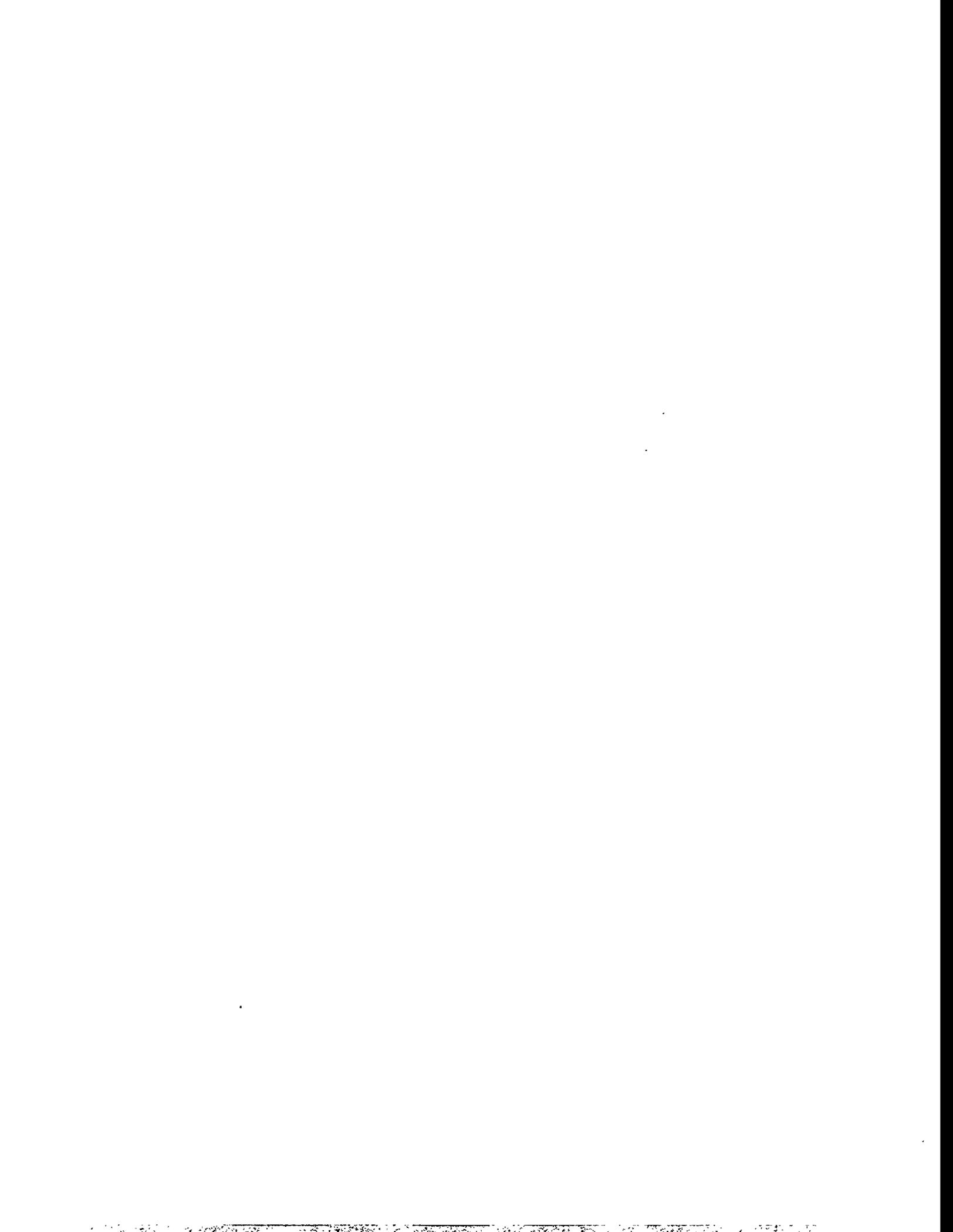
Fig. 14. GW-837 continuous water level, temperature, and conductivity monitoring.





<p>BCV TECH DEMO CONTAMINANT MIGRATION PATHWAY</p>	
<p>SAC Science Applications International Corporation</p>	
<p>0 200 400 SCALE: 1" = 400'</p>	
<p>LEGEND:</p> <p>..... ROADS BEAR CREEK & TRIBUTARIES Φ GW-835 . AUGERED PEIZOMETER</p>	
PROJECT NO.	96030
DRAWING NO.	/DWGS/581FIG12.DWG
REVISION DATE	REV. 1 / 11-18-96
XREF. FILES	9402D/XREF/XRBCV13 9402D/XREF/XRBCV14

Fig. 15. Contaminant migration pathways.



TABLES



Table 1. Bear Creek surface water screening parameters (collected 6/6/96 and 6/14/96*)

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)	Nitrate concentration (ppm)	Gross alpha (pCi/L)	Gross beta (pCi/L)	U. Fluor (ppm)
<i>Stream</i>								
BC 1430	BC1213	1.030	7.10	17.5	9			
BC 1350	BC1212	1.020	7.14	17.7	9			
BC 1300	BC1209	1.010	7.13	17.8	8			
BC 1250	BC1207	1.020	7.07	17.5	8			
BC 1200	BC1205	1.020	7.16	17.1	7			
BC 1150	BC1203	1.050	7.06	16.3	7			
BC 1100	Dry	---	---	---	---			
BC 1050	Dry	---	---	---	---			
BC 1000	BC1214*	1.000	7.40	18.0	3			
BC 950	BC1215*	1.000	7.40	18.0	3			
BC 900	BC1216*	0.990	7.20	17.9	3	133	53.3	0.43
BC 850	BC1217	0.493	7.01	18.1	2			
BC 800	BC1218*	0.990	7.01	18.9	3			
BC 750	BC1219*	1.770	6.99	18.7	3			
BC 700	BC1220*	1.930	7.09	18.5	2			
BC 630	BC1221*	1.970	6.69	18.4	4	149	34.4	0.49
BC 600	BC1222*	1.140	7.09	18.5	3			
BC 550	BC1223*	2.680	7.13	18.9	0			
BC 500	BC1224*	0.633	7.15	19.1	3	126	44.9	0.43

Table 1 (continued)

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)	Nitrate concentration (ppm)	Gross alpha (pCi/L)	Gross beta (pCi/L)	U. Fluor (ppm)
BC 450	BC1225*	0.630	7.17	19.0	3			
BC 400	BC1226*	0.606	7.21	19.8	3			
BC 350	BC1230*	0.585	7.23	20.0	2			
BC 300	BC1227*	0.550	7.20	20.3	3	67.4	30.2	0.27
BC 250	BC1228*	0.530	7.11	20.9	4			
BC 200	Dry	---	---	---	---			
BC 150	Dry	---	---	---	---			
BC 135	BC1229*	0.501	7.09	20.5	4			
				<i>Seep</i>				
BC 1330	BC1211	0.851	6.97	15.5	8	65	44	0.25
BC 1300	BC1210	1.100	6.96	18.4	0	52	23	0.26
BC 1280	BC1208	0.631	6.93	18.4	0	47	19	0.13
BC 1215	BC1206	0.679	6.84	19.7	0	46	16	0.12
BC 1150	BC1204	0.930	7.06	15.1	3	79	62	0.27
BC 1030	BC1202	1.080	6.70	14.3	3	80	38	0.48
BC 900	BC1216*	0.990	7.20	17.9	3	133	53.3	0.43

Table 2. NT-1 surface water screening parameters (collected 6/4/96)

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)	Nitrate concentration (ppm)	Gross alpha (pCi/L)	Gross beta (pCi/L)	U. Fluor (ppm)
<i>Stream</i>								
NT-1 000	N11201	1.370	6.84	22.1	50			
NT-1 050	N11202	1.750	6.54	20.6	50			
NT-1 100	N11203	1.640	6.56	20.3	50			
NT-1 150	N11205	1.470	6.68	20.3	50			
NT-1 200	N11206	1.240	6.66	20.5	50			
NT-1 250	N11208	1.180	6.89	20.5	49			
NT-1 300	N11209	0.960	6.91	20.4	42			
NT-1 350	N11210	0.680	5.83	20.3	30	6.6	37	0.004
NT-1 400	N11211	0.484	7.49	20.8	20			
NT-1 450	N11212	0.436	7.51	21.0	18			
NT-1 500	N11213	0.363	7.71	20.5	12			
NT-1 550	N11214	0.252	7.71	19.4	5			
NT-1 575	N11215	0.244	7.58	18.9	4			
<i>Seep</i>								
NT-1 075	N11204	22.300	6.08	20.5	50	83	910	0.016
NT-1 200	N11207	4.410	6.01	19.5	50	42	780	0.0017
NT-1 390	N11216	1.070	6.83	17.8	20	6.8	100	0.0049

Table 3. NT-2 surface water screening parameters (collected 6/5/96)

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)	Nitrate concentration (ppm)	Gross alpha (pCi/L)	Gross beta (pCi/L)	U.Fluor (ppm)
<i>Stream</i>								
NT-2 000	N21201	0.704	7.43	17.8	45			
NT-2 050	N21202	0.701	7.53	17.5	41			
NT-2 100	N21203	0.697	7.59	17.0	46			
NT-2 150	N21204	0.695	7.60	16.9	50			
NT-2 200	N21205	0.695	7.59	16.7	49			
NT-2 250	N21206	0.695	7.53	16.4	48			
NT-2 300	N21207	0.695	7.55	16.4	46			
NT-2 350	N21208	0.694	7.52	16.1	50			
NT-2 400	N21209	0.694	7.51	16.0	47			
NT-2 450	N21210	0.694	7.46	16.0	50			
NT-2 500	N21211	0.682	7.43	15.9	50			
NT-2 550	N21212	0.687	7.38	16.0	49			
NT-2 600	N21213	0.695	7.43	16.2	50			
NT-2 650	N21214	0.696	7.44	18.9	46			
NT-2 700	N21215	0.726	7.47	19.0	50			
NT-2 750	N21216	0.710	7.32	18.6	50			
NT-2 800	N21217	0.721	7.23	18.5	50			
NT-2 850	N21218	0.672	7.07	18.6	50			
NT-2 900	N21219	0.655	7.04	19.1	48			

Table 3 (continued)

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)	Nitrate concentration (ppm)	Gross alpha (pCi/L)	Gross beta (pCi/L)	U.Fluor (ppm)
NT-2 950	N21220	0.590	6.91	19.2	50			
NT-2 1000	N21221	0.141	7.38	19.2	17			
NT-2 1120	N21225	0.121	7.34	18.3				
				<i>Seep</i>				
NT-2 645	N21224	3.23	7.08	18.6	50	11	33	0.0023
NT-2 970	N21223	12.6	6.05	15.5	50	49	680	0.0015

Table 4. Groundwater seeps analytical results

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
Bicarbonate, mg/L	384	550	30	412	253					
Mercury, mg/L	<0.0002	0.0006	0.0045	<0.0002	<0.0002					
Aluminum, µg/L	<200	<200	723	110000	707	7210	<200	5170		
Boron, µg/L	62.3	94.9	49.7	420	<20	63.3	<20	55.3		
Barium, µg/L	72.1	285	728	958	4340	4910	4290	11000		
Calcium, µg/L	153000	164000	360000	>1000000	1100000	1100000	1120	>1000000		
Cadmium, µg/L	<20	<20	80.7	846	<20	252	<20	590		
Cobalt, µg/L	<20	<20	35.2	601	<20	71.8	<20	171		
Chromium, µg/L	<20	<20	<20	<20	<20	<20	<20	<20		
Copper, µg/L	<30	<30	<30	<300	<300	<300	<300	<300		
Iron, µg/L	<200	1610	<200	152	1000	3790	<200	<200		
Potassium, µg/L	3820	6150	7730	58400	4960	14900	4820	23800		
Magnesium, µg/L	21100	23200	52200	253000	139000	144000	139000	241000		
Manganese, µg/L	951	5050	11000	100000	5470	52400	5060	100000		
Molybdenum, µg/L	<40	<40	<40	<40	<40	<40	<40	<40		
Sodium, µg/L	54100	9890	50300	355000	92500	147000	92000	261000		
Nickel, µg/L	<40	<40	339	4930	<40	434	<40	1030		
Lead, µg/L	<200	<200	<200	<200	<200	<200	<200	<200		

Analysis

Table 4 (continued)

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
Thallium, µg/L	<100	<100	<100	<100	<100	102	<100	<100	<100	114
Vanadium, µg/L	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zinc, µg/L	27.2	<20	23.8	55.6	22.7	172	<20	98.8	<20	109
Selenium, µg/L	<500	<500	<500	<500	<500	<1000	<500	<500	<500	<1000
Silver, µg/L	24.9	<20	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic, µg/L	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Beryllium, µg/L	<2	<2	<2	<2	<2	35.7	<1.0	<10	<2	<10
Antimony, µg/L	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Lithium, µg/L	<10	<10	174	199	<10	14.1	53.9	13.1	52.9	<10
Phosphorous, µg/L										
Titanium, µg/L	<20	<20	<20	16.7	<20	<20	<20	49.3	<20	<20
Strontium, µg/L	333	327	709	723	1010	3520	4150	2910	4120	4730
Alkalinity, mg/L		400		550		30		410		260
Alpha activity, pC/L		89		16		56		170		63
Beta activity, pC/L		78		10		740		1700		850
Tritium, pC/L		170		3130		1300		370		370
Fluoride, mg/L		0.902		0.65		57		2.1		
Chloride, mg/L		42		9.5		180		60		58
Nitrite as Nitrogen, mg/L				<0.05		5.8				

Table 4 (continued)

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
Bromide, mg/L										
Nitrate as Nitrogen, mg/L		4.6		4.9		1800		720		1000
Ortho-Phosphate as Phosphorus, mg/L				<0.12						
Sulfate, mg/L		95		0.94		120		59		3.4
22-Sodium Activity, pC/L		1.1		0.2		-0.53		0.53		-0.76
40-Potassium Activity, pC/L		5.6		320		82		4		39
51-Chromium Activity, pC/L		1.3		-5		-4.3		6		1.7
54-Manganese Activity, pC/L		0.5		-1		0.18		-0.51		-0.52
57-Cobalt Activity, pC/L		-0.049		0.28		0.91		0.099		-0.35
58-Cobalt Activity, pC/L		0.17		-0.84		-0.67		-0.32		0.59
59-Iron Activity, pC/L		1.8		2.7		-0.75		2.6		-3.4
60-Cobalt Activity, pC/L		0.53		-1.1		2.1		0.23		1.9
65-Zinc Activity, pC/L		1.8		-4.2		-0.17		-1.6		3.8
95-Niobium Activity, pC/L		0.53		-0.34		0.85		-0.003		2.4
95-Zirconium Activity, pC/L		-0.75		1.8		-2.3		-5.5		-2.5
106-Ruthenium Activity, pC/L		7.7		-18		-5.3		-2.1		-18
125-Antimony Activity, pC/L		-5.3		2.6		-3.5		3.9		0.41
134-Cesium Activity, pC/L		-0.33		0.27		0.44		0.17		-2.5

Table 4 (continued)

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
137-Cesium Activity, pC/L		1.4		4.5		0.52		-0.61		0.005
144-Cerium Activity, pC/L		11		-9.1		-9.7		-7.2		-0.43
208-Thallium Activity, pC/L		-1.4		1.9		1		0.53		0.9
212-Bismuth Activity, pC/L		24		2.8		13		13		14
212-Lead Activity, pC/L		1.8		-4.8		4		0.19		1.3
235 Uranium Activity, pC/L		3.3		-14		13		2.6		16
Technetium -99, pC/L		17		-2		15000		5700		1900
Total Dissolved Solids, mg/L				620		12000		10000		
Total Strontium, pC/L		0.14		-0.08		6.3		24		1.3
Total Suspended Solids, mg/L		6		81		8		69		45
Uranium, µg/g		0.47		0.054		2.1		0.007		<0.002
Chloromethane, µg/L		10		10		10		10		10
Bromomethane, µg/L		10		10		10		10		10
Vinyl chloride, µg/L		10		10		10		10		10
Chloroethane, µg/L		10		10		10		10		10
Trichlorofluoromethane, µg/L		10		10		10		10		10
Methylene chloride, µg/L		10		10		4		7		3
Acetone, µg/L		2		9		8		6		5

Table 4 (continued)

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
1,1,2-Trichloro-1,2,2-trifluoroethane, µg/L		10		10		3		10		12
Carbon disulfide, µg/L		10		10		10		10		10
1,1-Dichloroethene, µg/L		10		10		10		10		10
1,1-Dichloroethane, µg/L		10		10		10		10		10
cis-1,2-Dichloroethene, µg/L		10		10		2		2		10
trans-1,2-Dichloroethene, µg/L		10		10		10		10		10
Chloroform, µg/L		10		10		1		6		5
1,2-Dichloroethane, µg/L		10		10		10		10		10
2-Butanone, µg/L		4		5		10		10		6
1,1,1-Trichloroethane, µg/L		10		10		10		10		10
Carbon tetrachloride, µg/L		10		10		10		10		10
Bromodichloromethane, µg/L		10		10		10		10		10
1,2-Dichloropropane, µg/L		10		10		10		10		10
cis-1,3-Dichloropropene, µg/L		10		10		10		10		10
Trichloroethene, µg/L		10		10		10		10		10
Dibromochloromethane, µg/L		10		10		10		10		10
1,1,2-Trichloroethane, µg/L		10		10		10		10		10
Benzene, µg/L		10		10		10		10		10

Table 4 (continued)

Sample no. (location) Collection date	BC1101 (BC 1030) 9/12/96		BC1102 (BC 1280) 9/20/96		NT1101 (NT1 200) 9/19/96		NT1102 (NT1 390) 9/19/96		NT2101 (NT2 970) 9/12/96	
	Filtered	Unfiltered								
trans-1,3-Dichloropropene, µg/L		10		10		10		10		10
Bromoform, µg/L		10		10		10		10		10
4-Methyl-2-pentanone, µg/L		10		10		10		10		10
2-Hexanone, µg/L		10		10		10		10		10
Tetrachloroethene, µg/L		10		10		52		45		10
1,1,1,2-Tetrachloroethane, µg/L		10		10		10		10		10
Toluene, µg/L		10		10		10		10		10
Chlorobenzene, µg/L		10		10		10		10		10
Ethylbenzene, µg/L		10		10		10		10		10
Styrene, µg/L		10		10		10		10		10
Xylene, µg/L		10		10		10		10		10

Table 5. Groundwater seeps field measurements (see Table 4).

Locations	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (C)
		<i>Seep</i>		
BC 1030	BC1101	0.994	6.61	22.0
BC 1280	BC1102	0.307	6.99	17.1
NT1 200	NT1101	0.522	5.42	20.7
NT1 390	NT1102	17.400	5.23	20.5
NT2 970	NT2101	0.579	5.79	17.8

Table 6. Push probe piezometer boring information

Location	Total depth [from TOC (ft)]	Casing stick-up (ft)	TD (BLS) (ft)	Depth to water [from TOC (ft)] 6/24/96	Depth to water [from BLS (ft)] 6/24/96	Water height (ft) 6/24/96
TPB-1	16.51	3.57	12.94	12.16	8.59	4.35
TPB-2	20.88	3.08	17.8	9.50	6.42	11.38
TPB-3	Abandoned	---	---	---	---	---
TPB-4	16.64	1.88	14.76	10.39	8.51	6.25
TPB-5	20.42	2.94	17.48	12.76	9.82	7.66
TPB-6	16.64	2.08	14.56	13.16	11.08	3.48
TPB-7	23.46	2.72	20.74	17.15	14.43	6.31
TPB-8	19.63	2.71	16.92	10.27	7.56	9.36
TPB-9	16.63	2.35	14.28	10.94	8.59	5.69
TPB-10	25.34	2.04	23.3	13.20	11.16	12.14
TPB-11	20.42	2.49	17.93	13.68	11.19	6.74
TPB-12	16.02	3.12	12.9	8.83	5.71	7.19
TPB-13	19.99	2.63	17.36	5.82	3.19	14.17
TPB-14	11.68	1.96	9.72	8.98	7.02	2.70
TPB-15	19.85	2.32	17.53	13.18	10.86	6.67
TPB-16	16.58	1.29	15.29	12.30	11.01	4.28
TPB-17	Abandoned	---	---	---	---	---
TPB-18	23.27	2.68	20.59	14.50	11.82	8.77
TPB-19	13.97	2.79	11.18	8.68	5.89	5.29

Table 6 (continued)

Location	Total depth [from TOC (ft)]	Casing stick-up (ft)	TD (BLS) (ft)	Depth to water [from TOC (ft)] 6/24/96	Depth to water [from BLS (ft)] 6/24/96	Water height (ft) 6/24/96
TPB-20	14.84	2.52	12.32	9.36	6.84	5.48
TPB-21	19.08	2.42	16.66	17.83	15.41	1.25
TPB-22	21.53	2.29	19.24	17.35	15.06	4.18
TPB-23	23.81	2.68	21.13	10.62	7.94	13.19
TPB-24	18.65	2.67	15.98	11.95	9.28	6.70
TPB-25	16.56	1.41	15.15	12.15	10.74	4.41
TPB-26	19.85	2.79	17.06	9.82	7.03	10.03
TPB-27	21.53	2.68	18.85	11.17	8.49	10.36
TPB-28	23.10	3.00	20.10	15.64 ^a	12.64 ^a	7.46 ^a
TPB-29	23.10	3.00	20.10	14.86 ^a	11.86 ^a	8.24 ^a
TPB-30	22.60	3.50	18.60	13.08 ^a	9.58 ^a	9.52 ^a
TPB-31	13.30	3.40	9.90	11.68 ^a	8.28 ^a	1.62 ^a
TPB-32	19.30	3.20	16.10	14.46 ^a	11.26 ^a	4.84 ^a

^aMeasurements made 11/6/96. These piezometers were installed in a later phase.

Table 7. Augered piezometer boring information

Location	Total depth [from TOC (ft)]	Casing stick-up (ft)	TD (BLS) (ft)	Depth to Water [from TOC (ft)]	Depth to water [from BLS (ft)]	Water height (ft)
GW-834	19.80	3.00	16.80	13.90 (8/20/96)	10.90	5.90
GW-835	22.10	2.90	19.2	13.23 (8/14/96)	10.33	8.87
GW-836	27.35	3.00	24.35	16.12 (8/28/96)	13.12	11.23
GW-837	30.90	3.00	27.90	12.94 (8/19/96)	9.94	17.96

Table 8. Groundwater analytical results

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)			
	8/20/96		8/14/96		8/19/96			
Collection date	Filtered		Unfiltered		Filtered		Unfiltered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Bicarbonate, mg/L			443		426		434	
Mercury, mg/L	0.0002		<0.0002		0.00049		0.0012	
Aluminum, µg/L	2760	2670	9860	8210	1220	4630	27900	25500
Boron, µg/L	102	<100	114	<100	108	<100	39.9	<100
Barium, µg/L	>23200	23800	23700	24300	83.5	483	578	587
Calcium, µg/L	>1000000	2629000	>1000000	2662000	163000	>1000000	>1000000	1681000
Cadmium, µg/L	411	391	427	404	<20	199	204	196
Cobalt, µg/L	216	212	222	211	<20	257	265	265
Chromium, µg/L	<20	<100	<20	<100	<20	<20	<20	<100
Copper, µg/L	65.2	<200	70.5	<200	<30	58.6	77.2	<200
Iron, µg/L	362	<800	5810	5700	712	207	14300	14300
Potassium, µg/L	29000	26500	32000	28200	6380	43200	47900	42400
Magnesium, µg/L	335000	322000	343000	327000	26000	152000	158000	151000
Manganese, µg/L	>100000	145000	>100000	147000	1120	100000	>100000	159000
Molybdenum, µg/L	<40	<200	<40	<200	<40	<40	<40	<200
Sodium, µg/L	506000	494000	516000	500000	17400	695000	705000	688000
Nickel, µg/L	1660	1710	1710	1750	<40	2130	2140	2210
Lead, µg/L	<200	<800	<200	<800	<200	<200	<200	<800
Thallium, µg/L	136	<500	139	<500	<100	143	169	<500
Vanadium, µg/L	<10	<50	<10	<50	<10	<10	<10	<50

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)						
	8/20/96		8/14/96		8/19/96						
Collection date	8/20/96		8/14/96		8/19/96						
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2					
Analysis	Filtered		Filtered		Filtered						
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2					
	Unfiltered		Unfiltered		Unfiltered						
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2					
Zinc, µg/L	33.5	<100	44.8	<100	<20	<20	97.6	<100	119	<100	105
Selenium, µg/L	<500	<3000	<500	<3000	<500	<500	<500	<3000	<500	<3000	<3000
Silver, µg/L	<20	<80	<20	<80	<20	<20	<20	<80	<20	<80	<80
Arsenic, µg/L	<100	<500	<100	<500	<100	<100	<100	<500	<100	<500	<500
Beryllium, µg/L	2	<5.0	2.5	<5.0	<1.0	<1.0	2.9	<5.0	4.5	<5.0	<5
Antimony, µg/L	<100	<500	100	<500	<100	<100	<100	<500	<100	<500	<500
Lithium, µg/L	41.8	<50	50.5	<50	30.6	32.4	119	93.8	143	93.8	124
Phosphorous, µg/L	547	<2000	668	<2000	<300	<300	562	<2000	724	<2000	<2000
Titanium, µg/L	<20	<80	189	96.2	<20	124	<20	<80	244	<80	161
Strontium, µg/L	660	6770	6670	6850	488	490	2390	2440	2450	2440	2500
Alkalinity, mg/L			420	310.1					410		
Alpha activity, pC/L			210	370					790		
Beta activity, pC/L			9000	280					4300		
Tritium, pC/L			1500	-46					1100		
Fluoride, mg/L			4.8	0.4					4.9		
Chloride, mg/L			260	28					320		
Nitrite as Nitrogen, mg/L			8.3	0.2					7.3		
Bromide, mg/L			NA	NA					NA		
Nitrate as Nitrogen, mg/L			2300	29					1400		

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)			
	8/20/96		8/14/96		8/19/96			
Analysis	Filtered		Filtered		Filtered		Unfiltered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Ortho-Phosphate as Phosphorus, mg/L		<5.0		<0.12		<5.0		<5.0
Sulfate, mg/L		14		150		390		390
22-Sodium Activity, pC/L		1.1		1.5		-1.5		-1.5
40-Potassium Activity, pC/L		52		50		42		42
51-Chromium Activity, pC/L		-1.2		8.1		9.7		9.7
54-Manganese Activity, pC/L		0.85		1.6		-0.095		-0.095
57-Cobalt Activity, pC/L		-0.57		0.84		0.31		0.31
58-Cobalt Activity, pC/L		-1.2		-1.4		0.49		0.49
59-Iron Activity, pC/L		0.9		-0.7		3		3
60-Cobalt Activity, pC/L		2.3		-1.7		2.9		2.9
65-Zinc Activity, pC/L		-0.63		-0.55		1		1
95-Niobium Activity, pC/L		3.6		-0.5		2.7		2.7
95-Zirconium Activity, pC/L		-1.9		-3.3		-1.6		-1.6
106-Ruthenium Activity, pC/L		-2.2		13		3.9		3.9
125-Antimony Activity, pC/L		-0.78		-2.9		2.4		2.4

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)	
	8/20/96		8/14/96		8/19/96	
Analysis	Filtered		Filtered		Filtered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
134-Cesium Activity, pC/L		-1.2		-0.52		1.2
137-Cesium Activity, pC/L		-0.77		-0.064		-2.4
144-Cerium Activity, pC/L		1.3		-3.5		-2.1
208-Thallium Activity, pC/L		4.5		3.4		3.1
212-Bismuth Activity, pC/L		13		13		1.8
212-Lead Activity, pC/L		18		6.4		12
235 Uranium Activity, pC/L		7.8		5		20
Technetium -99, pC/L		22000		150		10000
Total Dissolved Solids, mg/L				690		11000
Total Strontium, pC/L		-2.4		0.4		360
Total Suspended Solids, mg/L		190		9		
Uranium, -/g		0.0037		1.7		2.6
Unknown, µg/L		65				60
Acetaldoxime, µg/L		6				
1,2-EthanedioI, Dinitrate, µg/L		16				

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)	
	8/20/96		8/14/96		8/19/96	
Collection date	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Analysis	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1,5-Pentanediol, Dinitrate, µg/L		10				
Chloromethane, µg/L		10 U		10 U		3 J
Bromomethane, µg/L		4 J		10 U		2 J
Vinyl chloride, µg/L		10 U		10 U		10 U
Chloroethane, µg/L		10 U		10 U		10 U
Trichlorofluoromethane, µg/L		10 U		10 U		10 U
Methylene chloride, µg/L		14		10 U		18
Acetone, µg/L		12		9 BJ		43
1,1,2-Trichloro- 1,2,2-trifluoroethane, µg/L		10 U		5 J		3 J
Carbon disulfide, µg/L		10 U		10 U		10 U
1,1-Dichloroethene, µg/L		10 U		10 U		10 U
1,1-Dichloroethane, µg/L		10 U		10 U		10 U
cis-1,2-Dichloroethene, µg/L		6 J		10 U		3 J
trans-1,2-Dichloroethene, µg/L		10 U		10 U		10 U
Chloroform, µg/L		9 J		10 U		7 J
1,2-Dichloroethane, µg/L		10 U		10 U		10 U
2-Butanone, µg/L		4 BJ		3 BJ		8 BJ

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)	
	8/20/96		8/14/96		8/19/96	
Analysis	Filtered		Filtered		Filtered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1,1,1-Trichloroethane, $\mu\text{g/L}$		10 U		10 U		1 J
Carbon tetrachloride, $\mu\text{g/L}$		10 U		10 U		10 U
Bromodichloromethane, $\mu\text{g/L}$		10 U		10 U		10 U
1,2-Dichloropropane, $\mu\text{g/L}$		10 U		10 U		10 U
cis-1,3-Dichloropropene, $\mu\text{g/L}$		10 U		10 U		10 U
Trichloroethene, $\mu\text{g/L}$		10 U		10 U		10 U
Dibromochloromethane, $\mu\text{g/L}$		10 U		10 U		10 U
1,1,2-Trichloroethane, $\mu\text{g/L}$		10 U		10 U		10 U
Benzene, $\mu\text{g/L}$		10 U		10 U		10 U
trans-1,3-Dichloropropene, $\mu\text{g/L}$		10 U		10 U		10 U
Bromoform, $\mu\text{g/L}$		10 U		10 U		10 U
4-Methyl-2-pentanone, $\mu\text{g/L}$		10 U		10 U		2 J
2-Hexanone, $\mu\text{g/L}$		10 U		10 U		10 U
Tetrachloroethene, $\mu\text{g/L}$		2 J		4 J		14
1,1,2,2-Tetrachloroethane, $\mu\text{g/L}$		10 U		10 U		10 U

Table 8 (continued)

Sample No. (location)	PA1001 (GW-834)		PA1002 (GW-835)		PA1004 (GW-837)	
	8/20/96		8/14/96		8/19/96	
Collection date	8/20/96		8/14/96		8/19/96	
Analysis	Filtered		Filtered		Filtered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
	Unfiltered		Unfiltered		Unfiltered	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Toluene, µg/L		10 U		10 U		10 U
Chlorobenzene, µg/L		10 U		10 U		10 U
Ethylbenzene, µg/L		10 U		10 U		10 U
Styrene, µg/L		10 U		10 U		10 U
Xylene, µg/L		10 U		10 U		10 U
Ethane				4.03		
1,2-Dichloro-1,1,2-tr, µg/L						

Table 9. Groundwater field measurements (see Table 8)

Location	Sample no.	Conductivity (mS/cm)	pH (su)	Temperature (°C)
GW-834	PA1001	16.5	5.48	23.8
GW-835	PA1002	1.12	6.41	22.6
GW-837	PA1004	11.9	5.38	26.4

Table 10. Migration pathway chemical characteristics

Migration pathway	Sample location	Nitrate (mg/L)	Uranium (ug/g)	Gross alpha (pCi/L)	Gross beta (pCi/L)	Technetium (pCi/L)
1	GW-837	1400	2.6	790	4300	10,000
2	GW-835	29	1.7	370	280	150
3	GW-834	2300	0.0037	210	9000	22,000
3 (cont.)	TPBs -12, -13, -20	2- >50	<0.003-0.037	97-1581	78-824	N/A

APPENDIX B

**BEAR CREEK VALLEY TREATABILITY
STUDY SORPTION STUDIES**

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof.

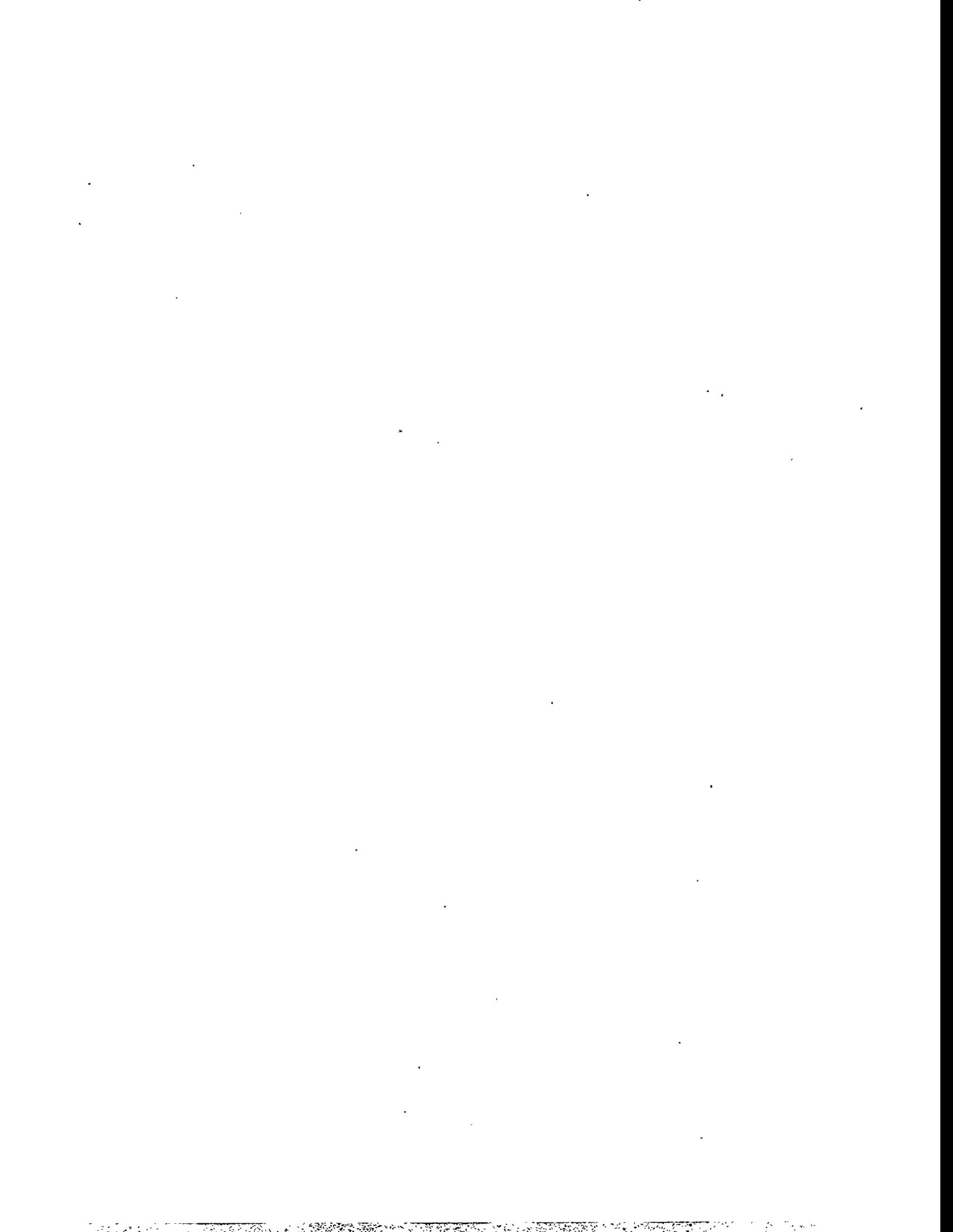
**BEAR CREEK VALLEY CHARACTERIZATION AREA
TECHNOLOGY DEMONSTRATION PROJECT:
SORPTION STUDIES**

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Paul A. Taylor

Chemical Technology Division

August 1996

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**BEAR CREEK VALLEY CHARACTERIZATION AREA
TECHNOLOGY DEMONSTRATION PROJECT:
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Background

Remediation methods are sought for reduction of uranium, metals, and organics [trichloroethylene (TCE), perchloroethylene (PCE)] from waters located at the Y-12 Plants. The main study focuses on waters denoted Boneyard Burnyard (BYBY) and North Tributary (NT-1)

The BYBY water contains mainly Al (3 ppm), Ca (56 ppm), Cl (30 ppm), Fe (2.5 ppm), Mg (6.5 ppm), K (5.5 ppm), Si (10 ppm), Na (14.5 ppm), sulfate (12 ppm), TCE (1 ppm), and PCE (2 ppm).

The NT-1 water contains mainly Al (81 ppm), Ba (20 ppm), Ca (>1000 ppm), Cl (180 ppm), Fe (37 ppm), Mg (224 ppm), Mn (>100 ppm), Ni (3 ppm), nitrate (8500 ppm), K (48 ppm), Na (379 ppm), and sulfate (12 ppm).

Objective and Scope

The scope of our studies is to investigate sorbents for reduction of uranium, metals, and organics (TCE, PCE) from waters located at the Y-12 Plants. The purpose of our experiments is to find a way to remove uranium and organics from BYBY water and metals from NT-1 waters.

Methods

Experimental Procedure for Uranium Sorption Screening Studies - Sorbent (0.25 g) was combined with 50 mL of groundwater, and 550 μ L of a 101-mg uranium/L solution was added to each tube. The experiments were carried out in 50-mL nominal volume polypropylene centrifuge tubes which were shaken for 24 h. Upon completion, the tubes were centrifuged at 1000 rpm for 5 min. The supernate was transferred to new centrifuge tubes before 100 μ L of concentrated nitric acid was added as a preservative. The samples were analyzed for uranium following the EPA method SW846-6010A for ICP analyses. For each sample, three burns were performed on a ICP-ES (Thermo Jarrell Ash, model 61E Trace), and the average of three burns was used in determining the results. The samples were filtered before analysis.

Experimental Procedure for Uranium Sorption Isotherm Studies - Sorbent (various amounts) was combined with 50 mL of groundwater, and 550 μ L of a 101-mg uranium/L solution was added to each tube. The experiments were carried out in 50-mL nominal volume polypropylene centrifuge tubes which were shaken for 24 h. Upon completion, the tubes were centrifuged at 1000 rpm for 5 min. The supernate was transferred to new centrifuge tubes before 100 μ L of concentrated nitric acid was added as a preservative. The samples were analyzed for uranium following the EPA method SW846-6010A for ICP analyses. For each sample, three burns were performed on a ICP-ES (Thermo Jarrell Ash, model 61E Trace), and

the average of three burns was used in determining the results. The samples were filtered before analysis.

Experimental Procedure for Metals Sorption Screening Studies - Sorbent (0.25 g) was combined with 50 mL of groundwater in each tube. The experiments were carried out in 50-mL nominal volume polypropylene centrifuge tubes which were shaken for 24 h. Upon completion, the tubes were centrifuged at 1000 rpm for 5 min. The supernate was transferred to new centrifuge tubes before 100 μ L of concentrated nitric acid was added as a preservative. The samples were analyzed for metals following the EPA method SW846-6010A for ICP analyses. For each sample, three burns were performed on a ICP-ES (Thermo Jarrell Ash, model 61E Trace), and the average of three burns was used in determining the results. The samples were filtered before analysis.

Experimental Procedure for VOC Sorption Studies - Sorbent (0.2 g) was combined with 40 mL of groundwater, 40 μ L of a TCE saturated water solution, and 400 μ L of a PCE saturated water solution; the experiment blank sample contained no sorbent. The experiments were carried out in 40-mL nominal volume glass vials which were shaken for 24 h. Upon completion, the tubes were centrifuged at 1000 rpm for 10 min. 150 μ L of the supernate was combined with 1000 μ L hexane for micro-extraction. The samples were analyzed for TCE and PCE using a gas chromatograph with electron capture detector. A three-point calibration method was used in analyzing the results.

Sorbents Used - A variety of sorbents are evaluated, ranging from natural materials (such as peat moss and zeolite) to highly engineered adsorbents (biobeads and ion exchange sorbents). A listing of the sorbents are below.

- Phosphate Rock (P-Rock), Loncala Phosphate Co., FL, \$0.03/lb
- TRW Coal-based Sorbent (TRW), TRW Inc., CA, \$0.15/lb (not commercially available)
- Granular Activated Carbon (GAC), Calgon Corp., PA, \$1.66/lb
- Zeolite, Robert Bowman, New Mexico Tech, N.M., \$0.04/lb
- Surfactant-modified Zeolite (SMZ), Robert Bowman, New Mexico Tech, N.M., \$0.13/lb (not commercially available)
- Dowex 21K Anion Exchange Resin, Dow Chemical Co., MI, \$4.19/lb
- Peat Moss, K-Mart, \$0.07/lb
- Cercona Zeolite (not commercially available)
- Biobeads (polymer beads with *Pseudomonas aeruginosa*), Mark Reeves, ORNL, TN, (not commercially available)
- Amberlite IRC-718, Rohm & Haas, PA, \$9.75/lb
- Ionac SR-4, Sybron Chemical Inc., N.J., \$10.22/lb
- MATS (cyanobacteria grown on glass fiber), MATS, Inc., GA., (not commercially available)

Result

Uranium Uptake: Screening Studies

Summary: Several of the sorbents, such as granulated activated carbon (GAC), coal based resin (TRW), peat moss, Dowex anion 21K exchange resin, phosphate rock (P Rock), and surfactant-modified zeolite (SMZ), worked well with the BYBY water. The TRW (coal-based sorbent) and the peat moss worked well for the NT-1 water.

Below are the results from screening studies conducted with BYBY and NT-1 waters.

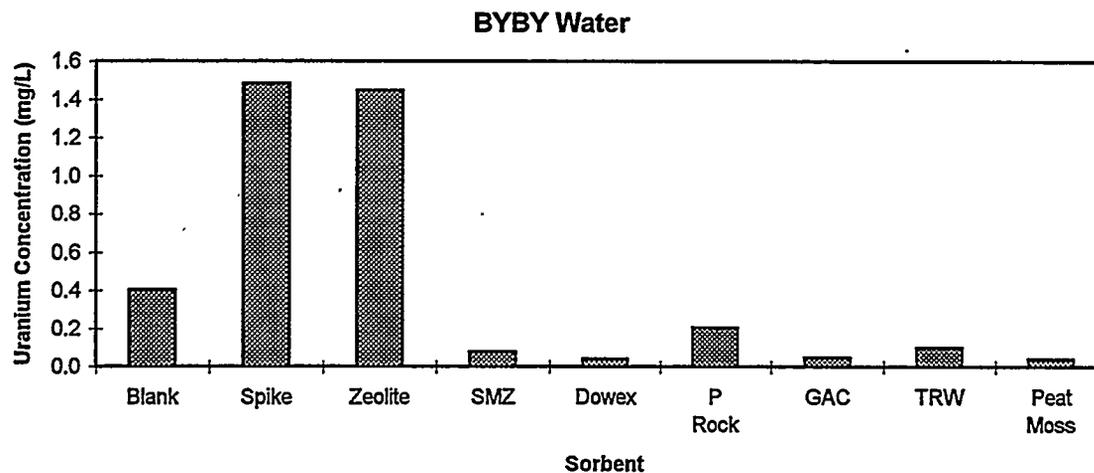


Figure 1. Screening study with various sorbents in BYBY water. In this study, several of the sorbents (granulated activated carbon [GAC], coal based resin [TRW], peat moss, Dowex anion 21K exchange resin, phosphate rock (P Rock), and surfactant-modified zeolite[SMZ] worked well with the BYBY water.

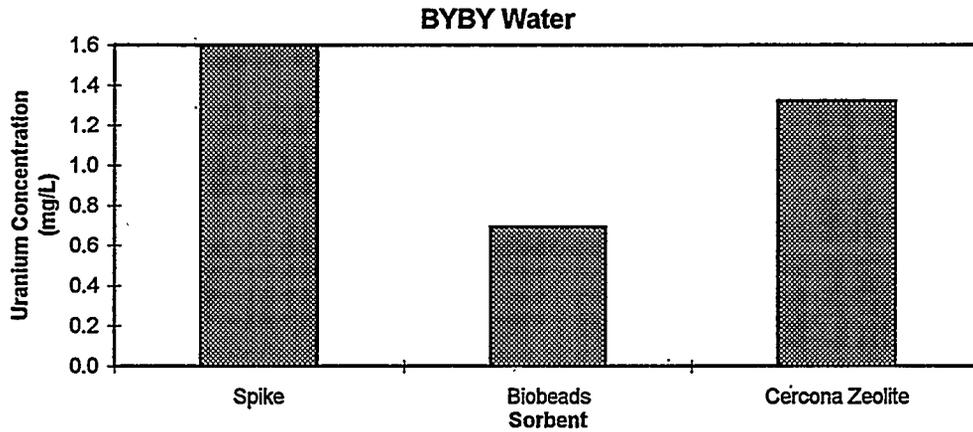


Figure 2. Screening study with various sorbents in BYBY water. In this study, the biobeads (with *Pseudomonas aeruginosa*) worked to some extent, but none of the sorbents worked very well.

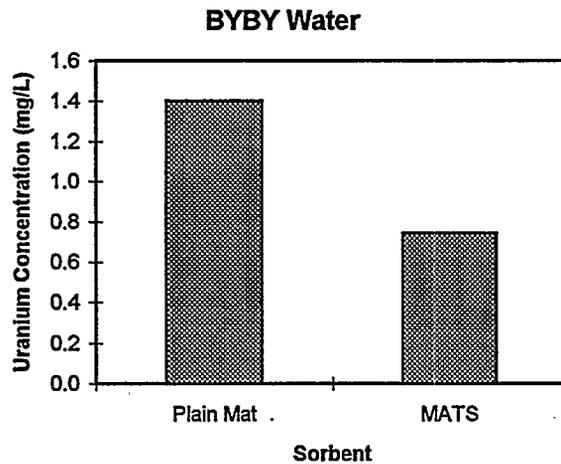


Figure 3. Screening study with MATS (microbial consortium dominated by cyanobacteria grown on glass fiber) in BYBY water; the blank was a plain glass fiber mat. As is noted, the microbial mat removed about 50% of the spiked uranium.

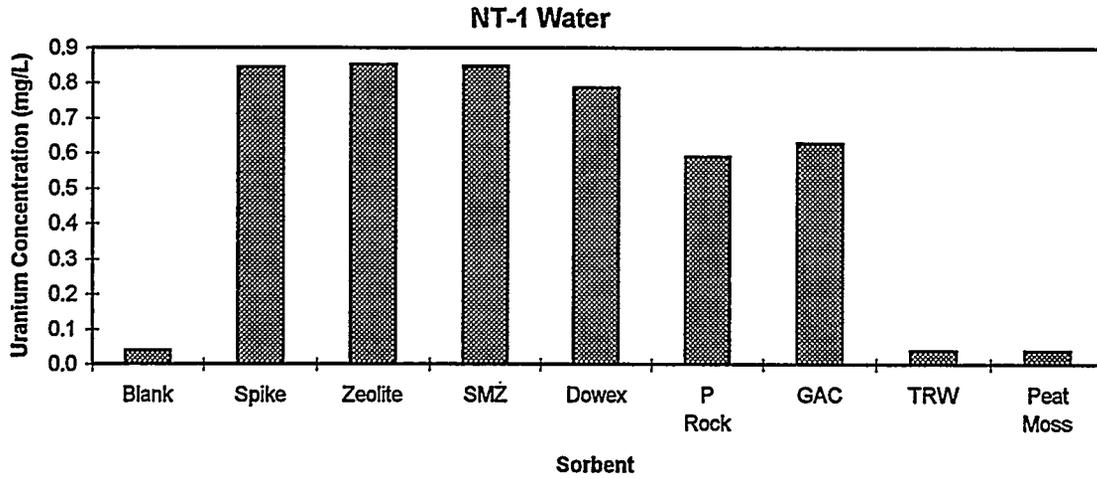


Figure 4. Screening study with various sorbents in NT-1 water. As is noted, the TRW (coal-based sorbent) and the peat moss worked well for the NT-1 water.

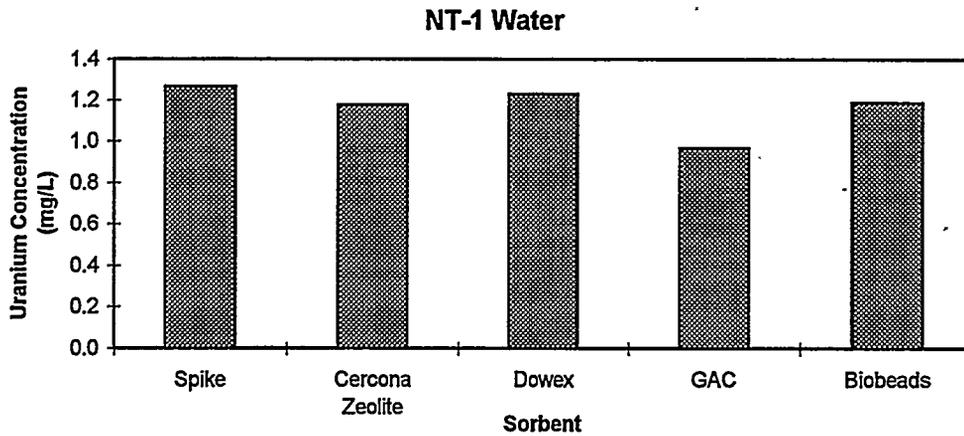


Figure 5. Screening study with various sorbents in NT-1 water. As is noted, none of the sorbents worked very well. (Some of the data are repeats from previous experiments.)

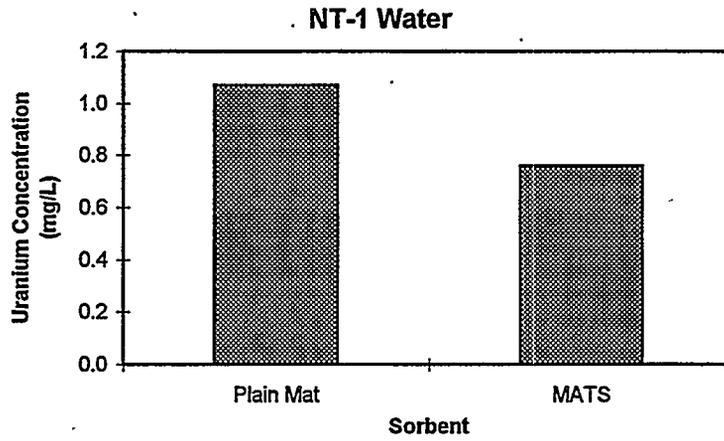


Figure 6. Screening study with MATS (microbial consortium dominated by cyanobacteria grown on glass fiber) in NT-1 water; the blank was a plain glass fiber mat. As is noted, the microbial mat removed about 40% of the spiked uranium.

Uranium Uptake: Isotherm Studies

Summary: Dowex 21K resin, peat moss, coal based resin (TRW) and granulated activated carbon (GAC) had high capacity for uranium in the BYBY water; the least expensive sorbent was peat moss at \$0.11/1000 gallon (1 ppm U). Peat moss had lower capacity for uranium in the NT-1 water but was better than TRW.

Below are the results from isotherm studies conducted with BYBY waters.

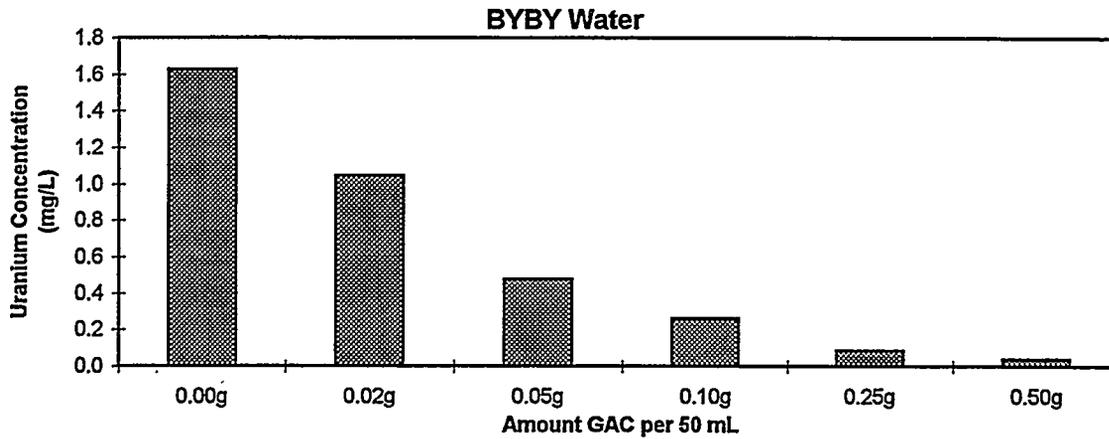


Figure 7. Study with various amounts of sorbents (granulated activated carbon [GAC]) in BYBY water. In this study, a typical isotherm behavior is clear. The isotherm is displayed in Figure 8.

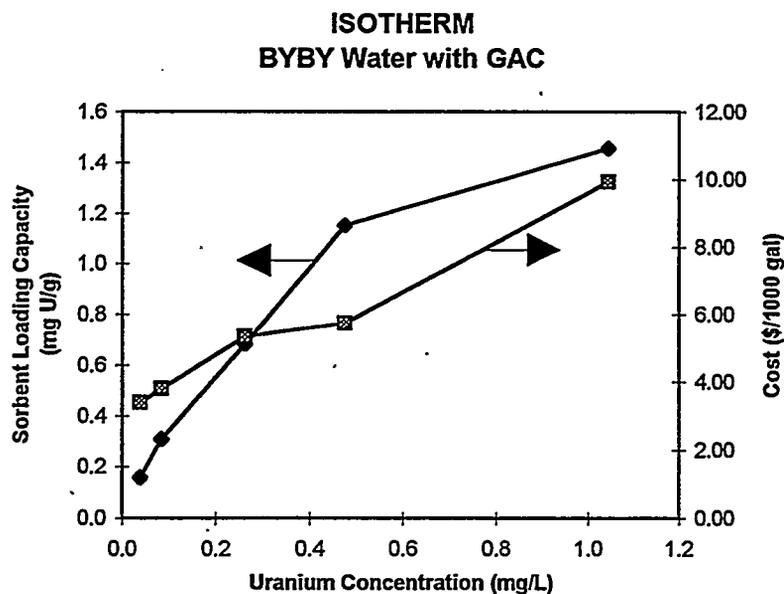


Figure 8. Data from Figure 7 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

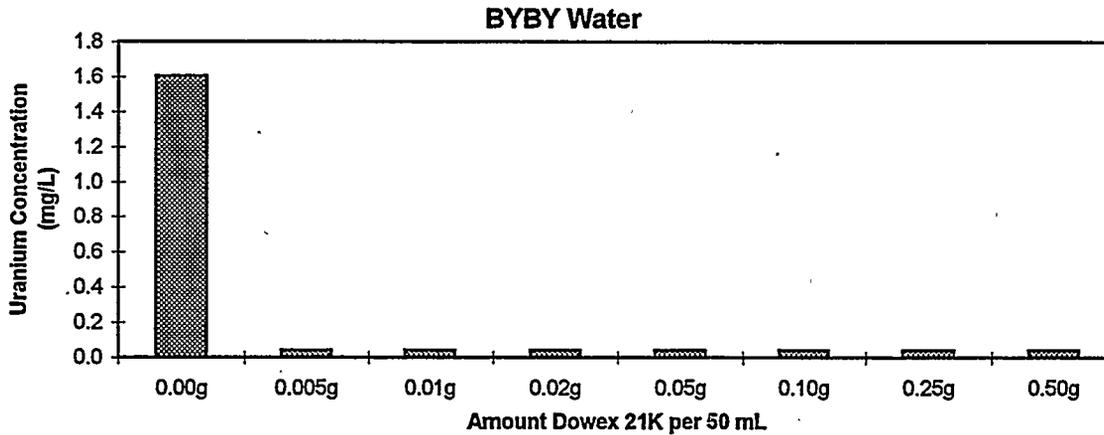


Figure 9. Study with various amounts of sorbents (Dowex 21K resin) in BYBY water. In this study, all levels of sorbent removed all of the uranium; thus, an isotherm cannot be constructed with this data. Thus, less than 0.1g per 1L BYBY water is needed for complete removal of uranium (at an initial value of about 1.6 ppm).

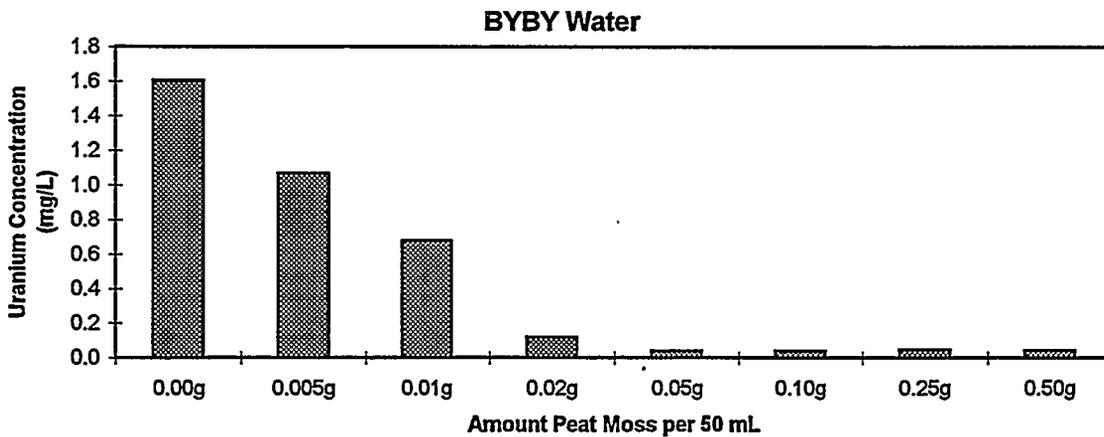


Figure 10. Study with various amounts of sorbents (peat moss) in BYBY water. The isotherm is plotted in Figure 11.

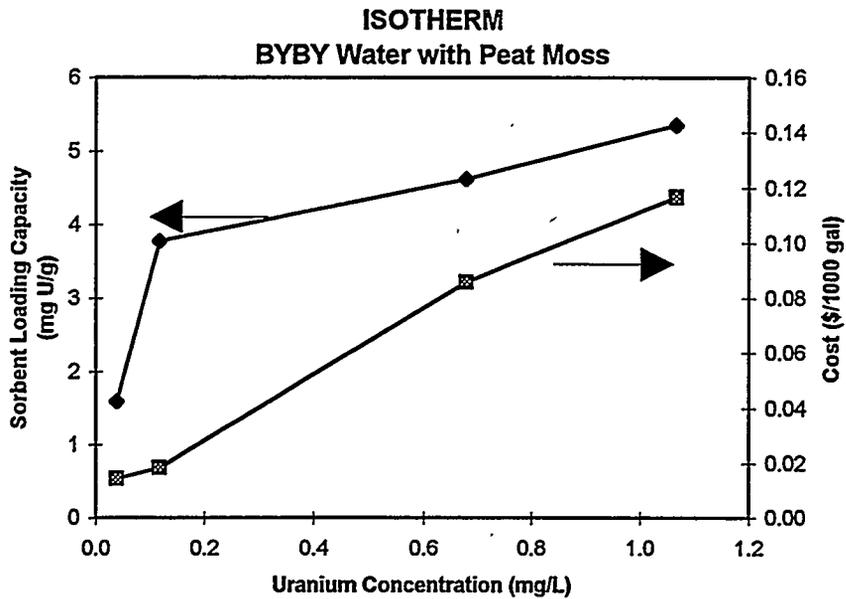


Figure 11. Appropriate data from Figure 10 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

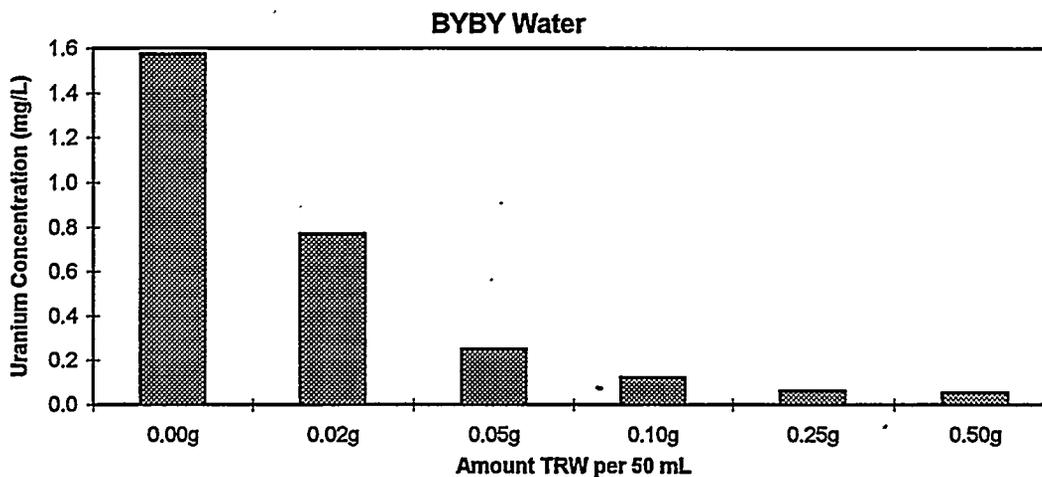


Figure 12. Study with various amounts of sorbents (TRW) in BYBY water. The isotherm is plotted in Figure 13.

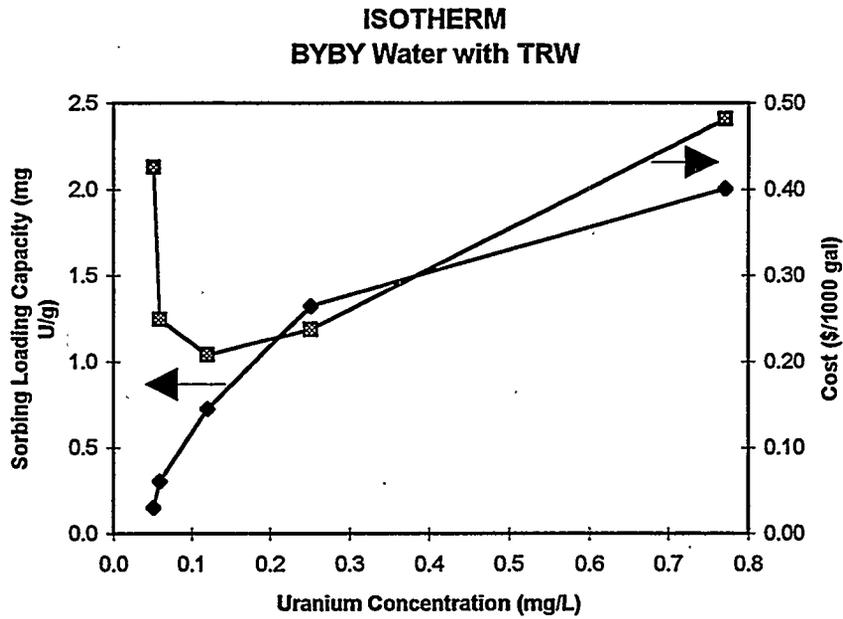


Figure 13. Data from Figure 12 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

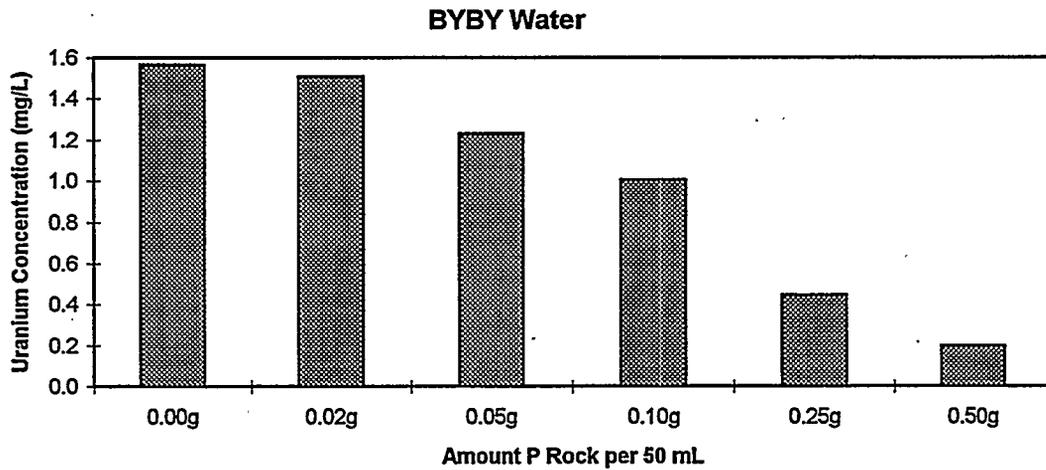


Figure 14. Study with various amounts of sorbents (P Rock) in BYBY water. The isotherm is plotted in Figure 15.

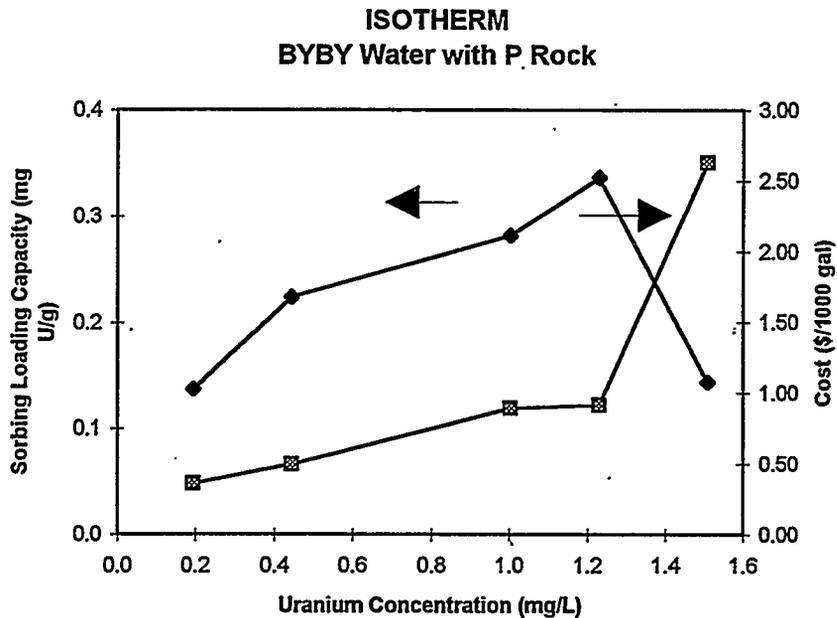


Figure 15. Data from Figure 14 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

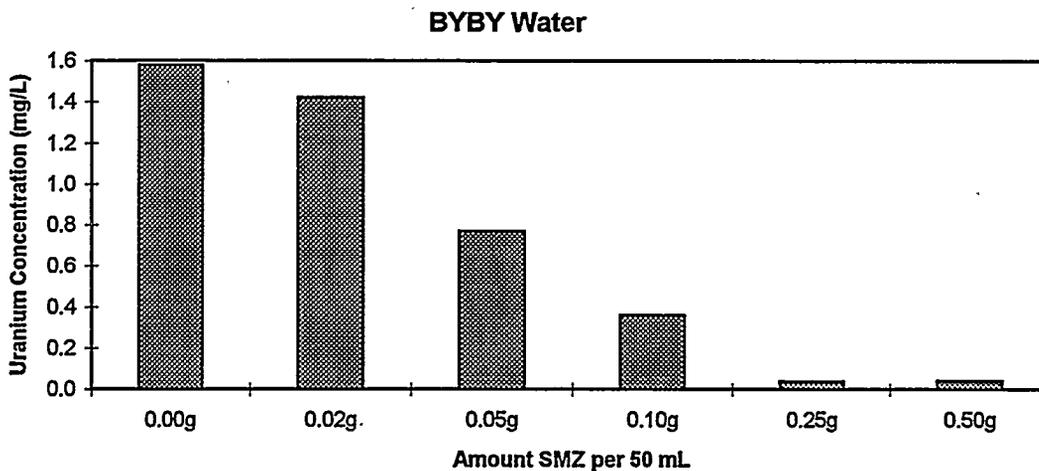


Figure 16. Study with various amounts of sorbents (SMZ) in BYBY water. The isotherm is plotted in Figure 17.

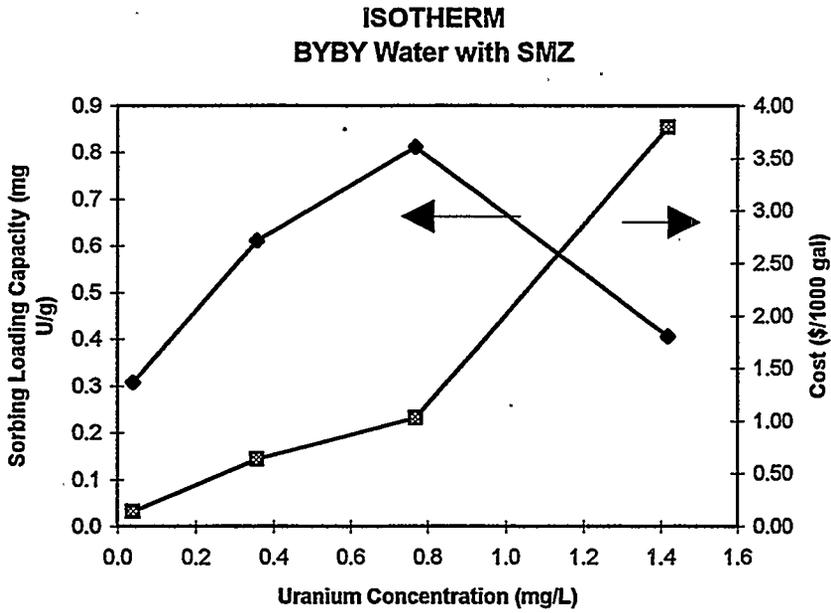


Figure 17. Data from Figure 16 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

Below are the results from isotherm studies conducted with NT-1 waters.

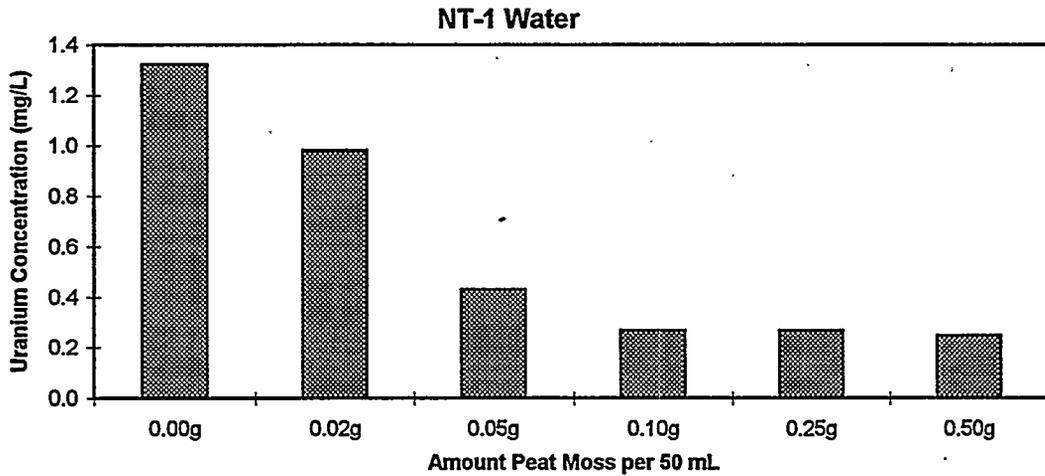


Figure 18. Study with various amounts of sorbents (peat moss) in NT-1 water. The isotherm is plotted in Figure 19.

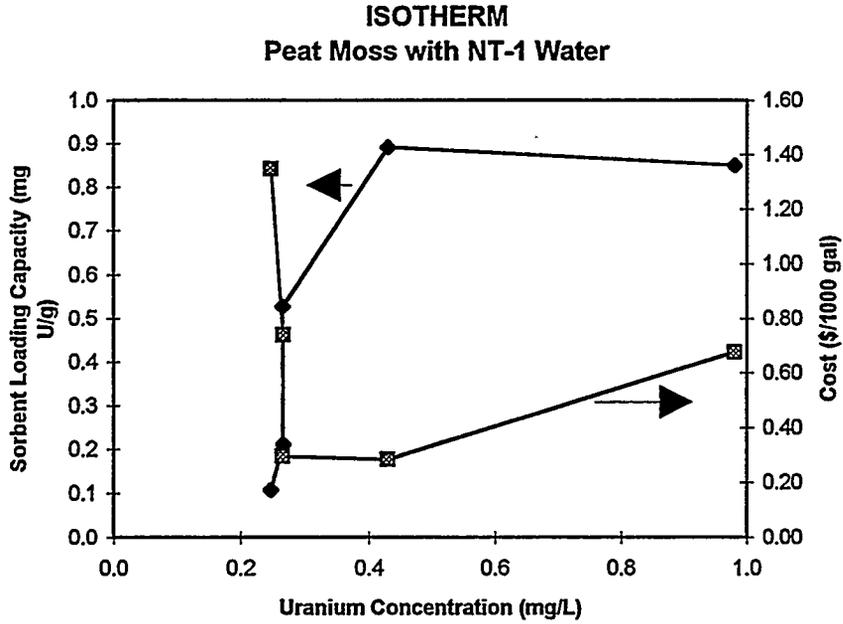


Figure 19. Appropriate data from Figure 18 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

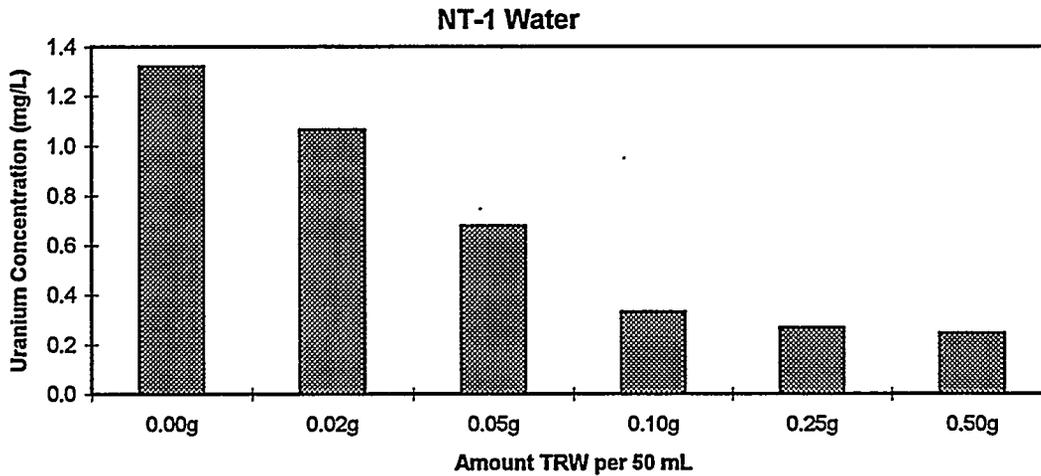


Figure 20. Study with various amounts of sorbents (TRW) in NT-1 water. The isotherm is plotted in Figure 21.

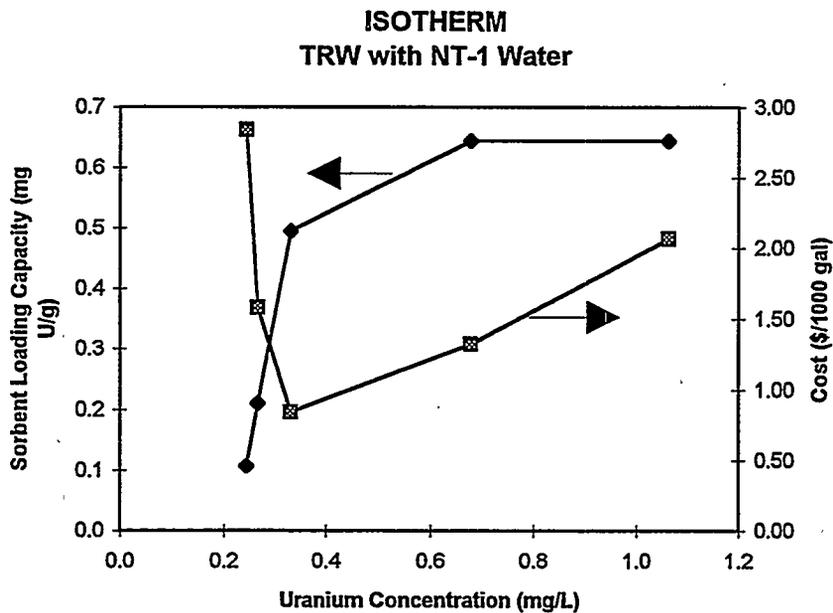


Figure 21. Appropriate data from Figure 20 has been plotted as an isotherm with the amount of uranium sorbed on the sorbent as a function of uranium concentration in the liquid at equilibrium.

Metals Uptake: Screening Studies

Summary: The only sorbents that show some promise for removing metals in general from NT-1 water are Amberlite IRC-718 and MATS.

Below are the results from screening studies conducted with NT-1 waters. In these figures, the left bars correspond to the concentration of metals in the spiked NT-1 water, and the right bars correspond to concentration of metals present in the solution after being in contact with the sorbent for 24 h. From the results displayed in these figures, it is clear that not many of the sorbents were effective in removing the metals. This is probably in part due to the very high concentration on calcium and sodium (>1000 and 379 ppm). The only sorbents that show some promise are Amberlite IRC-718 and MATS; the amount of MATS added have not been determined yet.

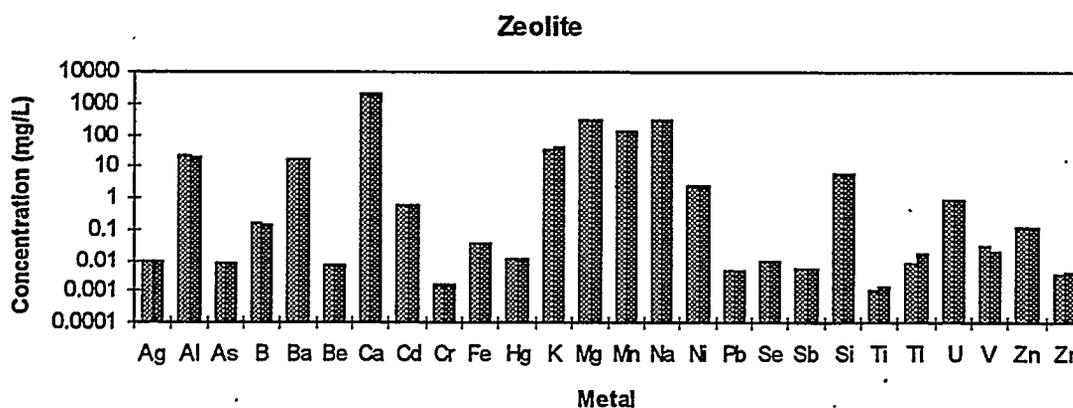


Figure 22. Results from screening study with zeolite in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions.

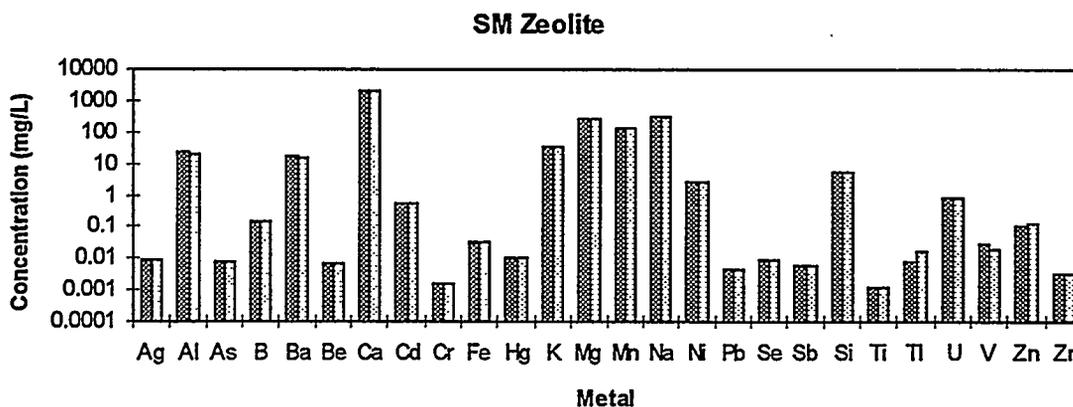


Figure 23. Results from screening study with surfactant-modified zeolite in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions.

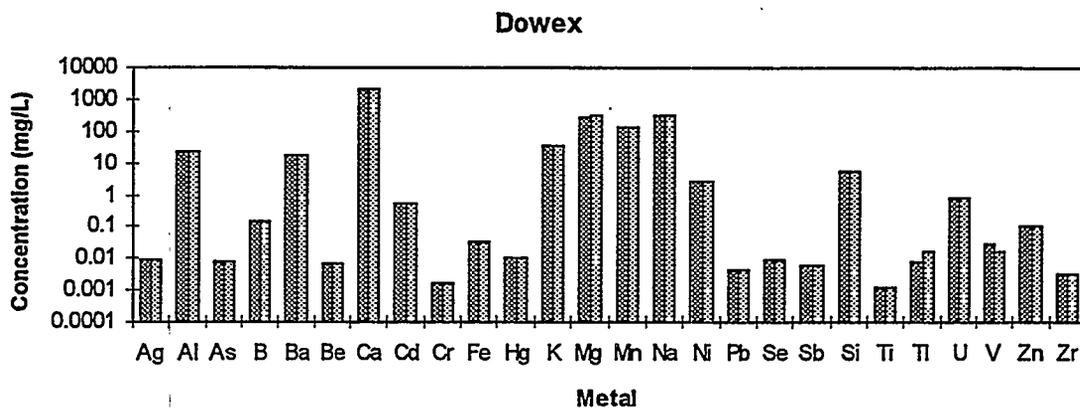


Figure 24. Results from screening study with Dowex 21K resin in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions. This is not surprising since the resin is a anion exchange resin.

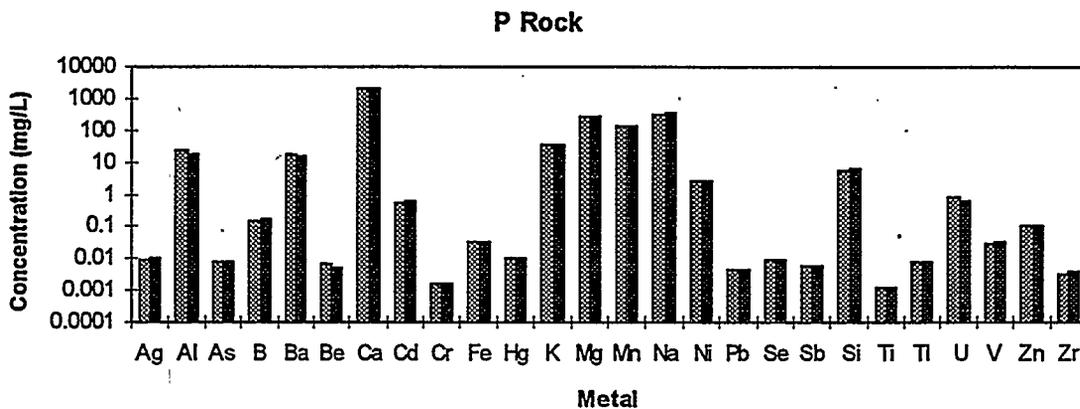


Figure 25. Results from screening study with phosphate rock in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions.

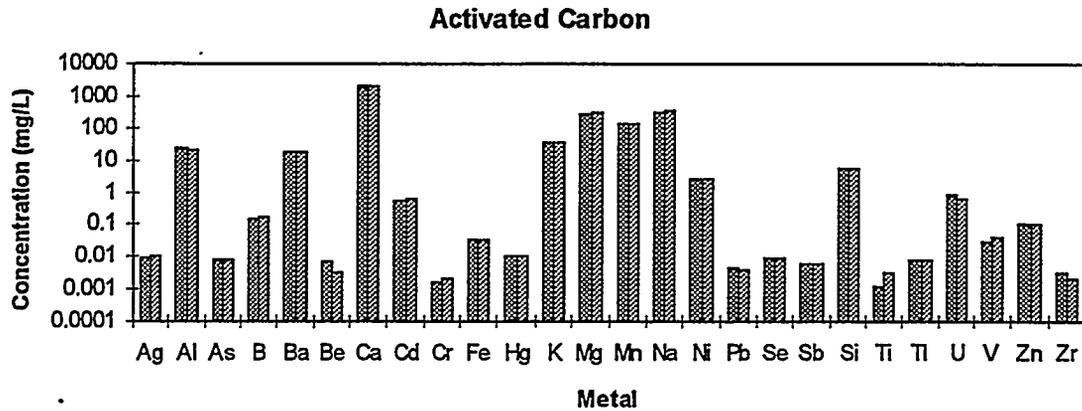


Figure 26. Results from screening study with granular activated carbon in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions.

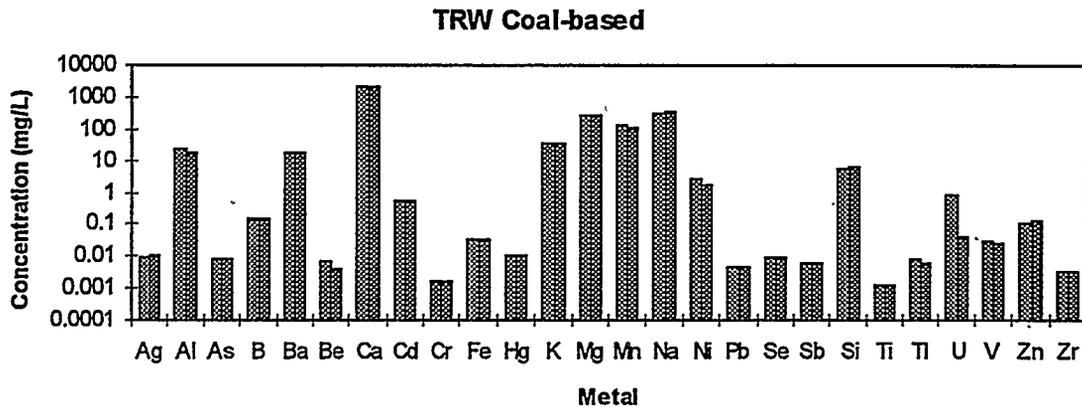


Figure 27. Results from screening study with TRW coal-based sorbent in NT-1 water. As is noted, the sorbent was able to remove uranium but not much of the other dissolved metal ions.

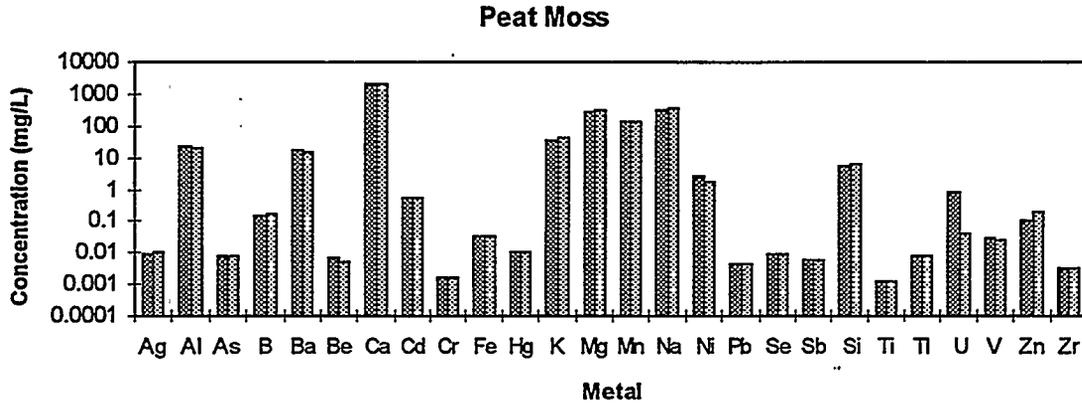


Figure 28. Results from screening study with peat moss in NT-1 water. As is noted, the sorbent was able to remove uranium but not much of the other dissolved metal ions.

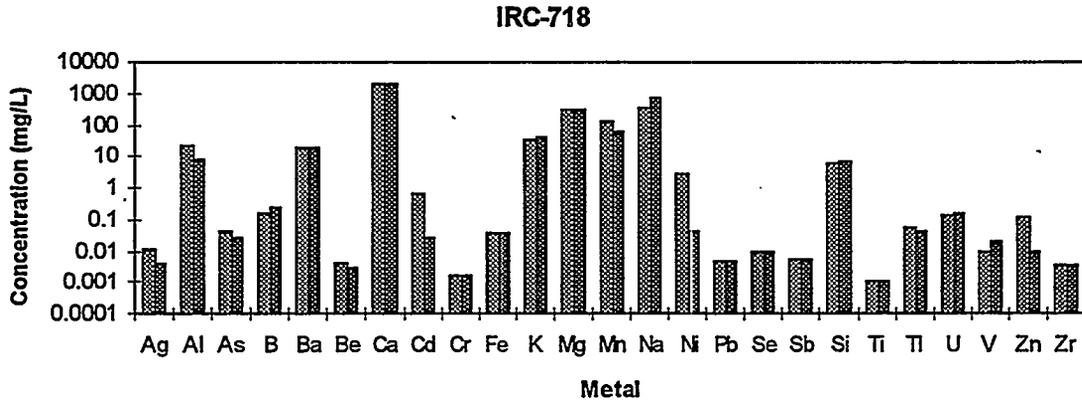


Figure 29. Results from screening study with Amberlite IRC-718 in NT-1 water. As is noted, the sorbent was able to remove some of the Ag, Al, As, Cd, Mn, Ni, and Zn. The Amberlite resin has traditionally been used for removing metals that form strong sulfides.

SR-4

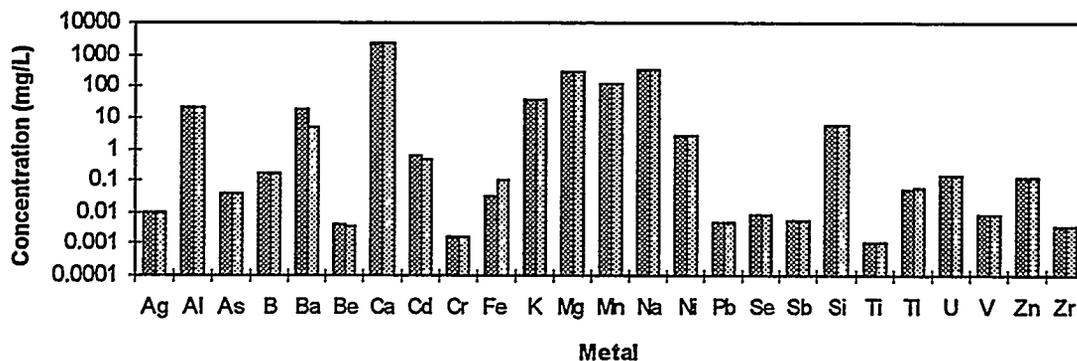


Figure 30. Results from screening study with Ionac SR-4 in NT-1 water. As is noted, the sorbent was not able to remove much of the dissolved metal ions.

MATS

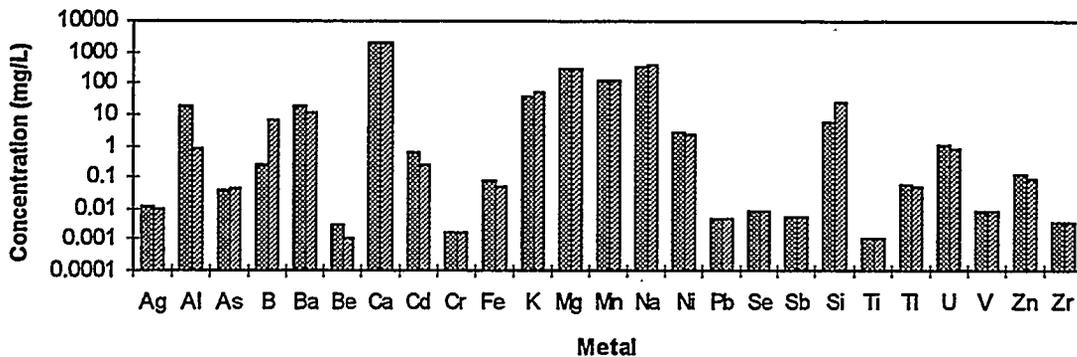


Figure 31. Results from screening study with MATS (microbial consortium dominated by cyanobacteria grown on glass fiber) in NT-1 water. As is noted, the sorbent removed small amounts of the Al, Ba, Be, Cd, Fe, U, and Zn. It appeared that B, Na, K, and Si was released from the culture or the overgrown glass fiber.

Volatile Organics Uptake: Screening Studies

Summary: Granular activated carbon (GAC) and peat moss was effective in removing TCE and PCE from BYBY water.

Below are the results from screening studies conducted with BYBY water.

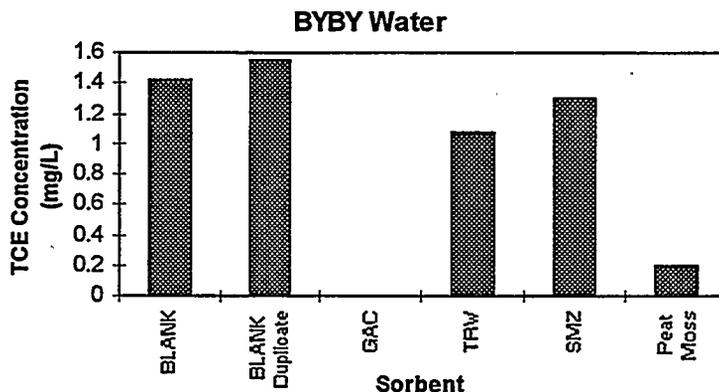


Figure 32. Screening study with various sorbents in BYBY water. In this study, two of the sorbents (granulated activated carbon [GAC] and peat moss) worked well for removing TCE. The duplicate blank provides an indication of error in analysis.

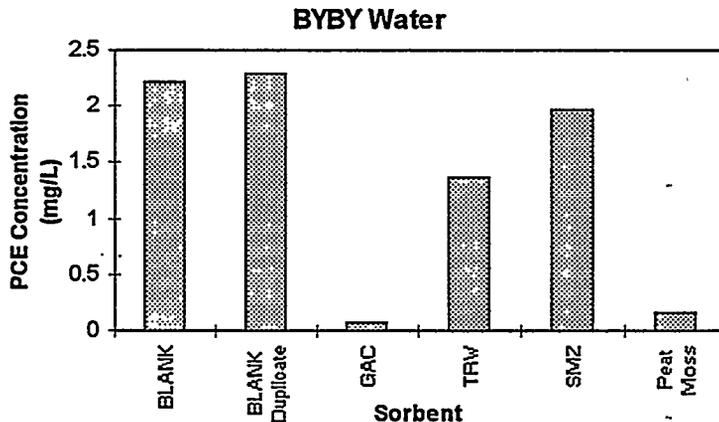
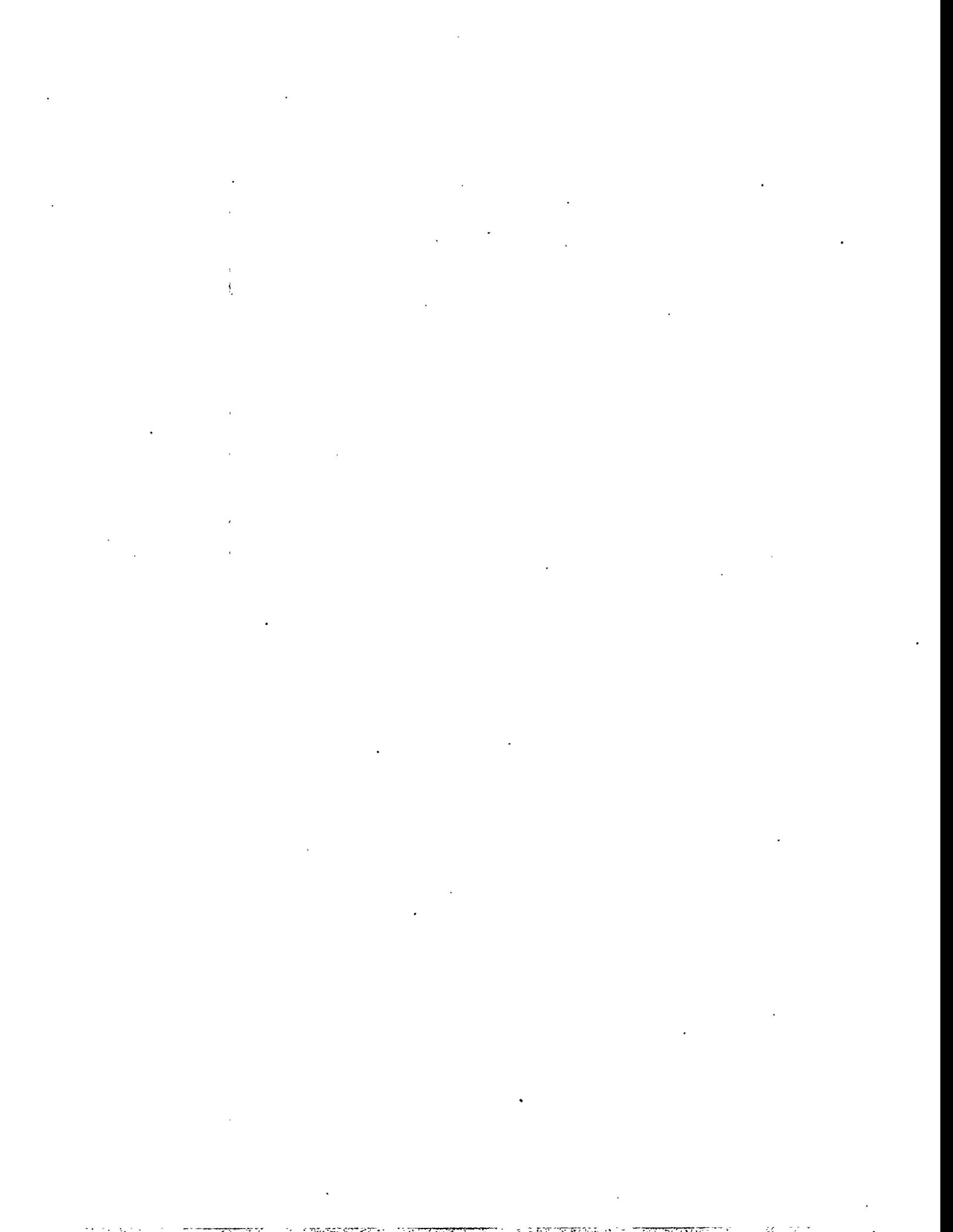


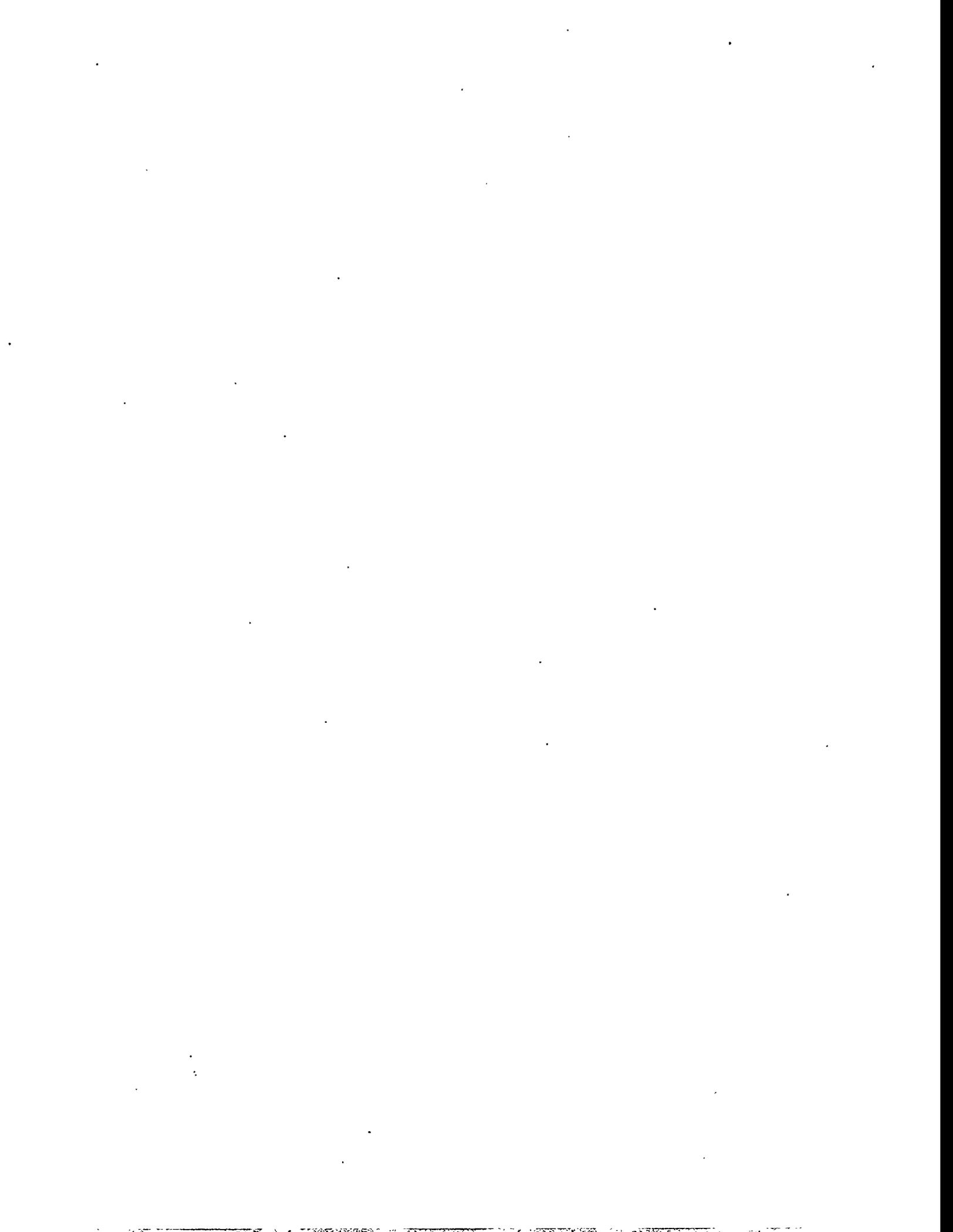
Figure 33. Screening study with various sorbents in BYBY water. In this study, two of the sorbents (granulated activated carbon [GAC] and peat moss) worked well for removing PCE. The duplicate blank provides an indication of error in analysis.

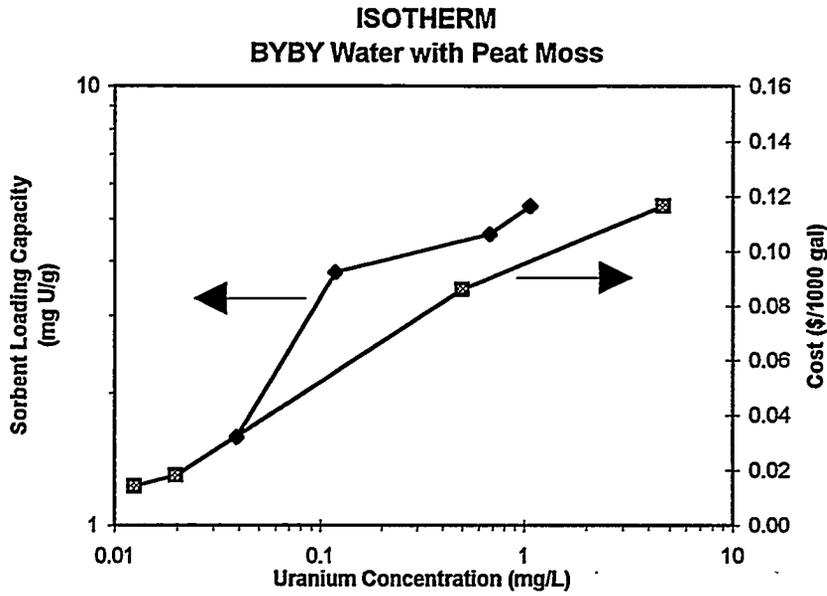
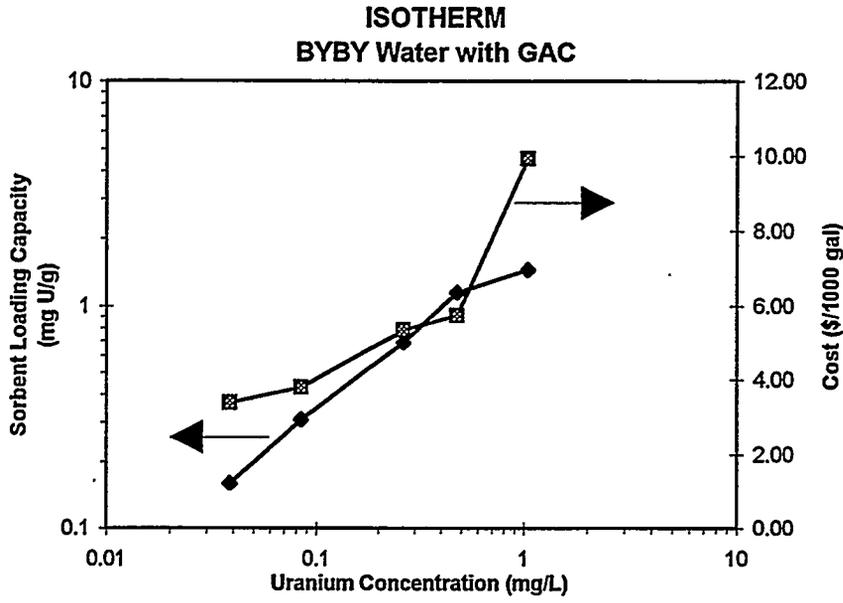
Conclusions and Recommendations

1. Several of the sorbents, such as granulated activated carbon (GAC), coal based resin (TRW), peat moss, Dowex anion 21K exchange resin, phosphate rock (P Rock), and surfactant-modified zeolite (SMZ), worked well with the BYBY water. Dowex 21K resin, peat moss, coal based resin (TRW) and granulated activated carbon (GAC) had high capacity for uranium in the BYBY water; the least expensive sorbent was peat moss at \$0.11/1000 gallon (1 ppm U). The TRW (coal-based sorbent) and the peat moss worked well for the NT-1 water. Peat moss had lower capacity for uranium in the NT-1 than in the BYBY water, water but was better than TRW.
 - **Recommendation:** Study peat moss, GAC, and Dowex 21K in column studies with BYBY water; Dowex 21K can be regenerated and reused. Study peat moss in column studies with NT-1 water. Do not use TRW since it is not commercially available and did not demonstrate superior performance that would warrant commercialization.
2. The only sorbents that show some promise for removing metals in general from NT-1 water are Amberlite IRC-718 and MATS.
 - **Recommendation:** Focus study on MATS in flow through mode since it is the least expensive. Note that this "sorbent" must be used in a open (to light) setting.
3. Granular activated carbon (GAC) and peat moss was effective in removing TCE and PCE from BYBY water.
 - **Recommendation:** Proceed with isotherm studies and evaluate performance before column testing.

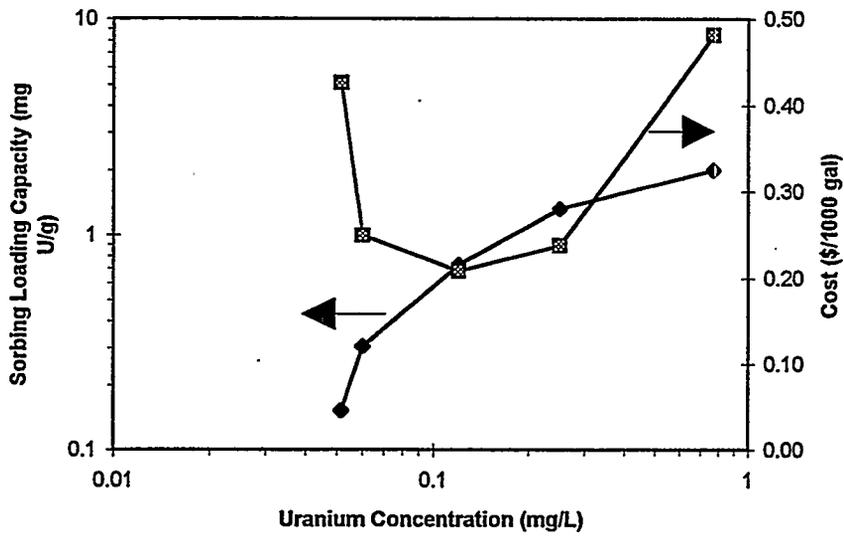


APPENDIX B
ATTACHMENT 1
ISOTHERMS AS LOG PLOTS

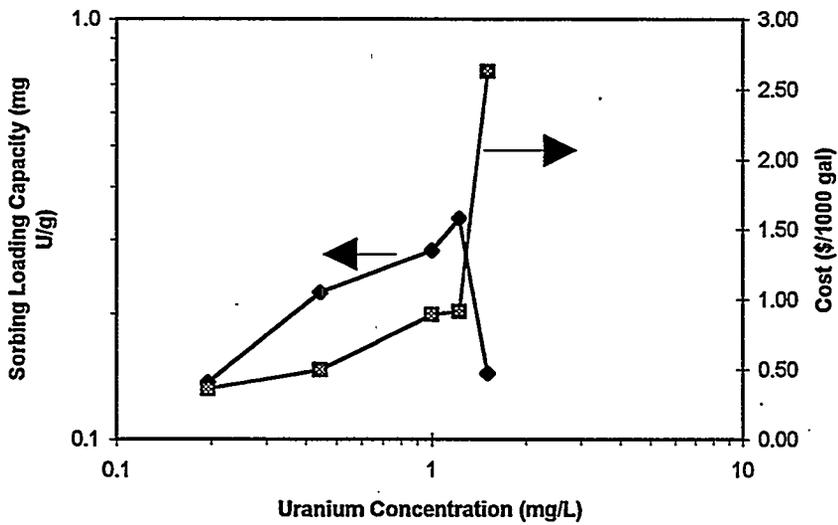




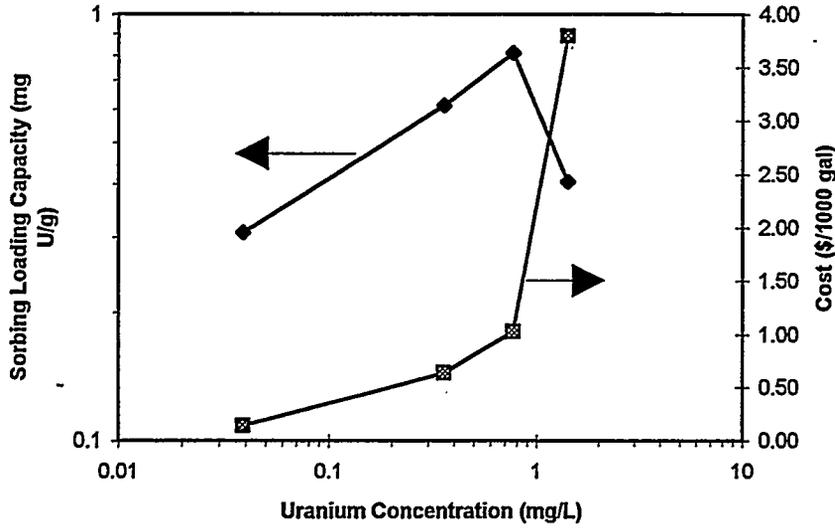
ISOTHERM
BYBY Water with TRW



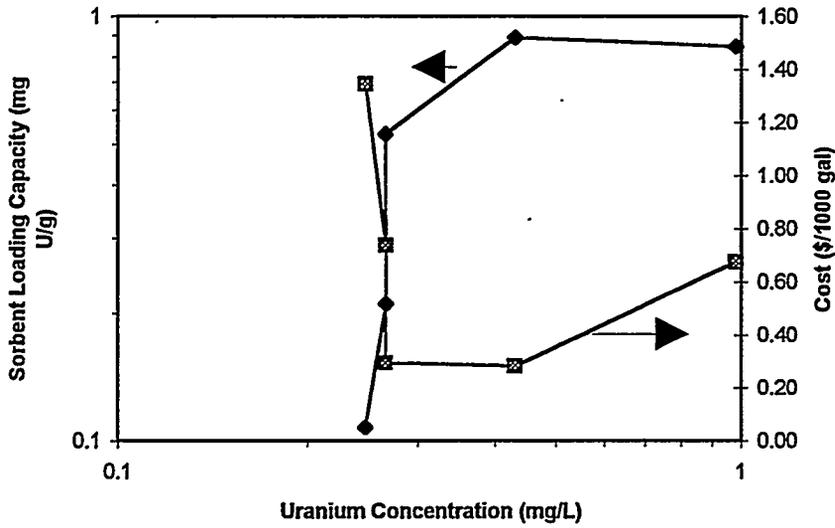
ISOTHERM
BYBY Water with P Rock



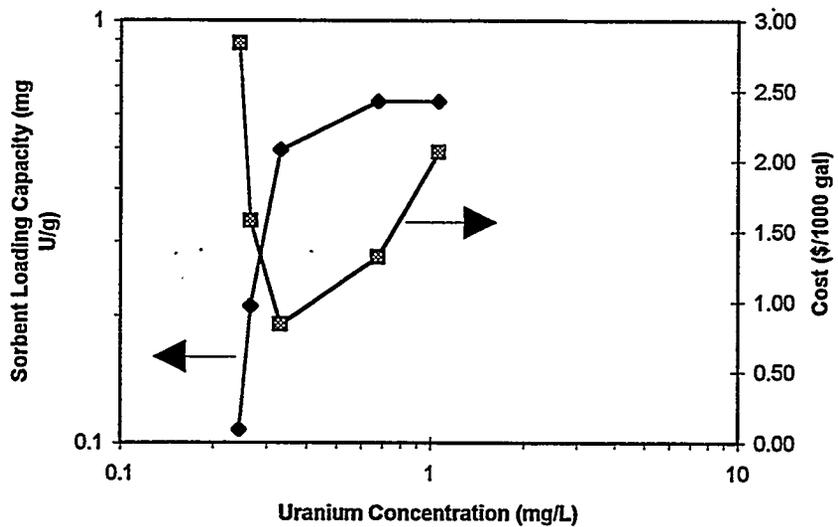
ISOTHERM
BYBY Water with SMZ



ISOTHERM
Peat Moss with NT-1 Water

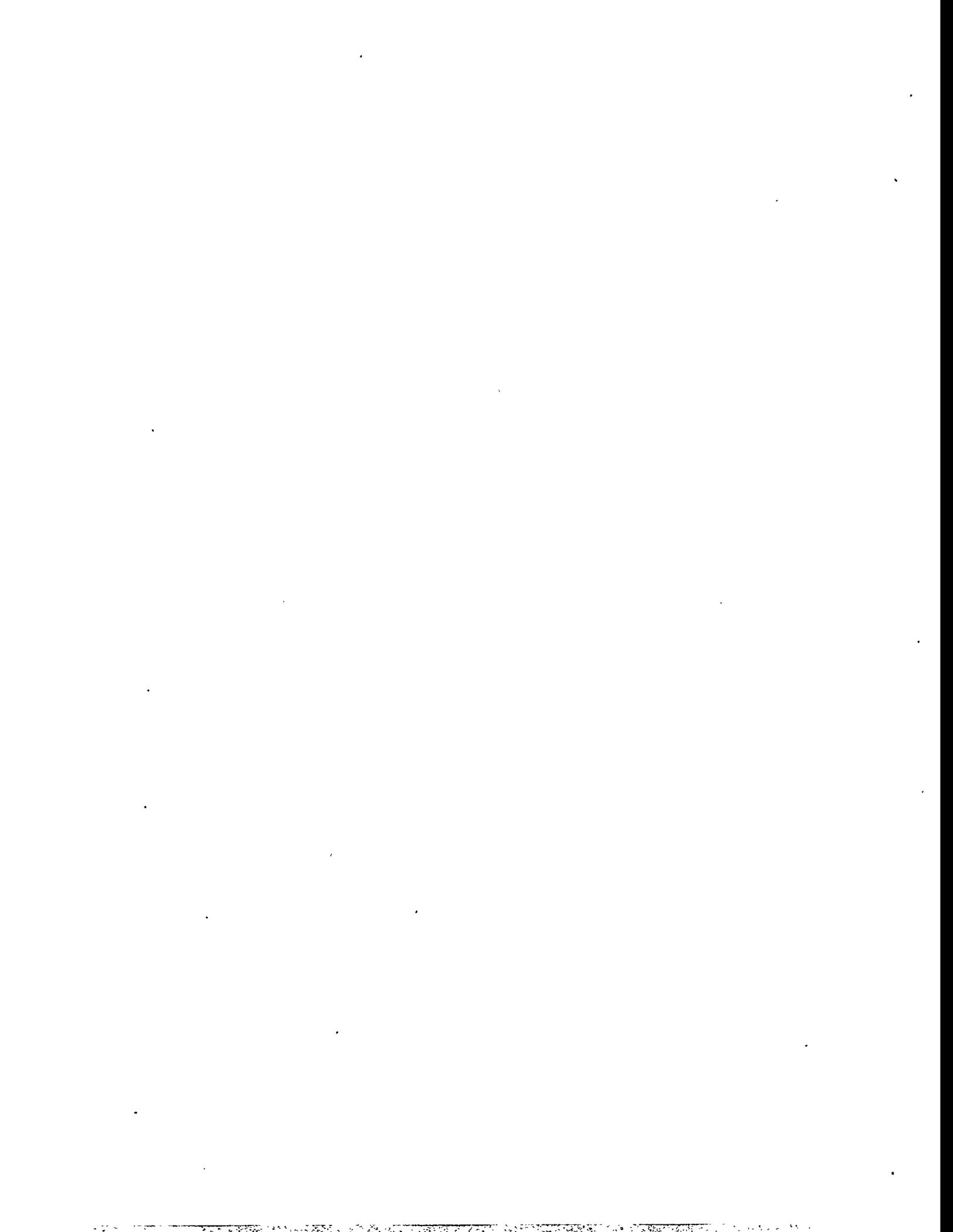


ISOTHERM
TRW with NT-1 Water



APPENDIX C

**REMOVAL OF CHLORINATED ORGANIC CONTAMINANTS IN
GROUNDWATER BY ZERO-VALENT IRON AND
PALLADIZED-IRON BIMETALS**



**REMOVAL OF CHLORINATED ORGANIC CONTAMINANTS IN
GROUNDWATER BY ZERO-VALENT IRON AND
PALLADIZED-IRON BIMETALS**

**Liyuan Liang
Matthew J. Dickey
Xiangping Yin**

October 1996



EXECUTIVE SUMMARY

The dehalogenation of chlorinated solvents by zero-valence iron has recently become the subject of intensive research and development as a cost-effective, passive treatment for contaminated groundwater through reactive barriers. The goal of our research was to determine what type (brand, mesh size, palladized or nonpalladized) of zero-valence iron was the most effective at degrading a variety of chlorinated contaminants (carbon tetrachloride, chloroform, trichloroethene (TCE), trichloroethane (TCA), and tetrachloroethene (PCE)) and their by-products (dichloromethane (DCM), methylchloride (MC), cis-dichloroethene (cDCE), 1,1-dichloroethene (1,1-DCE), vinylchloride (VC), and 1,1-dichloroethane (1,1-DCA)) in different types of groundwater.

Batch studies were performed by combining contaminated groundwater and one of the different types of iron filings in a zero headspace extractor. The extractor was placed on a rotator (30 rpm) and samples were periodically collected for gas chromatography (GC) analysis. Column studies were performed with Master Builder, Inc. medium mesh iron filings. Column lengths were varied by packing them with different amounts of filings. This allowed samples to be collected that been exposed to different amounts of reactive media. The columns were equilibrated with the contaminated groundwater for a minimum of an hour before samples were collected for GC analysis.

Elemental analysis was performed on the groundwater samples before and after exposure to the iron filings. A few elements were adsorbed by both the fine mesh, MB and 40 mesh, Fisher filings. In particular, Mn was strongly adsorbed by both filings. This may be partly due to Mn being reduced by the iron and precipitating out or plating onto the filings. Overall, the strongest adsorption was seen with NT-1 groundwater, probably due to its extremely high ionic strength.

All of the iron filings degraded the chlorinated contaminants they were exposed to, but certain forms of the filings were more effective than others. Fine mesh, no Pd, MB, fine mesh, 0.05% Pd, MB, and 40 mesh, 0.05% Pd, Fisher filings were the most effective at degrading the chlorinated contaminants. It was also discovered that the fine mesh, MB filings tended to produce fewer chlorinated by-products than the 40 mesh, Fisher filings, but this may be due to the MB filings adsorbing the chlorinated contaminants to a higher degree than the Fisher filings. There is concern that the performance of the MB filings may decrease once the adsorption capacity of the filings is reached. It is recommended that extended column studies be performed with the MB filings to determine the long term performance characteristics of this filing type. On a cost basis, the MB (\$0.20/lb) filings are much cheaper than the Fisher filings (\$40.0/lb) and therefore, much more cost effective.

1. INTRODUCTION

1.1 Background: Reduction of Chlorinated Solvents by Zero-valence Iron and Bimetallic Systems

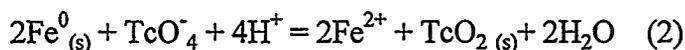
The dehalogenation of chlorinated solvents by zero-valence iron has recently become the subject of intensive research and development as a cost-effective, passive treatment for contaminated groundwater through reactive barriers [Gillham et al, 1992, 1994, O'Hannesin et al, 1992, 1993, Vogan et al, 1994, Korte et al., 1995; Liang et al., 1995, Liang et al., 1996a]. This treatment process is based on the well-known fact that zero-valence iron is an effective reducing agent relative to many redox-reactive species. Thermodynamically, dehalogenation occurs through a dual-electron transfer from Fe^0 to the halogenated hydrocarbons, resulting in an oxidized iron, a dehalogenated hydrocarbon, and a halogen ion, X^- :



Although detailed reaction pathways and mechanisms have not been determined, the reaction is believed to be a heterogeneous surface reaction. As such, degradation rates vary among iron filings obtained from different sources probably due to differences in surface characteristics [Horney et al., 1995; Liang et al., 1996]. Research conducted at Environmental Sciences Division of Oak Ridge National Laboratory (ESD-ORNL) suggest that chemisorption of halogenated organic molecules onto Fe^0 sites may be a rate limiting step. Other studies suggest that complete dechlorination (for example, from TCE to ethylene) in a single step is unlikely, and stepwise dechlorination must take place on the metal surface (O'Hannesin, 1993; Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Sivavec and Horney, 1995; Liang et al., 1995; Puls et al., 1995).

In a recent collaboration with University of Arizona, ESD-ORNL found that a bimetallic preparation of Fe with a small amount of Pd (0.05% by weight) was a superior reductant for trichloroethylene [Korte et al. 1995, Liang et al., 1996a]. The bimetallic system provided dechlorination kinetics that were 1 to 2 orders of magnitude faster than for zero-valence iron alone. Although palladization increases the cost of the iron material, the amount of filings required to achieve the same levels of dechlorination is significantly reduced due to more rapid degradation rates. Furthermore, more complete dechlorination than reduction by iron alone has been observed for the bimetallic system [Liang et al., 1996a].

Zero-valence iron has also been shown to be effective at removing technetium-99 (^{99}Tc) [Liang et al., 1996b] and Uranium (U) from contaminated groundwater. Pertechnetate oxyanion (TcO_4^-) is very water soluble, but can be reduced to insoluble TcO_2 with zero-valence iron via the redox reaction:



After reduction, the TcO_2 precipitates out or adsorbs to the iron and is immobilized. The immobilization of U by iron follows a similar pathway. The effect that high concentrations of

other cations and anions (i.e. Ca^{2+} and NO_3^- , respectively) may have on the immobilization of ^{99}Tc and U is not clear. Ions other than ^{99}Tc and U may adsorb to the iron and decrease the reducing power of the iron.

1.2 Objectives

Task 1: Preliminary evaluation using contaminated groundwater from Y-12

The feasibility of zero valence iron as a treatment for harsh ground waters was to be determined using batch experiments. The sources of iron are Fisher and MasterBuilder iron filings, and palladized iron. The target contaminants are organic solvents, such as PCE, TCE, TCA, and carbon tetrachloride. Three types of groundwater from Bear Creek Valley (BCV) are spiked with the organics, up to 6 ppm.

Task 2: Enhancement of dechlorination of the chlorinated solvents in groundwater

After Task 1 has been completed, solid materials (iron filings and foams, and bimetallic systems) were to be evaluated for enhanced dechlorination rates of PCE, TCA, and CT in groundwater.

Task 3: Column kinetic study for an extended period using Bear Creek Valley groundwater

Two types of solid materials were to be selected based on the results of the first two tasks to determine contaminant removal rate and efficiency in packed columns. Both VOCs and Uranium are sampled and analyzed. The rate constants will be used later in scaled-up applications.

2. COLUMN AND BATCH STUDY PREPARATION AND WATER CHEMISTRY OF SAMPLES

This section describes the preparation of the column and batch studies performed in this report and the water chemistry of the groundwater samples. The preparation of the column and batch studies was performed by personnel from the Environmental Sciences Division of Oak Ridge National Laboratory in Tennessee. The water chemistry determinations were performed by personnel from the Environmental Sciences Division and the Chemical Technology Division of Oak Ridge National Laboratory in Oak Ridge, TN and the Y-12 Analytical Services Organization managed by Lockheed Martin Energy Systems in Oak Ridge, TN.

2.1 Methods

Column and Batch Studies

The batch studies were prepared by placing 25 grams of iron filings in a zero headspace extractor and adding 125 mL of contaminated groundwater (VOC and/or Uranium were spiked to desired levels). The sample container was then sealed and placed on a rotator (30 rpm). Water samples were periodically withdrawn for analysis by gas chromatography (GC). Iron filings of 40 and 100 mesh were purchased from Fisher Scientific. For the studies with bimetallic substrates, the 40 and 100 mesh filings were chemically plated with palladium (0.05 or 0.25% of iron weight). Iron filings of medium and fine grade were purchased from MasterBuilder, Inc. The fine grade had an average size of approximately 40 mesh and was also chemically plated with palladium (0.05% of iron weight) for the bimetallic studies.

Glass columns of 1-2.5 cm in diameter and 2.7-24.6 cm in length were used. The columns were wet packed by adding a slurry of filings and water to the column and tapping the column to compact the filings, while maintaining a head of water to prevent air pockets. The columns were packed with medium mesh iron filings purchased from MasterBuilder, Inc (MB) that had been washed several times with water. The flow rate varied from 0.5 to 3 mL/min and the porosity was 0.6. After equilibrating the column by pumping contaminated groundwater through it with an HPLC pump for a minimum of an hour (> 30 bed volumes), samples were collected for contaminant and by-product analysis using gas chromatography.

2.2 Initial Chemical Composition of Groundwater Samples

The GW-087 and NT-1 groundwater types were each analyzed by Y-12 Analytical Services and the Chemistry Technical Division. The results are listed in Tables 1 and 2. GW-087 groundwater does not appear to have high concentrations of heavy metals, radionuclides, or dissolved and suspended solids. NT-1 groundwater is much harsher. It contains significant amounts of heavy metals, radionuclides, dissolved and suspended solids, and various chlorinated solvents. The number of dissolved and suspended solids is important because they may adsorb to the iron and interfere with the dechlorination and radionuclide adsorption reactions. There is also the possibility that the suspended solids may physically plug the pores when pumped through the porous media.

The different groundwater samples used in the studies were stored in sealed carboys and refrigerated. The CT groundwater initially contained ~0.6 ppm carbon tetrachloride. During storage, the carbon tetrachloride concentration slowly decreased, probably due to volatilization. This groundwater was later spiked with chloroform and used in further batch studies. The NT-1 groundwater was spiked with tetrachloroethene (PCE). GW-087 groundwater was spiked with PCE and trichloroethene (TCE) for two batch studies, trichloroethane (TCA) for two batch studies, and PCE and TCA for one column study. The groundwater samples were spiked to improve the detectability of by-products and the ability to determine the performance of the various iron filings.

Table 1. Chemical analysis of groundwater from well 087 at Barnyard/Boneyard (GW-087).

Analyte	Analyzed by Y-12 Analytical Services		Analyzed by Chemical Technology Division	
	Sample conc. (mg/L unless otherwise noted)	Qualifier	Sample conc. (mg/L)	Qualifier
Ag	<0.02	U	0.002	U
Al	1.67 (est)	D	0.07	D
As	<0.10	U	0.008	U
B	NA		0.207	D
Ba	0.0939	D	0.12	D
Be	<0.001	U	0.001	U
Ca	30.4	D	49	D
Cd	<0.020	U	0.028	D
Cr	<0.020	U	0.002	U
Fe	3.42	D	0.096	D
K	4.47	D	3.9	D
Mg	7.16	D	5.5	D
Mn	0.923	D	0.8	D
Na	14.4	D	12.5	D
Ni	0.0596	D	0.032	D
Pb	<0.20	U	0.004	U
Se	NA		0.009	U
Sb	NA		0.006	U
Si	NA		5.606	D
Tc	-40	U	NA	
Ti	NA		0.004	D
Tl	NA		0.006	U
U	0.0001	D	0.38	D
V	<0.01	U	0.009	U
Zn	0.0858	D	0.125	D
Zr	NA		0.003	U
Tritium	-180	U	NA	
Alkalinity	90	D	NA	
Fluoride	<0.05		NA	
Nitrate	1		NA	
Nitrite	<0.05		NA	
Sulfate	26		NA	
Total Radioactive Sr	-0.28	U	NA	
Total Dissolved Solids	160	D	NA	
Total Suspended Solids	22	D	NA	
pH	5.89		NA	

NA- Not applicable
U- Undetected
D- Detected

Table 2. Chemical analysis of groundwater from NT-1 near S3 pond (NT-1).

Analyte	Analyzed by Y-12 Analytical Services		Analyzed by Chemical Technology Division	
	Sample conc. (mg/L unless otherwise noted)	Qualifier	Sample conc. (mg/L)	Qualifier
Ag	<0.02	U	0.011	D
Al	81.3	D	21.85	D
As	<0.1	U	0.036	D
B	NA		0.383	D
Ba	20.1	D	18.47	D
Be	0.0103	D	0.004	D
Ca	>1000	D	2136	D
Cd	0.788	D	0.628	D
Cr	0.0758	D	0.002	U
Fe	37.4	D	0.033	U
K	48.2	D	36.77	D
Mg	334	D	300.3	D
Mn	>100	D	127.6	D
Na	379	D	350.1	D
Ni	3.18	D	2.844	D
Pb	<0.2	U	0.004	U
Se	NA		0.009	U
Sb	NA		0.006	U
Si	NA		5.947	D
Tc	15000 pCi	D	NA	
Ti	NA		0.001	U
TI	NA		0.049	D
Tritium	950 pC/L	D	NA	
U	0.006	D	0.144	D
V	0.0514	D	0.009	U
Zn	0.225	D	0.112	D
Zr	NA		0.003	U
Methylene Chloride	0.018	D	NA	
cis-DCE	0.019	D	NA	
Chloroform	0.017	D	NA	
PCE	0.12	D	NA	
Alkalinity	160		NA	
Fluoride	30	D	NA	
Nitrate	8500	D	NA	
Nitrite	16	D	NA	
Sulfate	12	D	NA	
pH	NA		NA	
Total Radioactive Sr	27 pC/L	D	NA	
Total Dissolved Solids	13000	D	NA	
Total Suspended Solids	370	D	NA	

NA- Not applicable

U- Undetected

D- Detected

3. Results

3.1 Volatile Organic Carbon (VOC) Degradation and Reaction Kinetics

Table 3 lists the initial contaminant concentration, by-product concentration at the end of the reaction, and estimated and calculated reaction half-lives for the VOC degradation on the various iron filing types used. The half-lives in Table 3 are also expressed graphically in Figures 1 and 2. The half-lives presented are initial half-lives and are expected to increase as the reactive media degrades (rust, sulfur poisoning, etc.). The half-lives were calculated using a first order reaction equation

$$dC / dt = -kC \quad (3)$$

where C is the concentration of the chlorinated contaminant, t is the reaction time, and k is the first order reaction constant. The half-life is defined as the reaction time at which 50% degradation is achieved (i.e. $C/C_0 = 50\%$):

$$t_{1/2} = \ln(C / C_0) / k = -0.69 / k \quad (4)$$

All of the different types and sizes of iron filings were effective in degrading the chlorinated contaminants present in the different groundwater types. The filing types did differ in their degradation efficiency, though. Figure 1 shows the half-lives of carbon tetrachloride on the different types of reactive media. The 40 mesh, 0.05% Pd, Fisher iron filings degraded carbon tetrachloride more quickly than the same iron filings without Pd. This is due to the Pd accelerating the dechlorination. The 100 mesh, 0.05% Pd, Fisher filings were electrolytically formed and were not porous like the 40 mesh filings. This lack of porosity decreases the surface area, which in turn decreases the dechlorination efficiency because of the reduced number of dechlorination sites. Therefore, the 100 mesh, 0.05% Pd, Fisher filings were not as effective as the 40 mesh, 0.05% Pd, Fisher filings. Fine, 0.05% Pd, MB filings and fine, no Pd, MB filings were very similar to each other in their degradation of carbon tetrachloride and were about as effective as the 40 mesh, 0.05% Pd, Fisher filings.

The half-lives of the dechlorination of chloroform in spiked CT groundwater on 40 mesh, Fisher iron filings with different amounts of Pd (Table 3) followed the same trend as the degradation of carbon tetrachloride. The iron filings with 0.05% Pd were significantly better at dechlorinating chloroform than the same filings with no Pd. Again, it is seen that the Pd improves the dechlorination process.

The half-lives of PCE in spiked NT-1 groundwater, TCA in spiked GW-087 groundwater, and a mixture of TCE and PCE in spiked GW-087 groundwater were measured on both fine mesh, MB and 40 mesh, Fisher iron filings (Figure 2). In each batch study, the fine mesh, MB iron filings were superior at dechlorinating the contaminants than the 40 mesh, Fisher iron filings. This is largely due to two reasons: 1. The surface area of the fine mesh, MB iron filings ($2.39 \text{ m}^2/\text{g}$) is 30% greater than the surface area of the 40 mesh, Fisher iron filings ($1.64 \text{ m}^2/\text{g}$).

This means that the MB iron filings have more dechlorination sites available per gram than the Fisher iron filings and will be more efficient, on a weight basis, at degrading the chlorinated contaminants. 2. Besides degrading the chlorinated contaminants, the MB filings also adsorb the chlorinated contaminants unlike the Fisher filings. This adsorption of the chlorinated contaminants by the MB filings causes it to appear that the half-lives of the contaminants on the MB filings are shorter than the half-lives on the Fisher filings when, in fact, it is a combination of dechlorination and adsorption. We do know that dechlorination happens on the MB filings and not just adsorption because we detect the dechlorination by-products.

3.11 By-product Distribution

3.111 Batch Studies

Each batch study showed a degradation of chlorinated contaminants over time, but certain reactive media were more efficient than others. Figure 3 shows the degradation of chloroform on Fisher iron filings, with and without 0.05% Pd. Both types of reactive media produced the same by-products (DCM, MC, and methane) but methane does not appear in Figure 3 because the GC used could not separate methane from the other hydrocarbons produced so an accurate methane concentration could not be measured. The palladized filings dechlorinated chloroform more quickly and showed an increased amount of MC and a decreased amount of DCM than the filings without Pd. The fact that the palladized filings produced more MC and less DCM than the nonpalladized filings indicates increased dechlorination by the palladized filings because MC is less chlorinated than DCM.

Figure 4 shows the breakdown of TCA on Fisher and MB iron filings. The by-products detected were 1,1-DCA, VC, and ethane. It is important to note that VC was detected throughout most of the experiment on the 40 mesh, Fisher reactive media but not on the fine mesh, MB reactive media until the very end of the experiment. VC is more toxic than PCE and TCE and has a MCL of 2 ppb, whereas PCE and TCE have MCLs of 5 ppb so it is very important that VC be removed. Long term column studies involving MB filings need to be performed to determine if VC is being degraded by the filings or initially adsorbed until saturation of the filings occurs and then flowing through the column without being further degraded. The Fisher filings produced more ethane but also more chlorinated by-products than the MB filings. The amount of ethane produced was an indicator of the degree of dechlorination because ethane is the final by-product. Ideally, ethane production should be high and the amount of chlorinated by-products detected should be low. If ethane production is low but the concentration of chlorinated by-products is also low, the filings may be adsorbing the chlorinated contaminants and not degrading them, as is suspected in the case of the MB filings. The MB filings may also show increased degradation due to their greater surface area than the Fisher filings. Figure 4 also shows the detection of PCE, TCE, and c-DCE. These were initially present in low concentrations in the GW-087 groundwater and should not be considered by-products of TCA degradation.

The degradation of PCE on Fisher and MB iron filings is seen in Figure 5. The reaction by-products were the same (TCE, cis-DCE, 1,1-DCE, VC, and ethane) except for TCE, which was not detected during the batch study using fine mesh, MB reactive media. Comparing the plots in Figure 5, the MB filings produced more ethane and fewer chlorinated by-products and degraded PCE to a higher degree than the Fisher filings. This improved performance by the MB filings when compared to the Fisher filings is likely due to the increased surface area of and adsorption by the MB filings.

Figure 6 shows the degradation of carbon tetrachloride in CT groundwater on different forms of Fisher iron filings. The by-products detected were dechlorinated hydrocarbons, DCM, and chloroform for each of the filing types except for the 100 mesh, 0.05% Pd filings where

DCM was not detected. The figure does not include the dechlorinated hydrocarbons because the GC used could not separate all the hydrocarbons (1,2, and 3 carbons) that were produced, so an accurate measurement of the amount of each hydrocarbon produced could not be obtained. The 40 mesh, 0.05% Pd filings degrade carbon tetrachloride to chloroform and DCM, whereas the 100 mesh, 0.05% Pd filings degrade the carbon tetrachloride to only chloroform. The presence of DCM, a less chlorinated by-product than chloroform, in the 40 mesh, 0.05% Pd batch study indicates that the 40 mesh, 0.05% Pd filings degraded carbon tetrachloride to a greater degree than the 100 mesh, 0.05% Pd filings. The 100 mesh, 0.05% Pd filings were electrolytically formed and were not porous like the 40 mesh, 0.05% Pd filings. This lack of porosity decreases the surface area, which in turn decreases the dechlorination efficiency because of the reduced number of dechlorination sites. Therefore, the 100 mesh, 0.05% Pd filings were not as effective as the 40 mesh, 0.05% Pd filings at dechlorinating carbon tetrachloride. The 40 mesh, 0.05% Pd also dechlorinated carbon tetrachloride more than the 40 mesh, no Pd filings (Figure 6). This is due to the accelerated dechlorination of carbon tetrachloride and its by-products caused by the Pd.

Fine mesh, 0.05% MB filings and fine mesh, no Pd MB filings degraded carbon tetrachloride in CT groundwater very similarly to each other (Figure 7). The only real difference between the two filings was that the chloroform by-product degraded more quickly on the nonpalladized filings than on the palladized filings. They both degraded carbon tetrachloride in a similar amount of time and produced about the same amount of DCM.

The degradation of PCE and TCE in spiked GW-087 groundwater on Fisher and MB filings produced ethane, VC, 1,1-DCE, cis-DCE, and TCE (Figure 8). The MB filings produced less ethane and lower concentrations of chlorinated by-products (particularly VC) than the Fisher filings. As discussed above, this may be caused by the MB filings adsorbing the chlorinated contaminants and not degrading them to the extent of the Fisher filings. Again, long term column studies with MB filings need to be conducted to determine if adsorption effects the dechlorination process.

3.112 Column Studies

In all of the column studies, the concentration of the initial chlorinated contaminant decreased down the length of the column. When carbon tetrachloride was the contaminant, chloroform, DCM, MC, and dechlorinated hydrocarbons were the by-products detected. The concentration of the by-products depended on the length of the column. Figure 9 illustrates the breakdown of carbon tetrachloride on medium mesh, MB iron filings. Figure 9 does not include the dechlorinated hydrocarbons because the GC used could not separate all the hydrocarbons (1,2, and 3 carbons) that were produced, so an accurate measurement of the amount of each hydrocarbon produced could not be obtained. The fact that by-products were detected indicated that the removal of carbon tetrachloride by MB filings was a dechlorination process, not just adsorption.

3.2 Water Chemistry

Elemental analysis was performed before and after treatment with the iron filings on the groundwater used in the column and batch studies. There was very little difference in the elemental analysis of samples taken before and after the column studies. Certain elements showed a strong affinity for the reactive media in the batch studies, though. A summary of those elements showing the strongest adsorption coefficients in the batch studies is found in Table 4. In the few applicable cases (Mn and Mg), the MB filings had higher adsorption coefficients than the Fisher filings. The Mn adsorption coefficient for Fisher iron filings and NT-1 groundwater was very high (6.24×10^4 mL/g). It is likely that the Mn was reduced by the iron and precipitated out or plated onto the filings. The high adsorption seen overall in the NT-1 groundwater is most likely due to the high ionic strength (the nitrate concentration is 8500 ppm) because as ionic strength increases, so does adsorption. Many of the elements were not initially present at high concentrations in the control samples (Tables 1 and 2), which contributed to the large variations seen in the adsorption coefficients.

Table 4. Adsorption coefficients of elements from different groundwater types onto different filings.

Element	Adsorption Coefficients for Different Groundwater and Iron Filing Types (mL/g)						
	NT-1, Fisher	GW-087 spiked with TCE and PCE. Fisher	GW-087 spiked with TCE and PCE. MB	GW087 spiked with TCA. Fisher	GW087 spiked with TCA. MB	CT. MB	CT. MB with 0.05% Pd
Al	2330.7	0.747664	0.25641	0.6435	-0.086	-4.17	-4.42
Ba	57.61	-2.55	-4.14	-0.13	-2.39	-1.56	-2.46
Be	30	NA	NA	NA	NA	NA	NA
Cd	1357.5	>60	>60	>60	>60	NA	NA
Mg	14.69	NA	NA	10.65	74.78	118.2	220.8
Mn	62439.44	1205	3625	396.1	>3605	NA	NA
Ni	186.85	>37.5	>37.5	>31.25	>31.25	NA	NA
Zn	76.67	>100	>100	>97.5	>97.5	23.51	50.53

Table 3. Half-lives of chlorinated contaminants on different iron filings.

Experiment number	Groundwater Type	Iron Type	Pd (% of iron weight)	Iron Mesh	Contaminant and conc., ppb	Batch study reaction time, hours. By-products at end of reaction, ppb	Batch half-life hours (calc)	Column half-life minutes (est)*
1	CT	Fisher	0.05	40	CT=605	170: DCM=7.2, CF=70, CT=nd	0.21	0.5
2	CT	Fisher	0	40	CT=524	72: DCM=32, CT=nd	0.37	0.9
3	CT	MB	0	Fine	CT=421	316: ethane=13, DCM=4, CF & CT=nd	0.21	0.5** (calc)
4	CT	MB	0.05	Fine	CT=421	317: ethane=37, DCM=7, CF & CT=nd	0.25	0.6
5	CT	Fisher	0.05	100	CT=523	29: CF=113	0.27	0.65
6	CT	Fisher	0.25	40	CF=2851	95: DCM=142	9	22
7	CT	Fisher	0.05	40	CF=2781	73: DCM=51	1.8	4.3
8	CT	Fisher	0	40	CF=2233	72: DCM=112	9.8	24
9	NT-1	MB	0	Fine	PCE=3027	192: PCE=9, cDCE=3, 1,1-DCE=9, VC=4, ethane=9	0.76	1.8
10	NT-1	Fisher	0	40	PCE=2252	191: PCE=295, TCE=17, cDCE=23, 1,1-DCE=40, VC=159, ethane=54	3.5	8.4
11	GW-087	MB	0	Fine	PCE=2682 TCE=2525	190: PCE=4.2, TCE=nd, cDCE=7, 1,1-DCE=nd, VC=5, ethane=171	0.68, 0.94	1.6, 2.3
12	GW-087	Fisher	0	40	PCE=1848 TCE=1972	190: PCE=28, TCE=6, cDCE=nd, 1,1-DCE=9, VC=112, ethane=256	12.5, 11.2	30, 27
13	GW-087	MB	0	Fine	TCA=2637 PCE=20 TCE=72.6 cDCE=34.6	190: ethane=63, 1,1-DCA=43, VC=1.4, TCE, cDCE, PCE, 1,1,1-TCA all = nd	1.21	2.9
14	GW-087	Fisher	0	40	TCA=2637 PCE=20 TCE=72.6 cDCE=34.6	189: ethane=211, 1,1-DCA=59, VC=101, TCE, cDCE, PCE, 1,1,1-TCA all = nd	4.18	10

* the column half-life was estimated from the batch half-life using the relationship

$$k_c \propto (S_b \times k_b) \div S_c$$

where k_c is the first order reaction constant in the column study, S_c is the surface area per L of the reactive media in the column study, k_b is the first order reaction constant in the batch study, and SA_b is the surface area of the reactive media per L of solution in the batch study. The ratio $S_c:S_b$ is approximately 25 for iron with the amount of iron used for the batch studies. k_c is then used with equation 4 to calculate the contaminant half-life expected in the column studies.

** This half-life was calculated from column data and not estimated.

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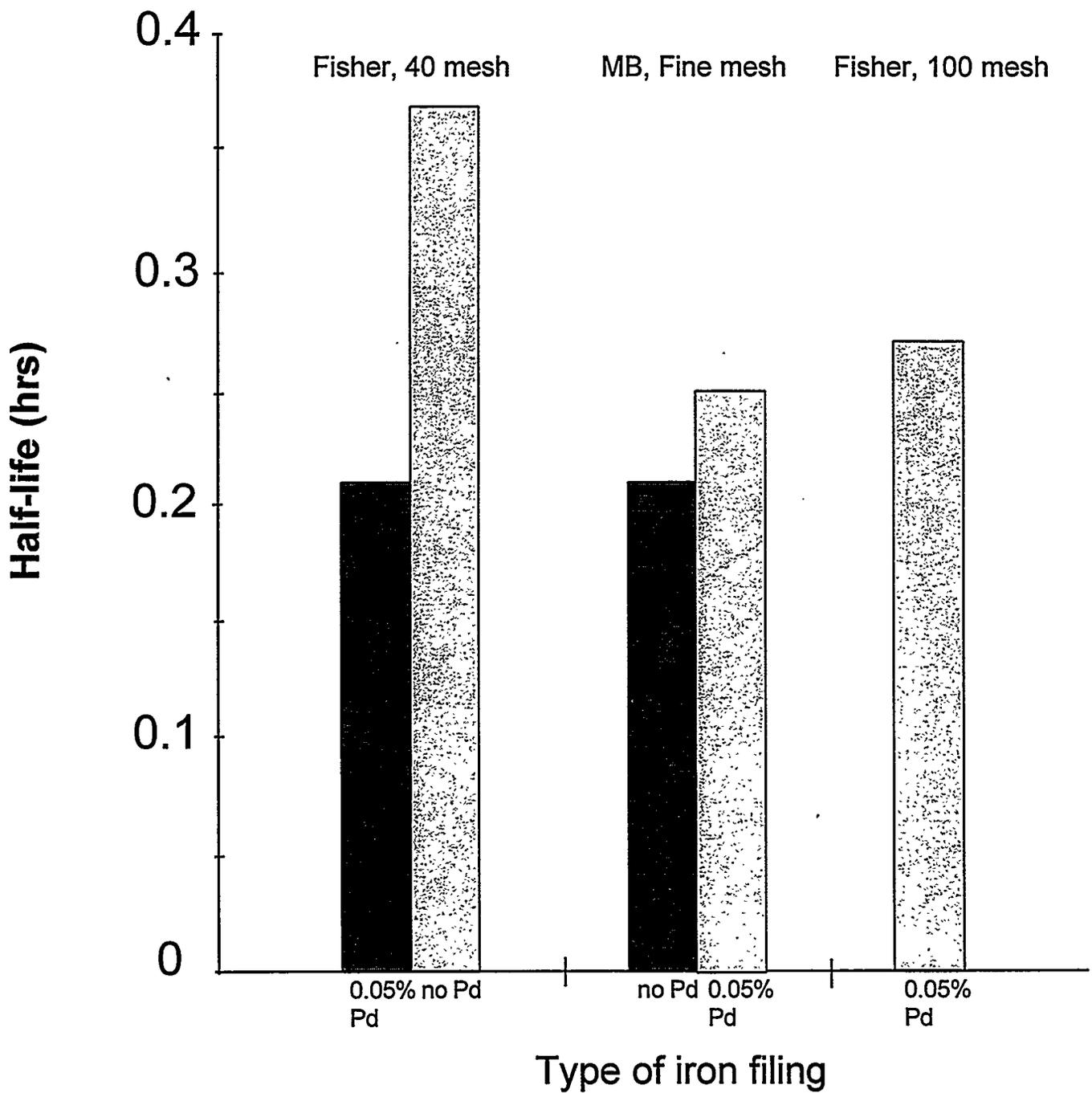


Figure 1. Initial half-lives of carbon tetrachloride in CT water on different types of iron filings. Calculated from batch studies.

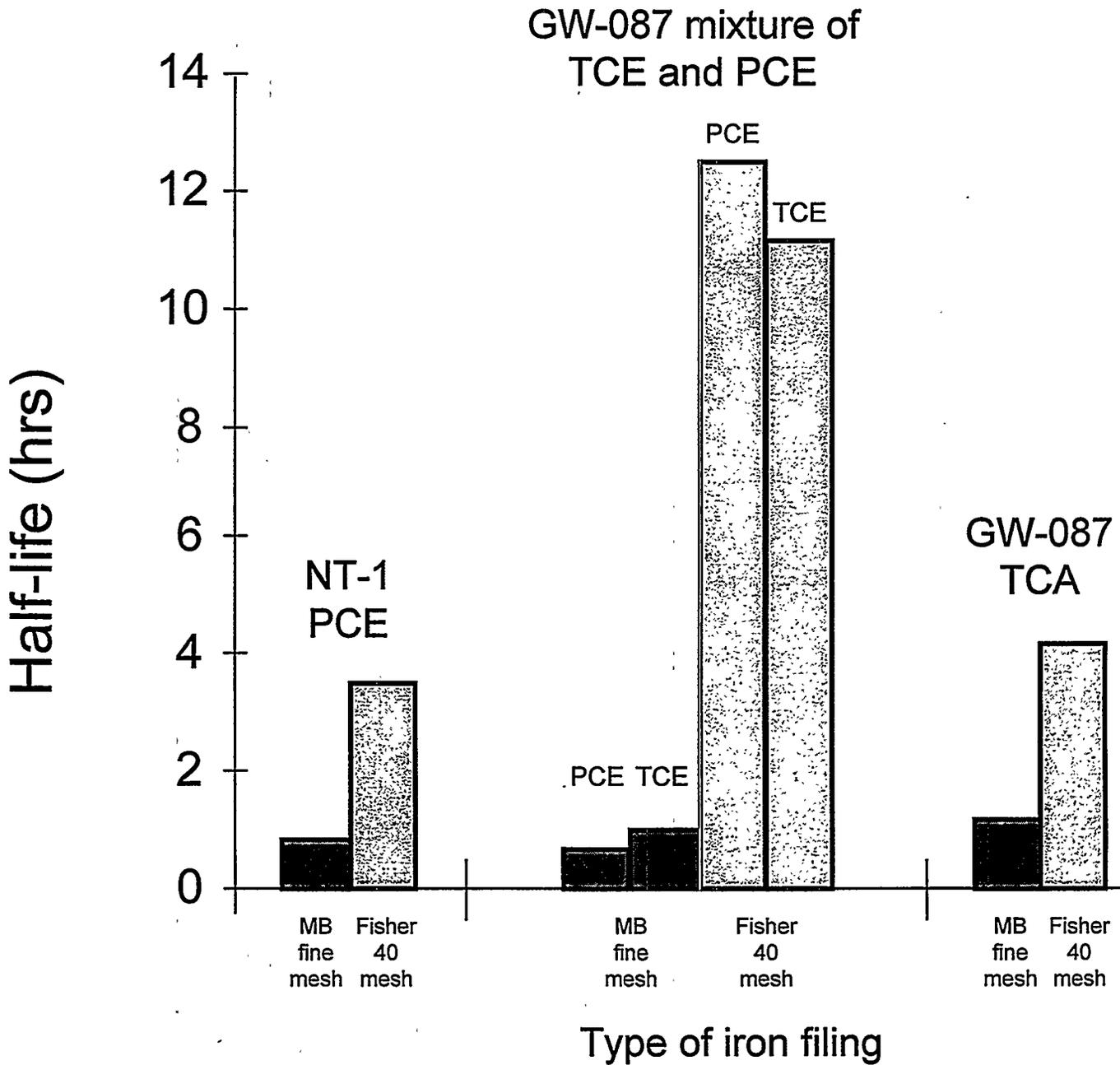


Figure 2. Initial half-lives of chlorinated contaminants on MB and Fisher iron filings not coated with palladium. All groundwater samples were spiked with the chlorinated contaminants.

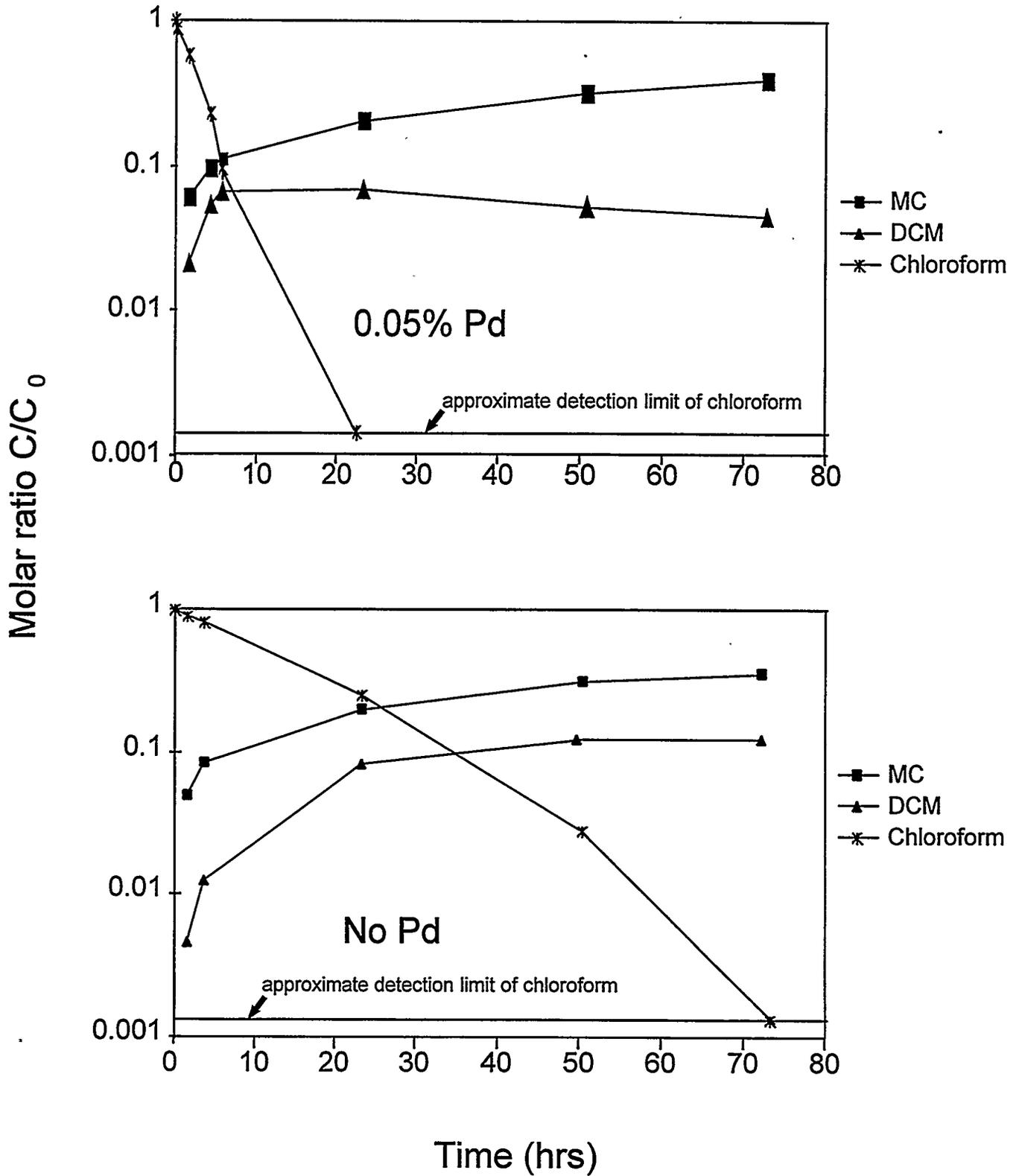


Figure 3. Chloroform and degradation by-products using chloroform spiked CT (Upper East Fork Poplar Creek) groundwater and 40 mesh, Fisher reactive media coated with and without Pd. C_0 is the initial concentration of chloroform.

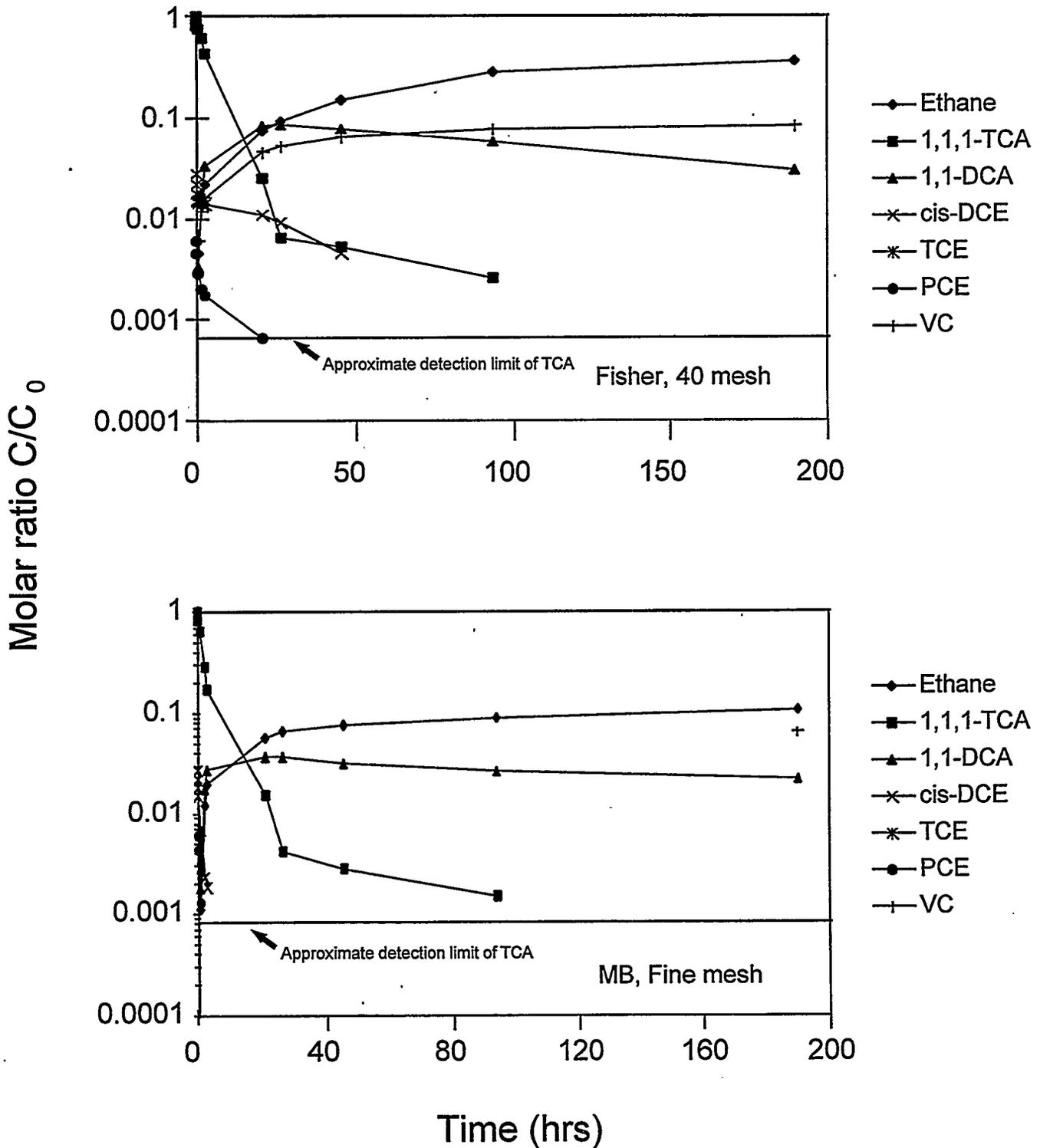


Figure 4. TCA and degradation by-products using TCA spiked GW-087 groundwater and Fisher and MB iron filings. C_0 is the initial concentration of TCA.

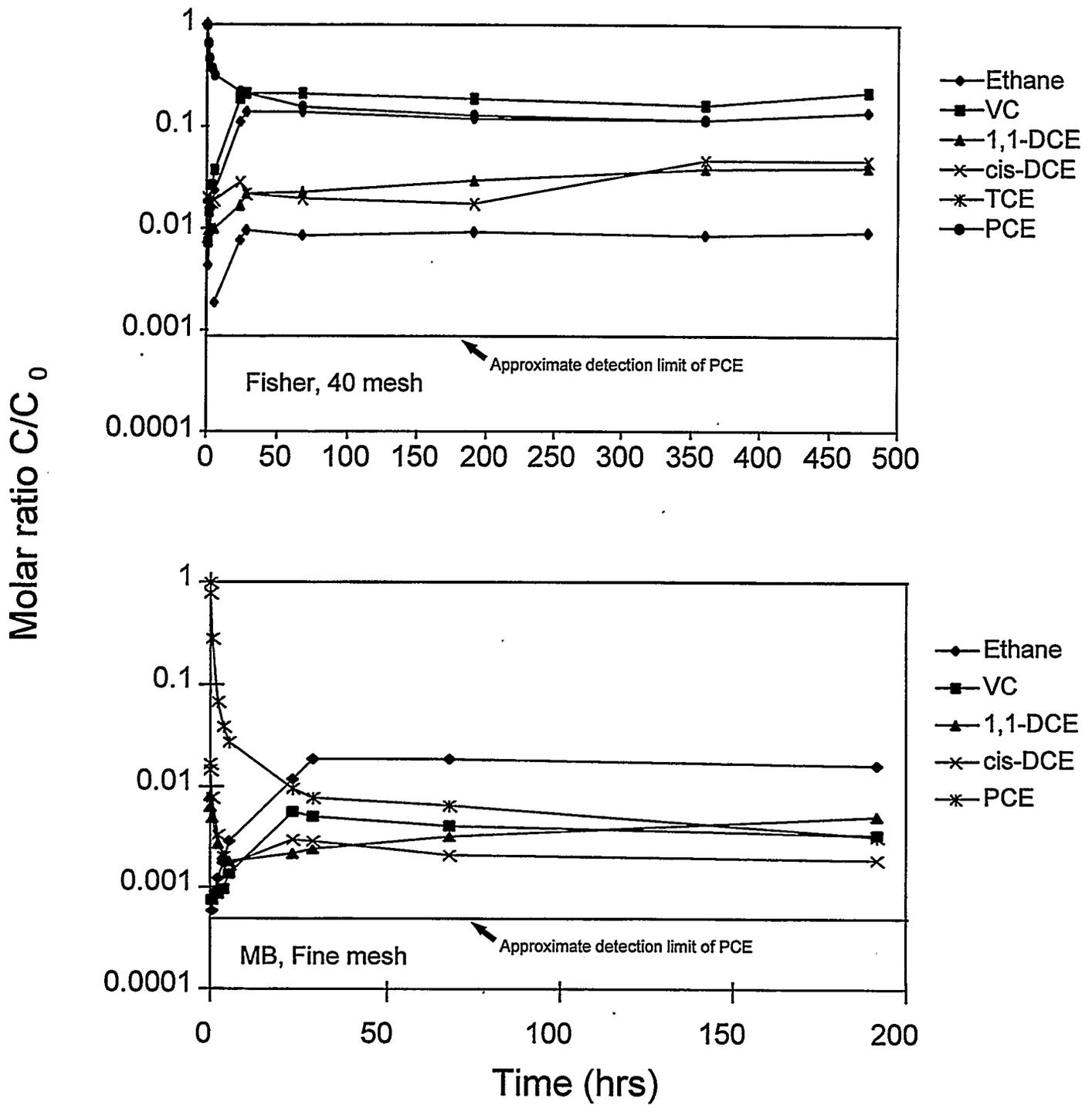


Figure 5. PCE and degradation by-products using PCE spiked NT-1 groundwater on Fisher and MB iron filings. CT_0 is the initial concentration of PCE.

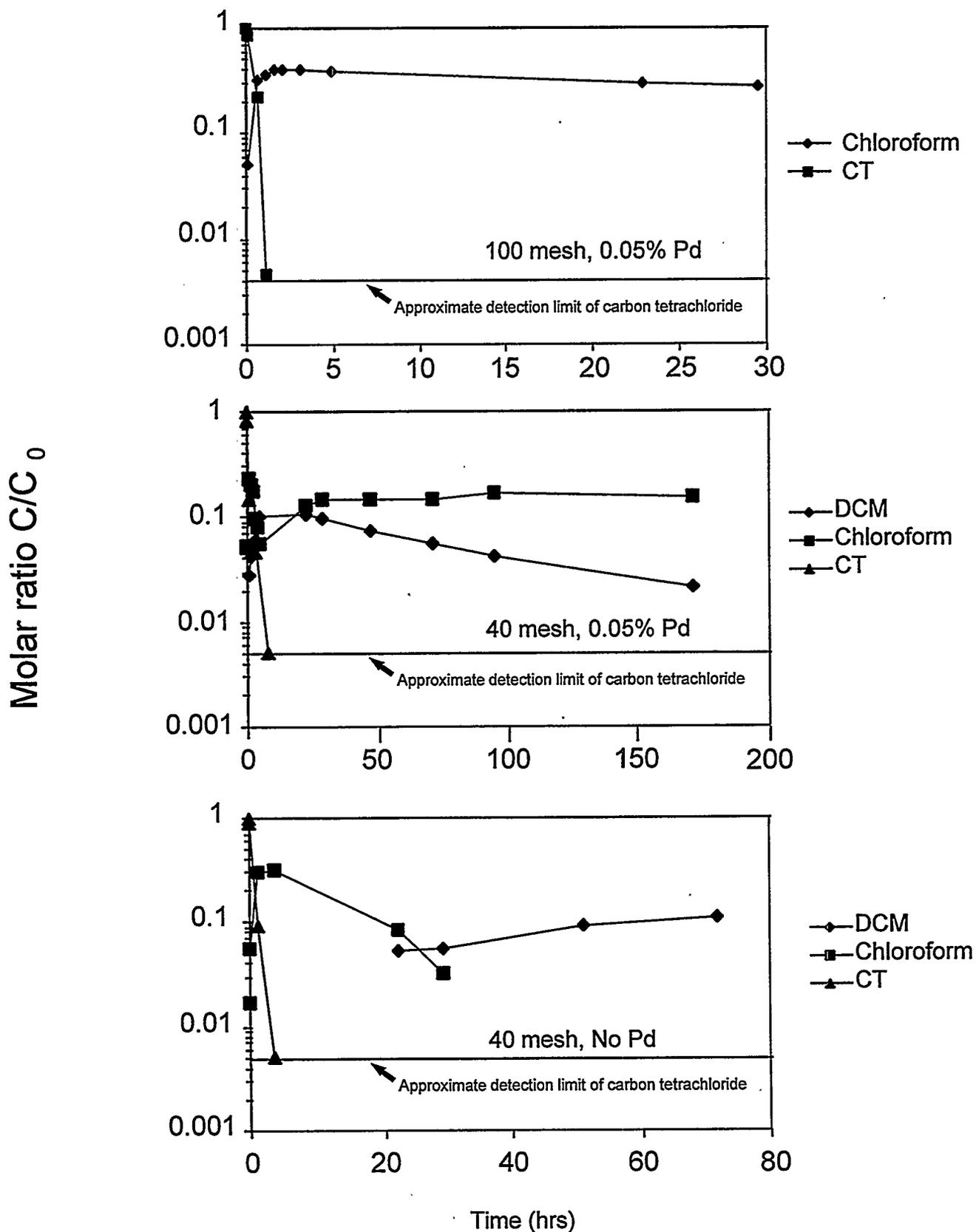


Figure 6. Degradation of carbon tetrachloride in CT groundwater on various forms of Fisher iron filings. C_0 is the initial concentration of carbon tetrachloride.

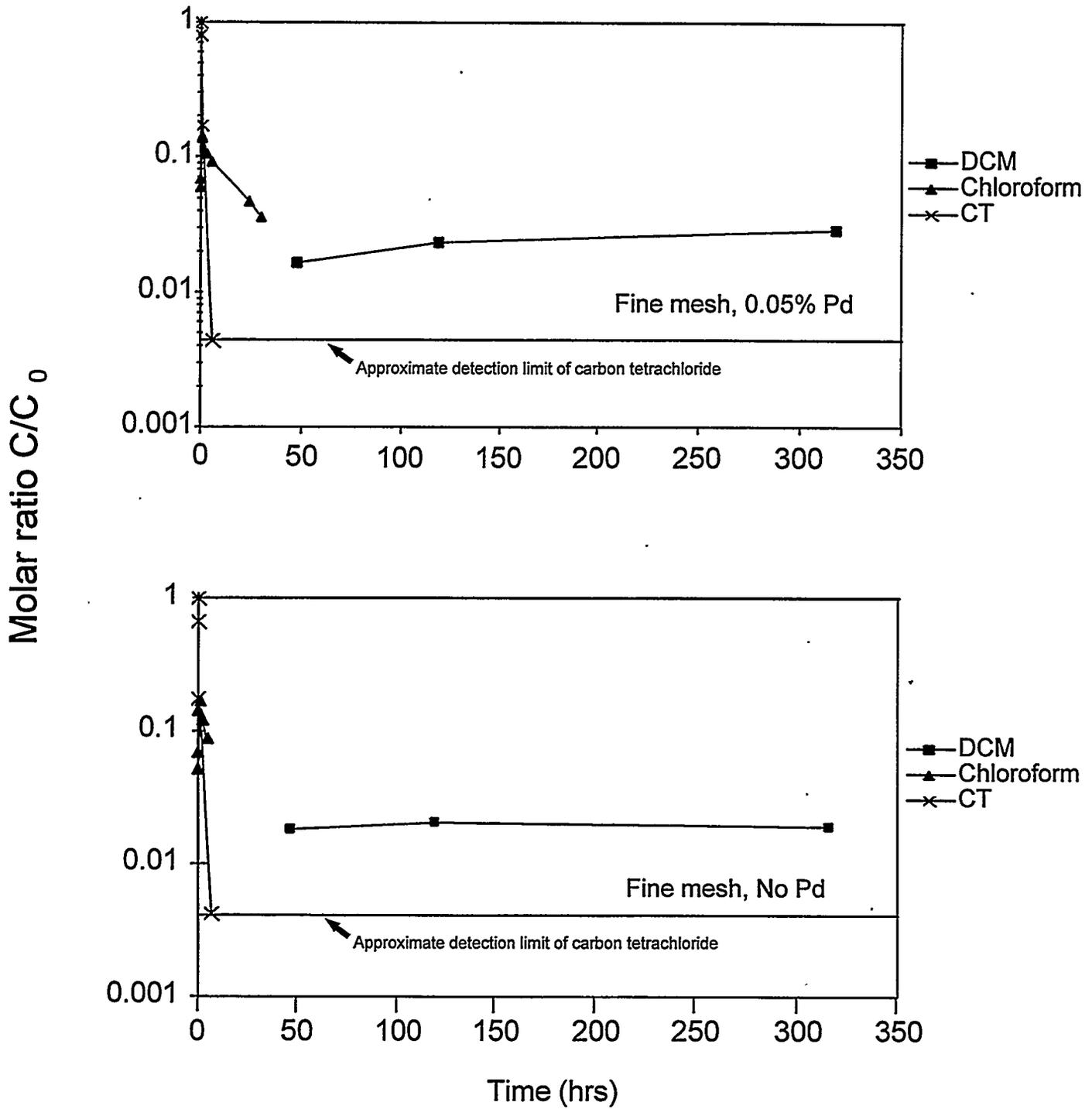


Figure 7. Degradation of carbon tetrachloride in CT groundwater on palladized and nonpalladized MB iron filings. C_0 is the initial concentration of carbon tetrachloride.

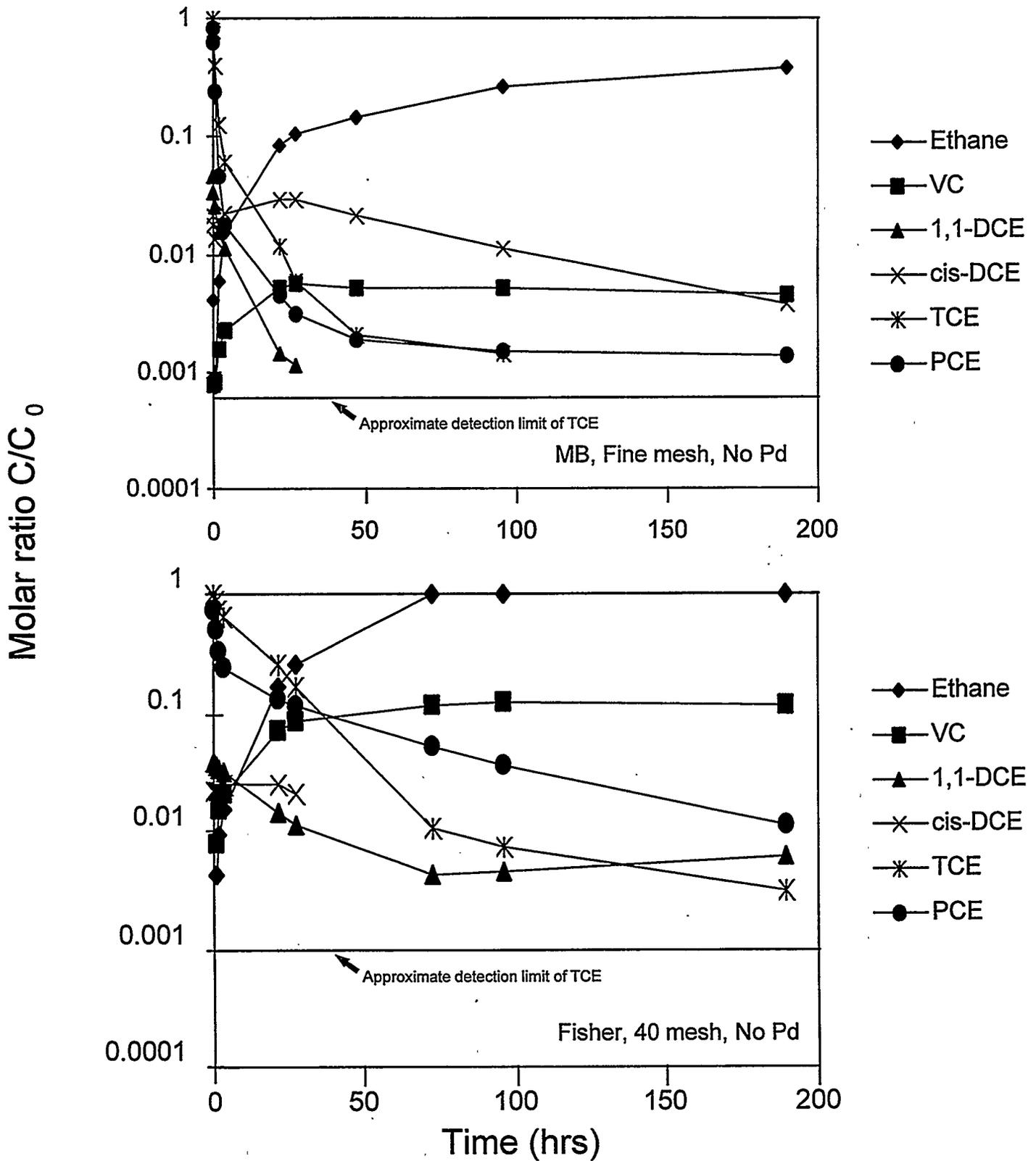


Figure 8. PCE, TCE, and degradation by-products using PCE and TCE spiked GW-087 groundwater and Fisher and MB iron filings. C_0 is the initial concentration of TCE.

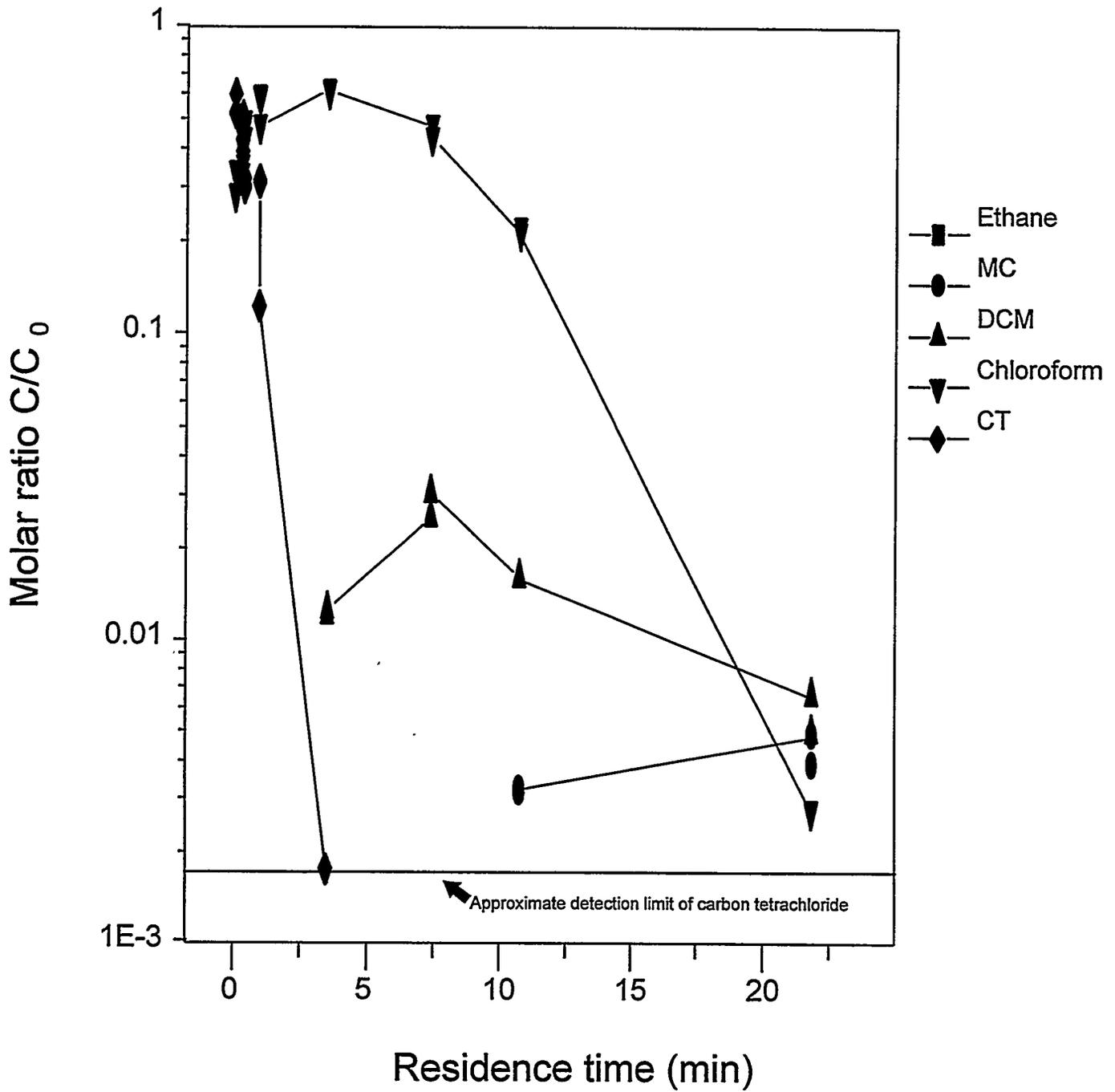
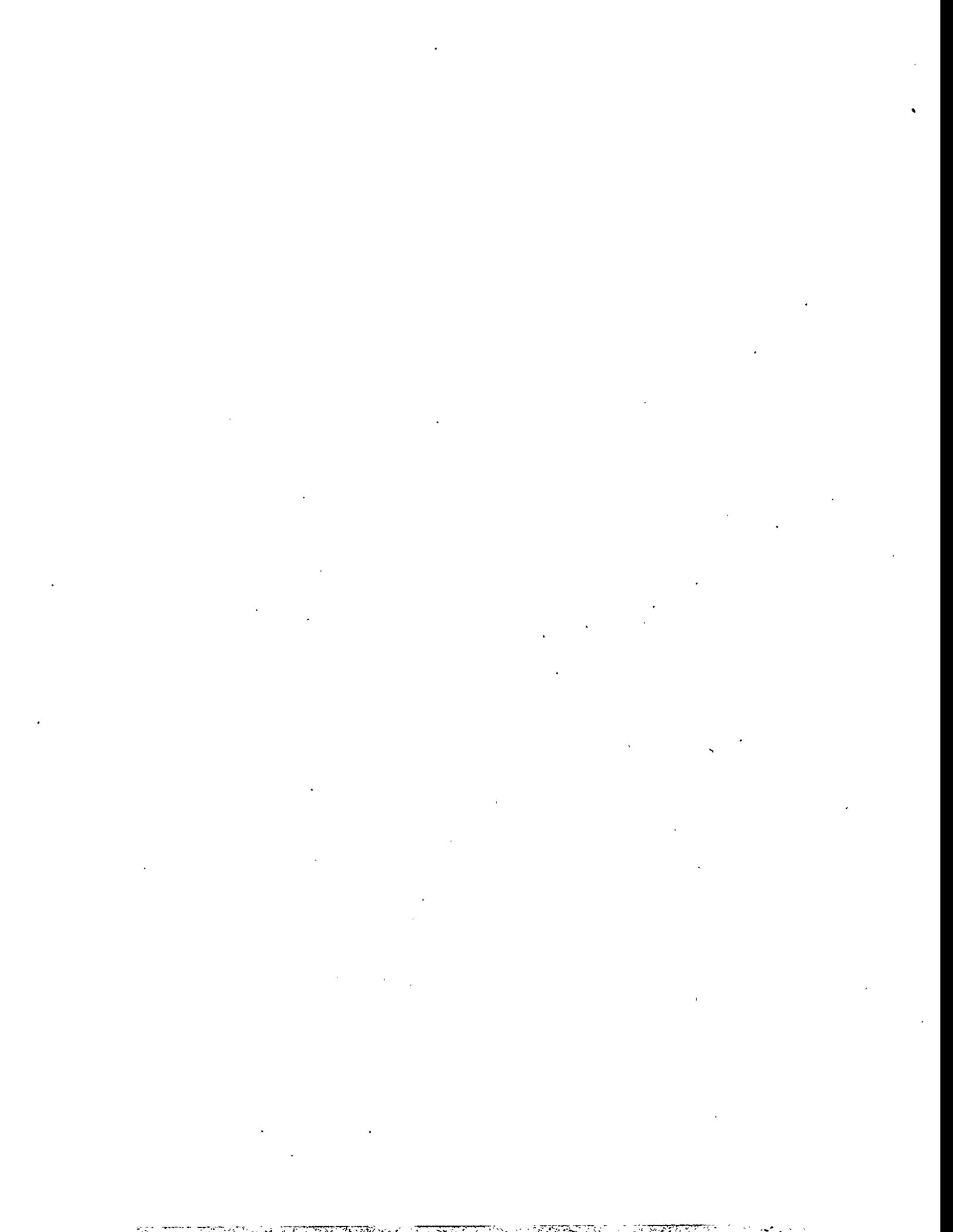
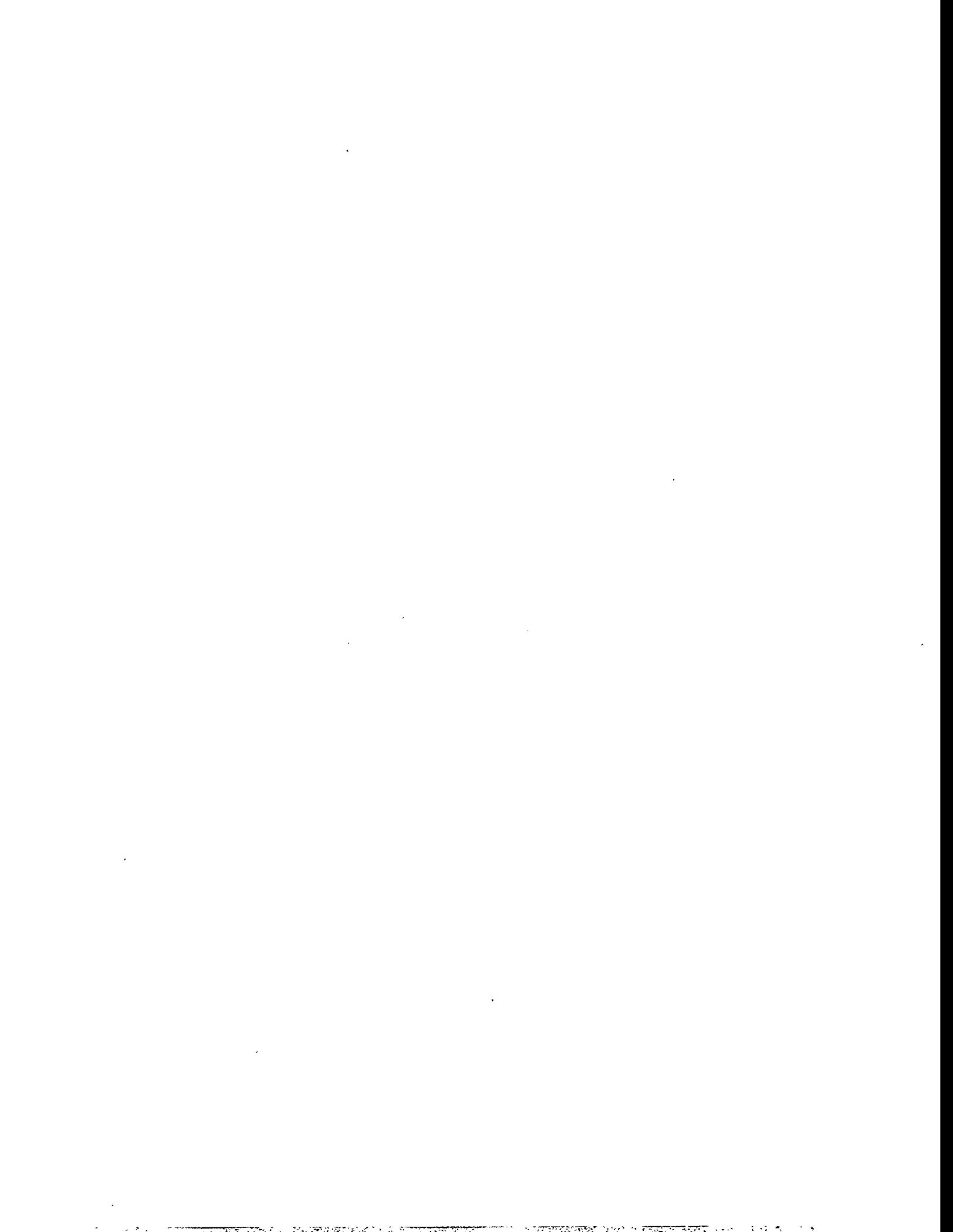


Figure 9. Carbon tetrachloride and degradation by-products from CT water) in a medium mesh, MasterBuilder reactive media filled column. C_0 is the initial concentration of carbon tetrachloride.



APPENDIX D

**ZERO-VALENT IRON AND METAL OXIDES
FOR THE REMOVAL OF SOLUBLE REGULATED METALS
IN CONTAMINATED GROUNDWATER AT A DOE SITE**



**ZERO-VALENT IRON AND METAL OXIDES FOR
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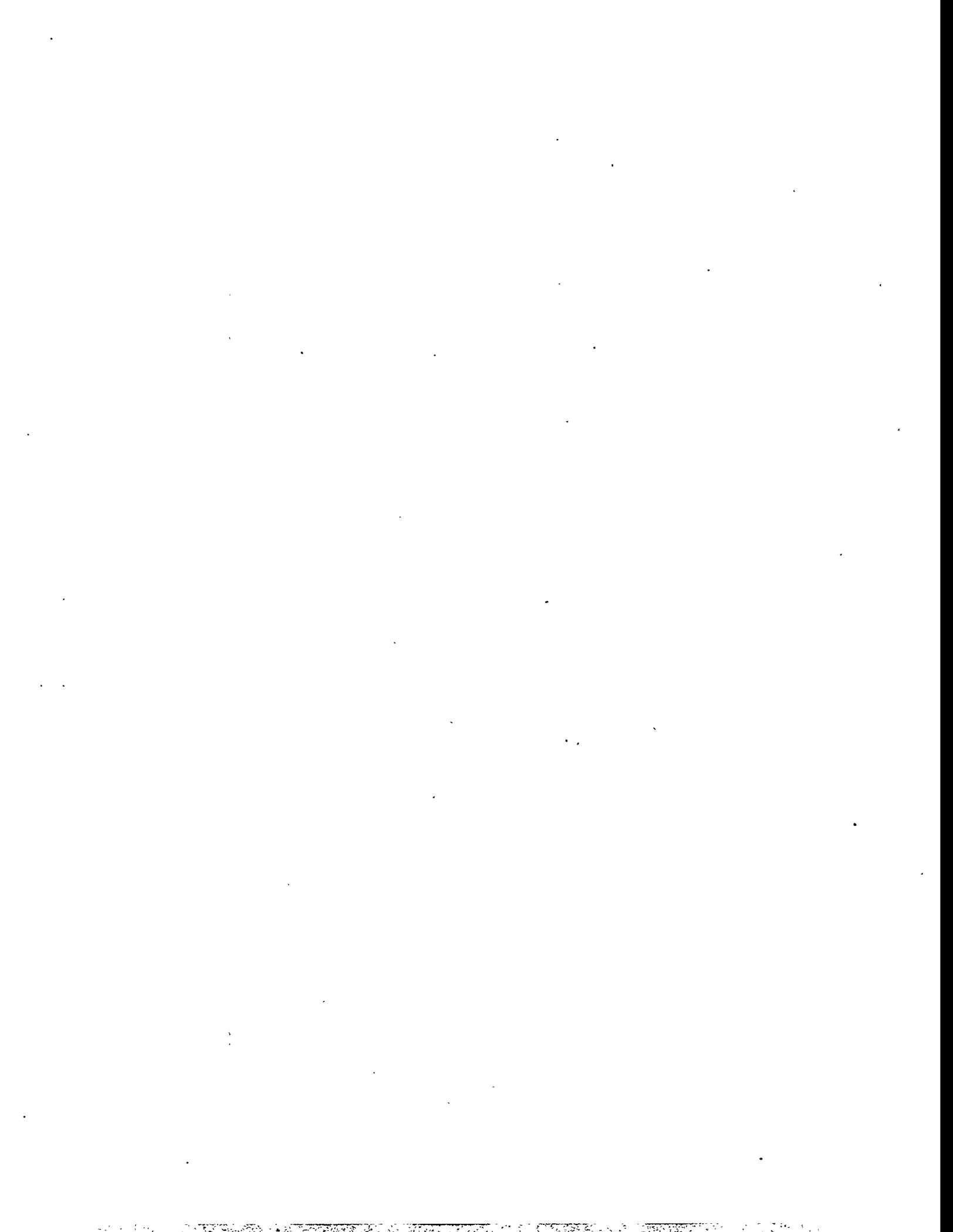
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ACRONYMS

BYBY	bone yard/burn yard area at the Y-12 Plant
DL	detection limit
E ⁰	Standard electrochemical cell potential (relative to the standard hydrogen electrode)
EDS	energy-dispersive X-ray spectroscopy
Eh	oxidation-reduction potential
EPA	U.S. Environmental Protection Agency
Fe ⁰	zero-valent iron
ICP	inductively coupled Plasma
ICD-ES	inductively-coupled plasma-emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
MCL	Maximum Contaminant Level permissible by the EPA for drinking water
NT-1	North Tributary 1
ppb	parts per billion
PRG	Preliminary Remediation Goal
PZC	point of zero charge
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
TDS	total dissolved solids
VOC	volatile organic compound
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

EXECUTIVE SUMMARY

Batch tests were performed on a number of zero-valent iron products and select adsorbents to test their ability to remove radionuclides and other regulated metal ions from groundwater. These investigations are in support of the remediation of the Bear Creek Valley watershed, located on the Oak Ridge Reservation at the Y-12 Plant. Metal ions identified as being contaminants of potential concern in the Y-12 aquifers include aluminum, barium, cadmium, manganese, nickel, technetium, and uranium. With the exception of barium, the solution phase concentration for each of these species could be lowered to the maximum contaminant level (MCL) criterion established by the U.S. Environmental Protection Agency (EPA) with use of either zero-valent iron or iron-oxide sorbents. Barium could be sorbed by pelletized material containing zeolite (clinoptilolite) or by treating the water with excess gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum maintains a low concentration of sulfate ion, precipitating barium as barite (BaSO_4).

To facilitate monitoring of the fate of select contaminants with use of rapid and sensitive counting techniques, we supplemented water samples with soluble radioisotope tracers (^{233}U as uranyl ion, ^{203}Hg as mercuric ion, and ^{99}Tc as pertechnetate ion). All zero-valent iron products tested appeared equally effective at removing these redox-active species. Removal of these metals by zero-valent iron occurred via reduction near the iron-solution interface to form less soluble species (the mechanism for removal of ^{99}Tc) or by adsorption of ions to ferric iron corrosion products (the predominant mechanism for the removal of uranium). The effectiveness of zero-valent iron was significantly diminished in the groundwater from the North Tributary 1 (NT-1) site (with high ionic strength or total dissolved solids primarily from calcium, nitrate, and bicarbonate), compared to the more dilute water from the Well 087 site. Batch testing indicated that the iron surfaces may become passivated at the elevated pH values that accompany corrosion of the iron. For zero-valent iron, relatively little reductive activity remains when the solution pH exceeds a value >9.5 , although ferric iron corrosion products continue to be effective sorbents for select contaminants. Passivation of the iron surface may also occur by adsorption/reduction of the redox active species themselves. Thus, the batch testing alone cannot confirm the long-term effectiveness of zero-valent iron for reductive precipitation

of priority pollutants, and investigations should be extended to conditions of dynamic flow (e.g., packed column testing), in which the hydroxyl ion reaction product may be swept from the reaction zone.

Zero-valent iron was also effective at removing other toxic metals regulated by the Resource Conservation and Recovery Act to levels below their respective MCL criteria. These metals include cadmium, manganese, and nickel. Again, the presumed dominant mechanism for removal of these metals is via adsorption or coprecipitation on iron corrosion products, although the transition metal contaminants are redox-active and can also be removed by reductive precipitation. In batch testing, soluble metal ion concentrations in the treated solution were often below their analytical detection limit; thus, meaningful adsorption isotherms cannot be generated for these species. Column testing will be required to determine the capacity and long-term effectiveness of zero-valent iron for removal of these metals and other species of concern.

A potential concern with use of zero-valent iron for treatment of radionuclides and toxic metals is that the toxic contaminants are not destroyed (as is the case for treatment of chlorinated organic pollutants). Metal ions may be sorbed and concentrated onto the corrosion products, which can detach from the surface of the iron substrate in the form of a fine particulate slurry that could be dispersible in high flow regimes. An alternate approach is to prepare aggregates of stable iron oxides for use as sorbent media.

Several of the stable iron oxides appear promising as adsorbents for treatment of the more dilute Well 087 water. Among the most effective adsorbents for uranium were purified magnetite, goethite, and hematite fine powders. However, use of these materials in a practical remediation scheme (e.g., as a permeable reactive barrier) will require binding the materials into a form that will allow sufficient hydraulic conductivity under conditions of dynamic flow. Under subcontract, Cercona, Inc., has produced several aggregate pellets or foamed ceramic products for evaluation as sorptive reagents. Of the pelletized form of sorbent materials, Cercona iron oxide aggregate (#113) performed best as an adsorbent material for uranium removal. In the Well 087 water, this material had a binding capacity for uranium of ~1 mg/g. However, the high ionic strength of the NT-1 water and the abundance of competing ions greatly reduced the effectiveness of all adsorbents tested. Because of the diminished sorptive capacity for the pollutants of

interest in water containing high concentrations (e.g., >8,000 mg/L) of nitrate ion, use of adsorbents may be unsuitable for a practical remediation scheme in the NT-1 water system.

For technetium removal, activated carbon was the most effective adsorbent material tested, especially for ^{99}Tc added to the low ionic strength Well 087 water. Removal of ^{99}Tc with use of activated carbon is considerably less effective in the NT-1 water, which contains high levels of strongly competing nitrate ion. In the latter medium, removal of ^{99}Tc by sorption with carbon is much less effective than is the case for reductive precipitation with use of zero-valent iron products or by electrochemically assisted removal of ^{99}Tc with use of a magnetite foam electrode.

Either iron or iron oxide products would be suitable for use in the Well 087 system. The most effective use of zero-valent iron may be to intermix the medium with either an inert (e.g., sand) or reactive (e.g., pelletized iron oxide) matrix; this would allow separation of the individual iron particles, so that they would not cement together and plug flow (due to the volume increase from rust formation) and perhaps allow for better dilution of the hydroxyl ion reaction product (minimizing the self-passivation of the iron substrate). This may also promote filtration or settling of the corrosion product fine particulate. The corrosion 'slough' has the potential to redisperse sorbed contaminant. The pH increase that accompanies iron corrosion could potentially enhance the sorption of cationic contaminants on pelletized iron oxide medium.

The NT-1 system, with a higher concentration of total metals and nitrate ion, is a greater challenge, perhaps requiring the use of multiple approaches. For example, the stream could first be treated with stable iron oxide, configured in a retrievable form (since the modest binding capacities for metals in this system would require frequent recharging of sorbent). This would remove the bulk of the heavy metal contaminants. Next, zero-valent iron could be used to remove residual heavy metals, including ^{99}Tc (which requires reduction); some halogenated organic compounds would also be treated, although these reactions are kinetically slow, compared to redox reactions with metal species. Barium is not appreciably removed by either iron or iron oxide and may require the use of gypsum as a precipitating agent. Finally, the solution, detoxified by removal of heavy metals, could be treated with biological agents to reduce the high concentration of nitrate ion. This

sequence of treatments would reduce the probability of loss of sorbed metals by colloidal iron corrosion product and would greatly reduce the water toxicity for biological treatment (and reduce the loading of toxic and radiologic metals in the biological treatment residuals).

1. INTRODUCTION

The goal of the present investigation is to identify candidate treatment materials that may be suitable for in-situ use in a permeable treatment trench or reactive barrier system for removal of inorganic contaminants in selected groundwater aquifers (Morrison and Spangler, 1993). Our research is focused on screening the efficacy of select inorganic matrix treatment media for the removal of soluble hazardous and radioactive metals from these contaminated waters at the Bear Creek Valley remedial action area at the Oak Ridge Y-12 Plant.

Groundwater at the Bear Creek Valley Operable Unit 2 has become contaminated with regulated metals and organic compounds due to former site activities and disposal practices. Contaminated water from the site can be characterized into distinct water types [Refer to *Bear Creek Valley Characterization Area Technology Demonstration Action Plan*, Y/EN-5479 (DRAFT), April 1996, and DOE/OR/01-1273/V1&D2 (Y/ER-182/V1&D2), January 1995]. Water Type 1, represented by water from North Tributary 1 (NT-1) near the former S-3 burial site, contains relatively high levels of metal ion contaminants and total dissolved solids (TDS); nitrate ion is present at levels $>7,000$ mg/L, and ^{99}Tc dominates the total radioactivity ($> 15,000$ pCi/L). Water Type 2, represented by water from Sampling Well 087 near the so-called boneyard/burnyard (BYBY) region of the site, contains relatively low levels of inorganic contaminants and TDS; the principle contaminants of concern in this system are trace volatile organic compounds (VOCs) and uranium. A third water type near exit pathways from the Y-12 site contains trace VOCs as the predominant contaminant. Representative analytical data for NT-1 and Well 087 waters are presented in Tables 1 and 2, respectively.

We report on the efficacy of zero-valent iron and metal oxide media for the removal of select contaminants of potential concern from Bear Creek Valley water samples. Some of the more important reactions that occur during treatment of contaminants with zero-valent iron (Fe^0) include the following five processes.

Table 1. Characteristics of NT-1 water (before treatment)

Characteristic	Historic data: NT-1		NT-1 (sampled 4/12/96)		NT-1 (sampled 7/11/96)	
	Y/EN-5479, Table 2.1 (sampled 2/26/96)	Raw (41-03)	Filtered (43-31)	Raw	Filtered	[Batch 2]
pH Value ^a		5.58	6.04	5.79	5.80	
Eh (vs SHE), (m V ^o)		+603		+670	+673	
Alkalinity (HCO ₃), (mg/L)	160					
Total Dissolved Solids	13,000					
Total Suspended Solids	370					
Total activity (pCi/L)	15,000		17,000	22,500	22,600	
Ag (mg/L)	<0.02	0.010	0.013			
Al (mg/L)	81	22.4	8.5		0.96	
As (mg/L)	<0.1	0.03	<0.008			
B (mg/L)		0.112	0.326			
Ba (mg/L)	20.1	18.7	18.8	14	15	
Be (mg/L)	0.010	0.006	<0.001			
Ca (mg/L)	>1,000	2230	2270		1800	
Cd (mg/L)	0.78	0.53	0.60	0.84	0.06	
Cr (mg/L)	0.076	<0.002	<0.002	0.009		<0.005
Fe (mg/L)	37.4	1.4	<0.033			<0.025
Hg (mg/L)	0.0002	0.024	<0.011	0.0011		<0.0005

Table 1. (continued)

Characteristic	Historic data: NT-1		NT-1 (sampled 4/12/96) [Batch 1]		NT-1 (sampled 7/11/96) [Batch 2]	
	Y/EN-5479, Table 2.1 (sampled 2/26/96)	NT-1 (41-03)	Raw (43-31)	Filtered	Raw	Filtered
K (mg/L)	48.2	33	43			
Pb (mg/L)	<0.2	<0.004	<0.004	<0.004	0.008	<0.003
Se (mg/L)		<0.009	<0.009	<0.009		
Sb (mg/L)		<0.006	<0.006	<0.006		
Si (mg/L)		8.0	4.9			
Ti (mg/L)		0.036	<0.001			
Tl (mg/L)	0.135	0.011	0.008			
U (mg/L)	0.006	(Spike)	(Spike)		0.008	0.008
V (mg/L)	0.051	<0.009	<0.009			
Zn (mg/L)	0.225	0.10	0.11		0.14	0.09
Zr (mg/L)		<0.003	0.004			
Chloride (mg/L)	180		223			258
Fluoride (mg/L)	30		48			
Nitrate (mg/L)	8,500		7,940			12,400
Nitrite (mg/L)	16		37			52
o-phosphate (mg/L)	<0.12		<1.0			
Sulfate (mg/L)	12		12.6			50

^aMeasured on date of testing (not *in-situ*)

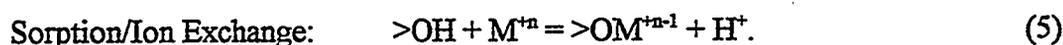
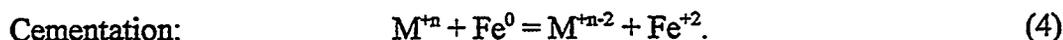
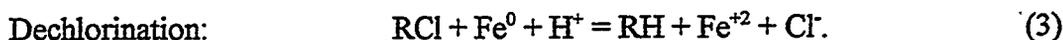
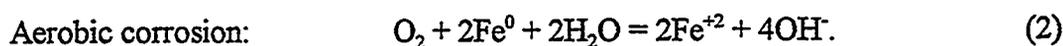
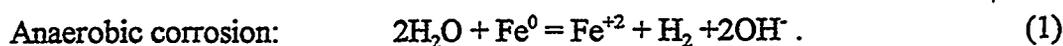
Table 2. Characteristics of Well 087 water (before treatment)

Characteristic	Historic Data: Well 087 ^a		Well 087 (sampled 4/12/96) [Batch 1]		Well 087 (sampled 7/11/96) [Batch 2]	
	Median (freq. detect)	Range	Raw (41-04)	Filtered (43-33)	Raw	Filtered
pH Value ^b			6.43	6.96	6.67	6.72
Eh (vs SHE), (mV) ^b			+598 ^d	+429	+641	+641
Alkalinity (HCO ₃) (mg/L)	181	81 - 238				
Total Dissolved Solids	292 (3/3)	232 - 342				
Total Suspended Solids	74 (4/4)	23 - 326				
Total activity (pCi/L)			1,500		730	10
Ag (mg/L)	ND (0/2)	<0.005	<0.002	<0.002		
Al (mg/L)	3.1 (1/1)		0.079	0.073	0.64	0.08
As (mg/L)	ND (0/2)	<0.0025	0.008 (ND)	0.008 (ND)		
B (mg/L)	0.15 (1/1)		0.360	0.204		
Ba (mg/L)	0.088 (1/1)		0.105	0.126	0.11	0.11
Be (mg/L)	ND (0/1)		0.001 (ND)	0.001 (ND)		
Ca (mg/L)	56.5 (4/4)	38 - 76	48.0	46.4	77	57
Cd (mg/L)	ND (0/3)	<0.001	0.002	0.004	0.006	0.004
Cr (mg/L)	0.0115 (4)		<0.002	<0.002	0.006	0.006
Fe (mg/L)	2.45 (2/2)	2.0 - 2.9	<0.033	<0.033	0.55	0.025
Hg (mg/L)	0.0006 (2/2)		<0.011	<0.011	<0.005	<0.005
Mg (mg/L)	6.1 (3/3)	5.1 - 8.5	6.63	6.57	5.8	5.1
Mn (mg/L)	0.52 (2/2)	0.48 - 0.57	0.893	0.938	0.76	0.69

Table 2. (continued)

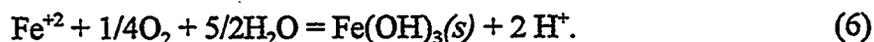
Characteristic	Historic Data: Well 087 ^a				Well 087 (sampled 4/12/96) [Batch 1]		Well 087 (sampled 7/11/96) [Batch 2]	
	Median (freq. detect)	Range	Raw (41-04)	Filtered (43-33)	Raw	Filtered	Raw	Filtered
Na (mg/L)	13.5 (4/4)	13 - 18	13.99	13.16	<5.0	<5.0	<5.0	<5.0
Ni (mg/L)	0.03 (1/1)		0.033	0.024	<0.0025	<0.0025	<0.0025	<0.0025
Pb (mg/L)	0.16 (4/4)	0.012 - 0.026	<0.004	<0.004	<0.003	<0.003	<0.003	<0.003
Se (mg/L)	0.005 (1/2)	0.003 - 0.007	<0.009	<0.009				
Sb (mg/L)	ND (0/1)	<0.025	<0.006	<0.006				
Si (mg/L)	10 (1/1)		5.38	5.12				
Ti (mg/L)	0.06 (1/1)		<0.001	<0.001				
Tl (mg/L)			<0.006	0.006				
U (mg/L)	0.46	0.14 - 0.52	(Spike)	(Spike)	0.23	0.23	0.23	0.24
V (mg/L)	0.005		<0.009	<0.009				
Zn (mg/L)	0.052 (1/1)		0.02	0.028	0.06	0.06	0.06	0.08
Zr (mg/L)	ND (0/1)	<0.0025	<0.003	0.003				
Chloride (mg/L)	32.5 (4/4)	20 - 33		9.1				16
Fluoride (mg/L)	0.05 (1/3)	0.1		<0.55				
Nitrate (mg/L)	ND (0/4)	<0.055		<1.0				<1.0
Nitrite (mg/L)	ND (0/4)			<1.1				<1.0
o-phosphate (mg/L)				<40				
Sulfate (mg/L)	11 (4/4)	8 - 19		26				21

^aMeasured on date of testing (not *in-situ*)^bFrom Report Y/EN-5479



In the equations above, R represents the organic portion of a chlorinated hydrocarbon molecule, M^{+n} represents a cationic metal contaminant, and $>\text{OH}$ represents an exchangeable site on the hydrous metal oxide at the iron substrate or on its detached corrosion product. [Note in the simplified Eq. 5 that, depending upon the solution pH, the surface site may have a net positive ($>\text{OH}_2^+$) or negative ($>\text{O}^-$) charge. The exchange of protons to and from the oxide surface creates specific site types available for adsorption (Ford, 1992)].

In addition, the ferrous iron (Fe^{+2}) reaction product in Eqs. 1–4 can be oxidized by air to form ferric ion (Fe^{+3}), which can subsequently hydrolyze and precipitate from solution at near-neutral and alkaline pH values, as illustrated in the simplified Eq. 6:

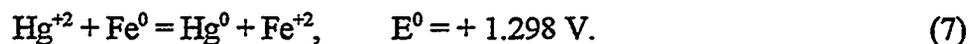


Hydrolyzed ferric iron [$\text{Fe}(\text{OH})_3(s)$, and its polymer, ferrihydrate] and iron oxide minerals are effective reagents for removing many toxic and radioactive trace element contaminants from solution by sorption (as depicted in Eq. 5) or a combination of coprecipitation and sorption (Venkataramani et al., 1978; EPRI, 1987; Ford 1992, Theis et al., 1994). Sorption of uranyl ion to these and other mineral phases is well documented (Langmuir, 1978; Hsi and Langmuir, 1985; Giblin et al., 1981; Ho and Miller, 1986; Koss, 1988; Hakanen and Lindberg, 1992). Excellent and comprehensive recent reviews of the

chemistry of radionuclides in the geosphere have been prepared by Leiser (1995) and by Silva and Nitsche (1995).

Reaction 3 describes the degradation of chlorinated organic hydrocarbons, such as perchloroethene or carbon tetrachloride, that occurs in aqueous solution in the presence of iron metal; this topic has recently been reviewed by Wilson (1995) and Tratnyek (1996).

The so-called "cementation" reaction described by Eq. 4 refers to the process by which a metal deposits by reaction of its ion with a more readily oxidized metal. Iron is most commonly used as the sacrificial anode for the galvanic couple (Cooney, 1992; Manahan, 1994). For example, mercuric ion (Hg^{2+}) is readily removed from solution by cementation with the use of zero-valent iron (Bostick et al., K/TSO-6; Grau and Bisang, 1995; Anaciato et al., 1996):



The large positive value for the standard cell potential, E^0 , indicates that the reaction as written is thermodynamically favored.

In a field application of zero-valent iron for the remediation of metal ions in solution, many of the mechanisms for metal removal may occur simultaneously. This can be illustrated by chromate ion, found as a groundwater contaminant near certain industrial sites. Toxic hexavalent chromium (Cr(VI)) can be reduced to the insoluble trivalent species with use of either zero-valent iron (Bowers et al., 1986, Cantrell, 1995) or soluble ferrous ion (Anderson and Bolto, 1984; James, 1996). Furthermore, chromium ions are readily sorbed onto ferrihydrate (Zachara et al., 1987) or iron corrosion products and other iron-containing minerals (EPRI EA-4544). All of these mechanisms may occur during subsurface treatment with use of zero-valent iron (Davis et al., 1993; Powell et al., 1995).

In addition, the presence of strong ligands or complexing agents in a water system can strongly affect metal ion solubility and sorptive properties. This topic is beyond the scope of the present report, although we briefly examine the effect of added bicarbonate ion on the sorption of uranyl ion by ferrihydrate under oxic (aerobic) conditions.

All of the reactions described above are sensitive to the solution pH value. Note in Eqs. 1 and 2 that corrosion of zero-valent iron in water raises the solution pH value (due to an increase in hydroxyl ion concentration). This phenomenon can affect metal ion removal in many ways, confounding the interpretation of batch-test results. For example, metal ions may hydrolyze and precipitate at these elevated pH values.

Sorption of ions to mineral surfaces is strongly dependent on the solution pH value, which affects the surface charge distribution on the sorptive substrate. As the pH increases above the point of zero charge (pzc) for the substrate, the surface becomes more negatively charged and the sorption of cations generally increases. Conversely, sorption of anions is generally favored at pH values below the pzc of the substrate. For iron-containing minerals, the pzc is typically in the range of ~6–8.5 (Silva and Nitsche, 1995). Thus, depending upon the pH of the slurry, iron-containing minerals may be used to sorb oxyanions (such as CrO_4^{-2} , AsO_4^{-3} , SeO_3^{-2} , etc.) or cations (Cr^{+3} , Pb^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Ni^{+2} , etc.) (EPRI, 1987).

At sufficiently high pH values, the surface of the iron metal becomes passivated, and both the corrosion rate and redox activity of the iron substrate is diminished. This effect is illustrated in Fig. 1, which compares the pH-dependency for the removal of soluble Tc(VII) from a carbonate salt solution by sorption onto anion exchange resins and by reduction with steel to form an insoluble Tc(IV) product (Bostick et al., K/TCD-1120; K/TCD-1141). In the absence of strong reducing agents, ^{99}Tc exists in the form of the pertechnetate ion (TcO_4^-), which does not hydrolyze at high pH values nor readily sorb to iron corrosion products or to soil and sediment particulate matter (Leiser and Bauser, 1987; Gu and Dowlen, 1996). Thus, the relative ineffectiveness of iron as a treatment reagent at pH values above ~9.5, as illustrated in Fig. 1, is attributed to surface passivation phenomena (Pourbaix, 1974).

The effectiveness of several forms of zero-valent iron (e.g., reagent-grade metal filings, reclaimed scrap material, beaded aggregate or foamed product) for the removal of select contaminants was assessed by batch-test using two types of water from Bear Creek Valley (*viz.*, NT-1 and Well 087 or BYBY water). Uranium was identified as a principle contaminant of concern; therefore, the waters for testing were supplemented with soluble hexavalent uranium, as uranyl ion (UO_2^{+2}). The removal of added U(VI) by all forms of

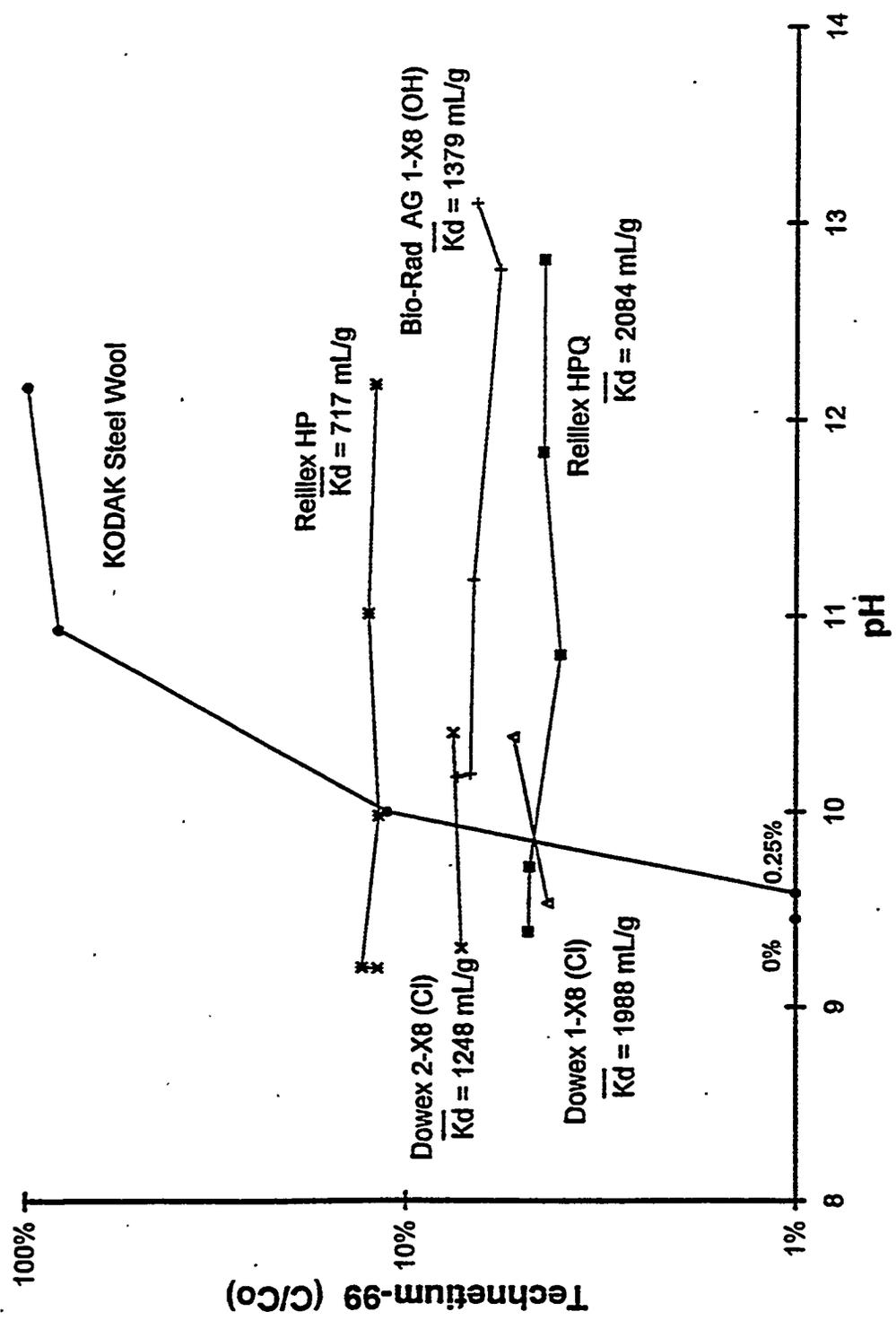


Fig.1. Adsorbent removal efficiency as a function of pH (0.01 g as-received adsorbent/mL simulated NGLLLW solution).

iron gave essentially equivalent apparent kinetics for a given water system (with removal rates in the high-ionic-strength NT-1 water being lower by a factor of approximately 20, compared to the performance in the BYBY water). In our testing, the predominant mechanism for the removal of soluble uranium by zero-valent iron reagent appeared to be sorption of U(VI) to hydrolyzed ferric iron corrosion product, rather than reduction of uranium to a lower valence state. Porous beads prepared from stable iron oxide products are also shown to be effective sorbents for many toxic metals and radionuclides. Performance characteristics for several media are compared in the text.

2. MATERIALS

2.1 WATER SAMPLES

We received samples of water labeled "NT-1 (sampled 4/12/96 and 7/11/96) and "Well 087 (sampled 4/17/96 and 7/10/96). Well 087 water is characteristic of groundwater originating from the so-called "bone yard/burn yard" (BYBY) area at the Y-12 plant. Selected characteristics of these two waters are given in Tables 1 and 2. These samples, as-received, have very low uranium concentrations and were supplemented with uranium (i.e., "spiked") for testing in our laboratory; NT-1 contains relatively high ^{99}Tc , plus (low, but detectable) ^3H (tritium) and radio-strontium.

2.2 TREATMENT AGENTS

As a benchmark treatment agent, we have selected Fisher I-57 degreased iron filings (Fisher Scientific Co., Fair Lawn, NJ), nominal 40/60 mesh (~0.25-0.35mm diameter). We have demonstrated the effectiveness of this material in batch-test studies for the removal of soluble Tc(VII), Cr(VI) and Hg(II) in decontamination brine (Bostick et al., 1988) and Tc(VII) in simulated groundwater (Bostick et al., 1995). Similarly, Cantrell et al. (1995) have used this reagent in batch-test studies for the removal of Cr(VI), Tc(VII) and U(VI) from groundwater. Fisher iron has been used in a continuous-flow, packed-column configuration to remove pertechnetate ion from simulated high-nitrate decontamination brine (Del Cul and Bostick, 1995), and from contaminated groundwater (Liang et al., 1996). Other forms of zero-valent iron and iron oxides have been proposed for the treatment of toxic metals in industrial wastewaters (Smith, 1995) and groundwater (Powell, 1995).

Developmental samples of ceramic foam and aggregate material (prepared for this project by Cercona, Inc., Dayton OH 45404, under subcontract PY251G18) have also been evaluated. Material selected for evaluation was assigned a K-25 Material Sciences Department number (MSD-96-XXX); a brief material descriptive summary is presented in Table 3. In general, samples of aggregate material and other sorbents selected for testing

Table 3. Selected characteristics of Cercona foam aggregate and related materials

Sample code	Description	BET surface area (m ² /g)	Dry bulk density (g/cm ³)	Crystallographic characterization (XRD)	Elemental composition (EDS)
MSD-96-109	Porous synthetic magnetite pellets: ~98% magnetite (from Isaac iron oxide), + Norlig G binder. Fired in CO ₂ @800° C.	0.70	1.4	Major: magnetite (Fe ₃ O ₄); minor: quartz (SiO ₂)	Fe; trace Ca, Si, Mn
MSD-96-110	Porous zero-valent iron pellets: ~98% Fe (National Steel), + Norlig G binder. Fired in 7% H ₂ @ 1080° C.	0.92	2.4	Major: iron; minor: fayalite (Fe ₂ SiO ₄), wustite (FeO)	Fe; trace Ca, Si, Mn, Cr
MSD-96-111	Porous zero-valent iron pellets: ~93% Fe (National Steel), + Cercona binder. Fired in 7% H ₂ @ 1080° C.	~0.01	2.1	Major: fayalite; wustite; minor: iron	Fe; trace Ca, Si, Mn, Cr
MSD-96-112	Porous zero-valent iron pellets: ~98% Fe (from Isaac iron oxide), + Norlig G binder. Fired in N ₂ + 50% H ₂ @ 1080° C.	0.05	2.5	Major: iron, wustite	Fe; trace Ca, Si, Al, S
MSD-96-113	Porous iron pellets: ~93% mixed oxide (from Isaac iron oxide), + aluminosilicate binder (unfired).	13.3	1.3	Major: magnetite, hematite	Fe; trace Al, Si, Ca, Mn
MSD-96-114	Porous zero-valent iron pellets ~94% Fe (US Metal), + aluminosilicate binder. Fired in N ₂ + 7% H ₂ @1080° C.	3.94	2.4	Major: iron; minor: hematite (Fe ₂ O ₃)	Fe; trace Mn, Ca, Al, Si, Ti, S
MSD-96-115	Porous zero-valent iron pellets: ~92% Fe + aluminosilicate binder. Fired in N ₂ + 7% H ₂ @1080° C.	0.24	2.5	Major: iron; minor: hematite, magnetite	Fe; Al, Si; trace Mn
MSD-96-116	Foamed zero-valent iron aggregate: ~92% Fe (US Metal), + Cercona binder. Fired in N ₂ + 50% H ₂ @1080° C.	0.8	1.2	Major: iron; minor: magnetite, fayalite, hematite	Fe; Al, Si; trace, Mn, Cr, C
MSD-96-118	Porous zeolite (clinoptilolite) + 20 wt % FeOOH, + Cercona binder (unfired).	13.4	0.8-1.0	Major: goethite (FeOOH), clinoptilolite; minor: quartz, biotite	Fe; Al, Si; trace Ca, K

Table 3. (continued)

Sample code	Description	BET surface area (m ² /g)	Dry bulk density (g/cm ³)	Crystallographic characterization (XRD)	Elemental composition (EDS)
MSD-96-119	Porous zeolite + ~70 wt % Fe (US Metal), + Cercona binder (unfired).		1.6	Major: iron, clinoptilolite; minor: quartz, biotite	Fe, Al, Si, trace Ca, Mn
MSD-96-120	Porous zeolite + ~20 wt % FeS ₂ + Cercona binder (unfired).		1.0	Major: pyrite (FeS ₂), clinoptilolite; minor: quartz, biotite	Fe, S, Si, Al, trace Ca, K
MSD-96-134	Foamed zero-valent iron: ~94% Fe + (US Metal), + Cercona binder. Fired in N ₂ + 50% H ₂ @1080°C.	~0.5	~1		
MSD-96-192	Porous zeolite pellets (aluminosilicate bonded clinoptilolite, unfired)		0.6		
MSD-96-193	Foamed bimetallic steel: ~70% Fe (US Metals) + 23% high-silicon steel (Duriron), balance Cercona binder. Fired in N ₂ + 5% H ₂ @1080°C		1.8		
MSD-96-194	Foamed iron + 2% FeS ₂ , Cercona binder. Fired in N ₂ + 5% H ₂ @ 1080°C.		1.9		
Iron filings	Fisher I-57, ~40 mesh	5.89			
Iron filings	Master Builder's Steel (MBS), ~40 mesh	2.11	2.6		
Activated carbon	Nucon Mersorb-3	767			
Fe ₃ O ₄	Magnetite (Alfa Products)	5.55			
α-FeOOH	Goethite (NOAH Chemicals)	12.7			
Fe ₂ O ₃	Hematite (Alfa Products)	9.39			

were dry sieved to select -8/+ 12 mesh particles (i.e., diameters ~1.4–2.4 mm). Photomicrographs of representative Cercona material are provided in Fig. 2.

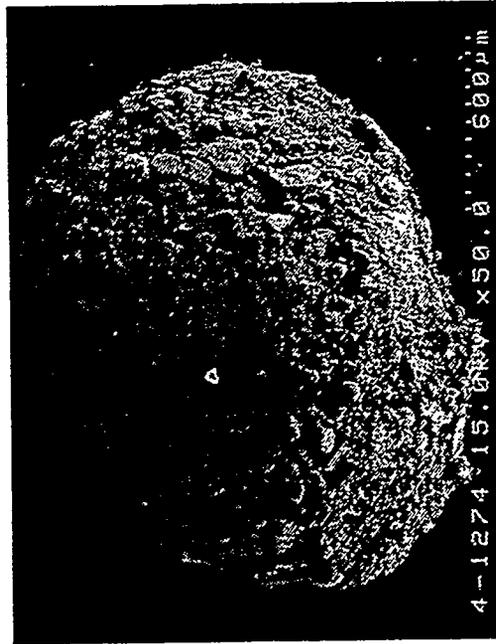
2.3 CERCONA TECHNOLOGY

The Cercona technology is based on the gelation of soluble silicates with soluble aluminates. The combination of these two aqueous solutions will gel in a reproducible and controllable manner depending on the specific concentration, temperature and ratio of each material. The Cercona process utilizes this concept by forming two slurries of these solutions with the additional "customized" aggregate and powdered materials desired. The resultant final composition, therefore, is typically 5–15 wt % silicate and aluminate with the balance being any inorganic material desired, such as metallic iron, iron oxides, zeolites, clays, or speciality ceramic materials.

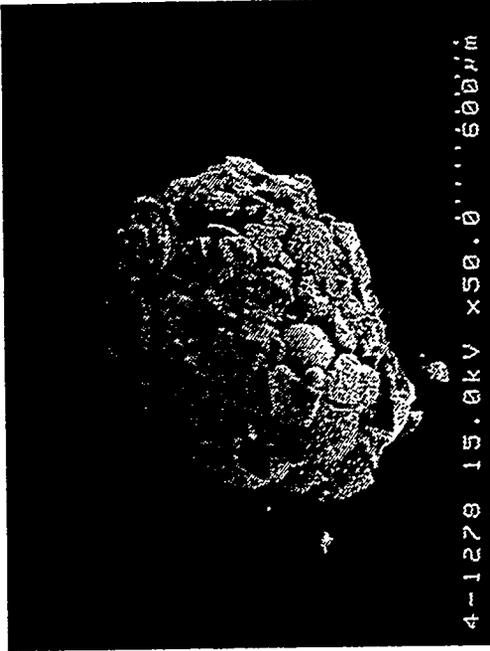
In the production of foamed shapes, foaming takes place prior to gelation. The incorporation of specialty gassing agents, surfactants, and gel modifiers controls the amount, size, and degree of openness in the final foam structure in much the same manner as used in the production of urethane foams. After the foamed articles (products) have sufficiently set, they are further processed to improve durability and then dried, baked, and fired in a controlled reducing atmosphere (if necessary). Because over 85% of the raw material used can be varied, control over the final composition allows for the production of "site specific" reactive media systems.

In the production of porous pellets and the like, the hydrogel binder system is used simply to pelletize, or agglomerate fine particulate materials together (controlled composition), bonding them in place with or without foaming. The size of the particulates, amount of binder liquid phase, and pelletizing conditions controls the final pellet size, shape, and degree of porosity.

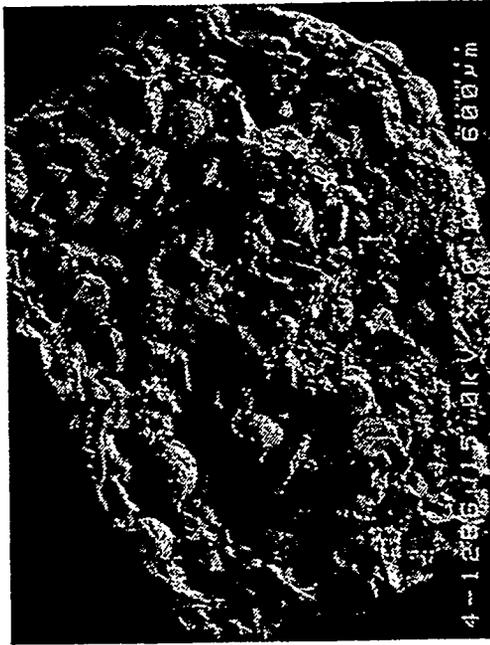
One of the advantages of the Cercona process is the relatively low cost of the raw materials used in the manufacturing process. Both the silicate and aluminate binder materials are low cost, readily available commodity chemicals. In the production of iron



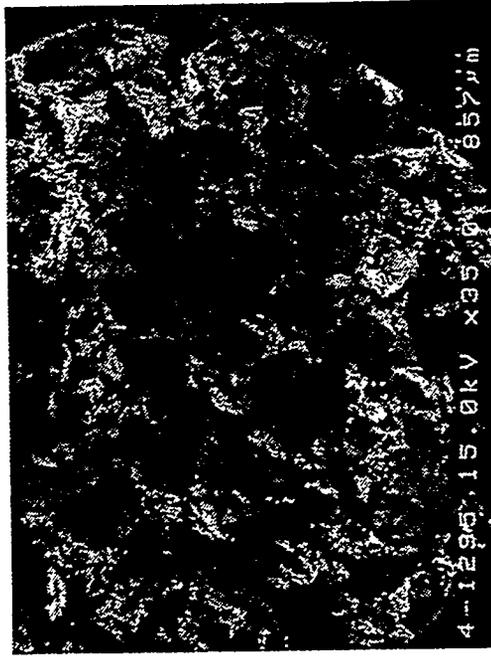
96-109: Magnetite aggregate pellet



96-110: Iron aggregate pellet



96-111: iron aggregate pellet



96-134: Iron Foam pellet

Fig.2. Micrograph images of representative Cercona pellet and foam products.

and iron-based porous material systems, the iron used is primarily fines from scrap iron processing. A combination of scrap iron, iron ore (oxides), and baghouse dust materials are combined in suitable proportions depending on the final product characteristics desired such as composition, strength, surface area, and porosity.

2.4 SPIKE AND TRACER CHEMICALS

2.4.1 Mercury

Nonradiological mercury was added in the form of mercuric chloride (HgCl_2). Radiologically traced mercury solutions were prepared by the addition of small quantities of $^{203}\text{HgCl}_2$ (Amersham International), which allowed quantitation by gamma-counting (Bostick et al., 1996).

2.4.2 Uranium

Natural uranium was added in the form of uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Solutions submitted for inductively coupled plasma emission spectroscopy (ICP-ES) analysis were spiked to contain a nominal concentration of 1 mg-U/L. To enhance in-house monitoring of the fate of uranium by gamma-counting, we supplemented some uranium solutions with a tracer solution enriched in isotope ^{233}U .

3. METHODS

3.1 DAVIES-GRAY TITRATION

The Davies-Gray (1964) procedure, as refined by Eberle et al., (1970), is a highly accurate method for moderately concentrated solutions of uranium, and can be used to differentiate U(VI) from reduced forms of uranium (e.g., U(IV)). We have used this technique to quantitate uranium in the relatively high concentration range (e.g., ~100–1000 mg/L).

3.2 ELECTRODE POTENTIAL (Eh) AND SOLUTION pH

The oxidation-reduction potential (Eh) of an aqueous solution is measured using a platinum-calomel combination electrode, and the result is corrected for the potential difference between the calomel reference electrode and the standard hydrogen electrode (SHE). Measurement of the solution pH and redox potential may provide a useful frame of reference when used in conjunction with thermodynamic prediction of species predominance domains under equilibrium conditions (Pourbaix, 1974; Garrels and Christ, 1965). However, as Manahan (1994, p. 99) warns; "attaching any quantitative significance to the Eh value measured directly with an electrode is a very dubious practice, (since) most (low ionic strength) aquatic systems do not yield meaningful values of Eh."

However, the measured Eh value is more reliable when poised by a dominant reversible redox couple, such as Fe(II)/Fe(III). Thus, in a system equilibrated with zero-valent iron, the measured Eh value is a practical indicator of the iron redox couple, but it may have limited value as a master variable for thermodynamic predictions of the speciation of other couples that may not be in complete equilibrium (Fish, 1993).

3.3 EQUILIBRIUM TESTING

Unless otherwise indicated, solid phases were tested *as-received*, without preconditioning. Known amounts of solid reagent and aqueous solution are contacted by shaking the slurry in a sealed container for 16–24 hours before separating the phases.

Solution samples for in-house gamma counting were filtered through 0.2- μm Acrodisc membranes; whereas, samples for ICP-ES were filtered through 0.45- μm Nalgene membranes.

Additional batch experiments were conducted by adding 0.01, 0.03, or 1.0 g of iron to 10-ml aqueous samples spiked with total uranium at concentrations up to 8 mg/L, traced with ^{233}U isotope. The vials in both experiments were agitated for approximately 18 hours with a wrist action shaker and sampled. After the day 1 sampling, the vials were sealed to allow further reaction. After 30 days elapsed, the vials were again sampled for aqueous uranium levels. All samples were analyzed for aqueous uranium via gamma counting with a Packard Auto-Gamma 500C instrument.

A third type of batch experiments involved placing iron coupons (1.43 cm diameter, 0.15 cm thick) in 500-ml sample bottles containing waters with differing background electrolyte compositions. All bottles were spiked to 927 mg of uranium per liter with a ^{233}U tracer. To create anaerobic conditions, the sample bottles were continuously purged with nitrogen gas. Aqueous samples were withdrawn from each bottle and analyzed via gamma counting.

3.4 ALPHA/BETA LIQUID SCINTILLATION COUNTING

Total alpha/beta activity is monitored with use of a Packard 2550 TR/AB Analyzer. This instrument utilizes a multidimensional analysis to allow significant resolution of alpha and beta radioactive decay for identifying radionuclide activities in a mixture.

3.5 GAMMA COUNTING

Solutions traced with gamma-emitting radionuclides (^{203}Hg , ^{233}U) are counted on a Packard Auto-Gamma 500 instrument.

3.6 INDUCTIVELY COUPLED PLASMA-EMISSION SPECTROSCOPY (ICP-ES)

After treatment and phase separation (filtration), solutions traced with natural uranium were preserved with the addition of 2% (by volume) ultrapure nitric acid reagent and then submitted to C. H. Mattus at Oak Ridge National Laboratory for analysis. Although ICP-ES is not the preferred method of analysis for some of the constituents of interest (notably Hg and U), the technique does permit simultaneous monitoring for many of the metallic elements in solution.

3.7 INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY (ICP-MS)

Additional acid-preserved samples were submitted to the K-25 Site Analytical Services Organization for analysis by ICP-MS. This technique is more sensitive for uranium, with a reported detection limit of 0.025 mg/L (or 25 ppb).

3.8 MICROCHARACTERIZATION

Samples of ceramic foam and aggregate product were examined by electron microscopy (for surface morphology), energy-dispersive X-ray spectroscopy (EDS) (for determination of elemental content), and by X-ray diffraction crystallography (XRD) (for determination of major *crystalline* phases).

3.9 ESTIMATION OF DISTRIBUTION COEFFICIENTS

In order to compare reagents, we computed a conditional distribution coefficient, K_d , using the relationship:

$$K_d = S/C \quad (8)$$

where S = mass of contaminant 'sorbed' at equilibrium per mass of 'sorber' and
 C = equilibrium concentration of soluble contaminant in aqueous phase.

If C is given in g/ml, then K_d has the units ml/g.

An adsorption isotherm is a model to define the relationship between the amount of a substance sorbed (S in Eq. 1) and its concentration in solution (C) at equilibrium at a constant temperature. Note that Eq. 8 is also the expression for a simple linear sorption isotherm, which often adequately describes sorption under a defined set of conditions over a limited range of equilibrium concentrations of solute. Note also that the experimental sorption isotherm for a given metal species with use of a relatively nonspecific sorbent can deviate significantly from linearity when the test solution contains other metals that can successfully compete for the same binding sites (Bostick and Guo, 1996). An alternative model, often providing a better predictive outcome over a wide range of contaminant concentrations, is the Freundlich isotherm:

$$S = K_f C^{1/N} \quad (9)$$

This model assumes that there are a finite number of sorption sites, and it attempts to account for the heterogeneity of these sites. In an empirical linear form, the Freundlich isotherm becomes where K_f and $1/N$ are empirical constants.

$$\log S = \log K_f + (1/N) \log C \quad (10)$$

Eq. 10 has been used to extrapolate data to predict packed bed capacity factors (Section 5.4) at varying influent levels of contaminant.

It is recognized that redox ('cementation') reactions are not generally well-described by sorption isotherms, but the conditional K_d value derived from Eq. 8 does allow an approximate (if simplistic) quantitative comparison among media for contaminant removal efficiency under a defined range of test conditions (solution pH, concentrations of competing ions or complexing agents, etc.).

4. RESULTS

4.1. SCREENING OF TREATMENT MEDIA

4.1.1. Multielement Survey by Inductively-Coupled Plasma (ICP) Analysis

Multidosage testing of selected sorbents with use of uranium-spiked Well 087 and NT-1 waters was performed, and the residual concentrations of metallic elements in the filtered treated waters were surveyed by ICP spectroscopy. Results are plotted in Figs. 3–10. For reference treatment goals, we have used the concentration values for Preliminary Remediation Goals (PRGs) and EPA MCLs for drinking water cited in DOE/OR/01-1273/V1&D2. The reported detection limit (DL) for contaminants with use of the ICP-ES system is also plotted (the ICP-MS system generally gives lower detection limits). Each of the identified contaminants of potential concern were amenable to remediation by either zero-valent iron or sorbent, although treatment to target goals required higher dosages for the NT-1 water. A brief summary, by contaminant, is given below.

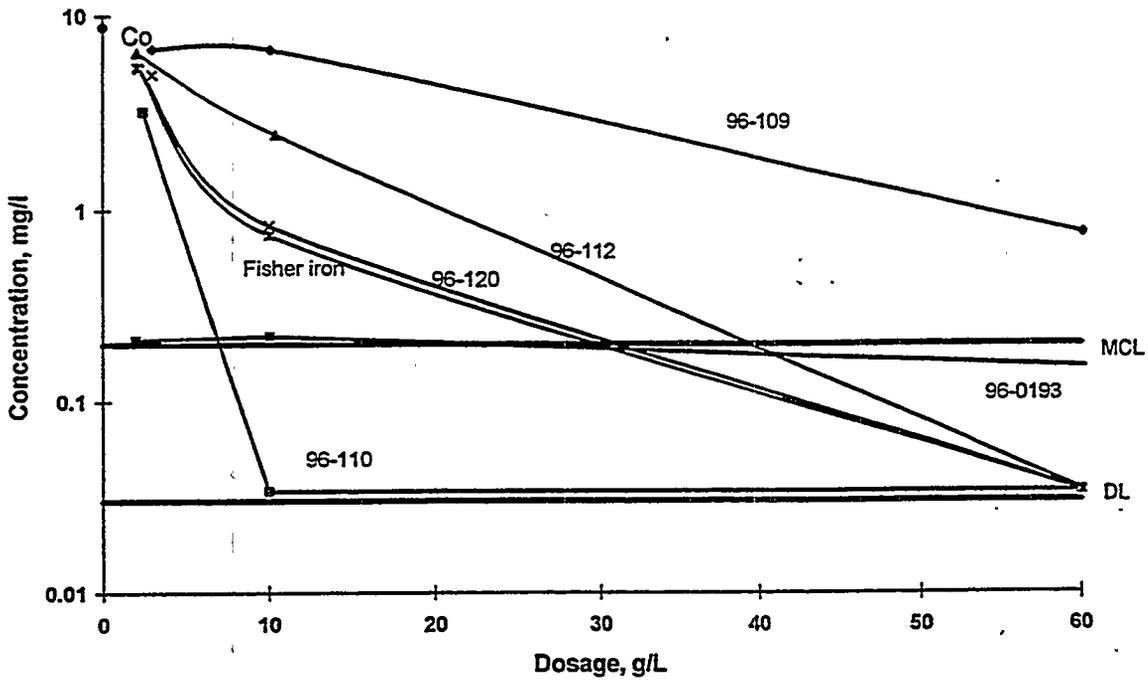
4.1.2 Aluminum (Al) (Fig. 3; MCL = 0.2 mg/L)

Aluminum is removed by coprecipitation or sorption to ferric iron corrosion product or sorbent. Cercona material 96-120 is an unfired product containing an aluminosilicate binder; this material appears to leach out soluble or colloidal Al.

4.1.3 Barium (Ba) (Fig. 4; MCL = 2 mg/L, PRG = 2.6 mg/L)

Barium is present in relatively high concentrations (15–20 mg/L) in the NT-1 water. It is not removed appreciably with use of zero-valent iron or iron oxide sorbents. Cercona materials 96-118, 96-120, and 96-192 contain zeolite in the form of clinoptilolite, which is somewhat effective in removing soluble Ba. Chemical treatment, with sparingly-soluble gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, appears to be a more effective means to control barium

REMOVAL OF Al FROM NT-1 WATER



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REMOVAL OF Al FROM WELL 087 WATER

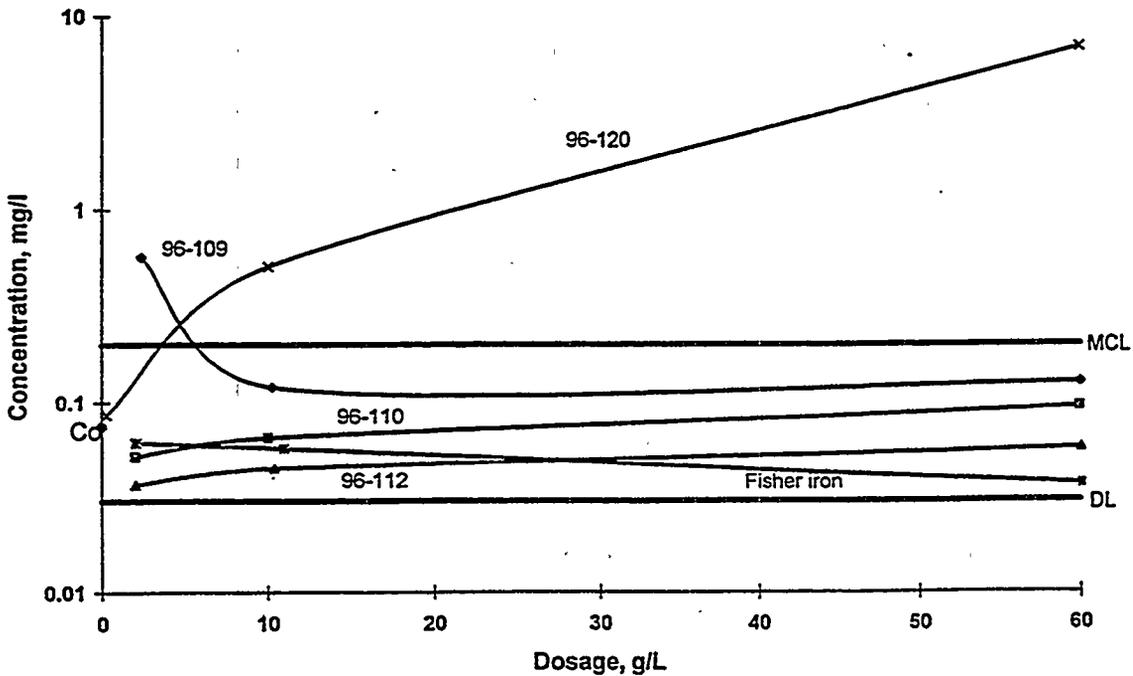


Fig. 3. Removal of soluble Aluminum from Y-12 waters.

8/27/96

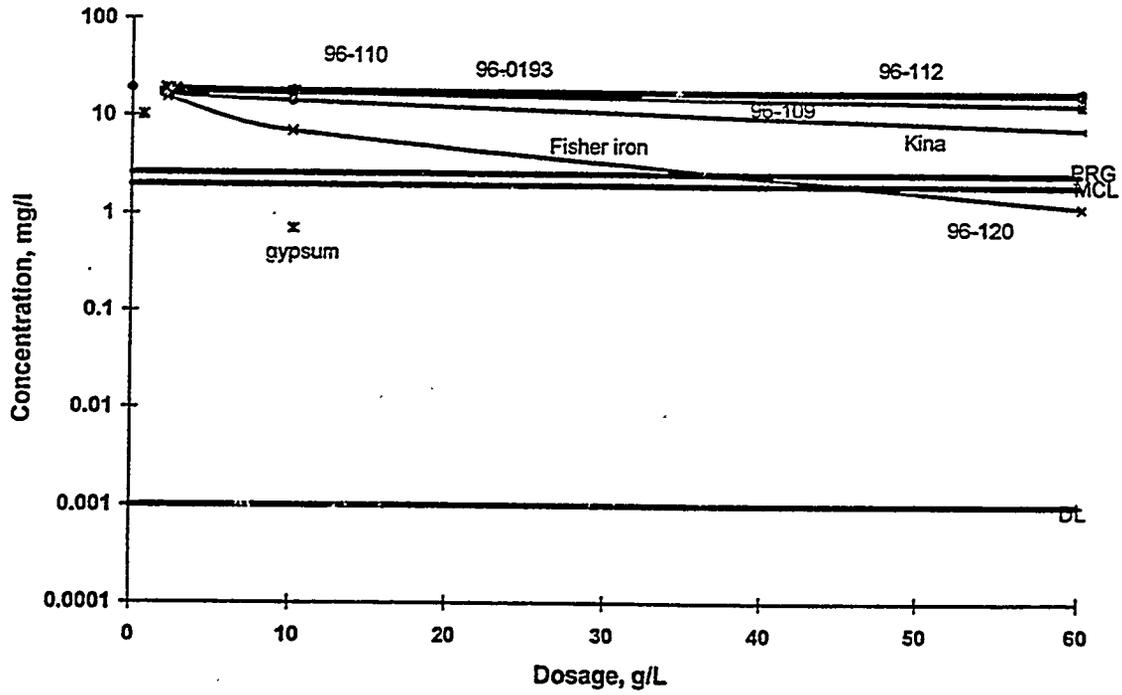


Fig. 4. Removal of Barium from NT-1 water.

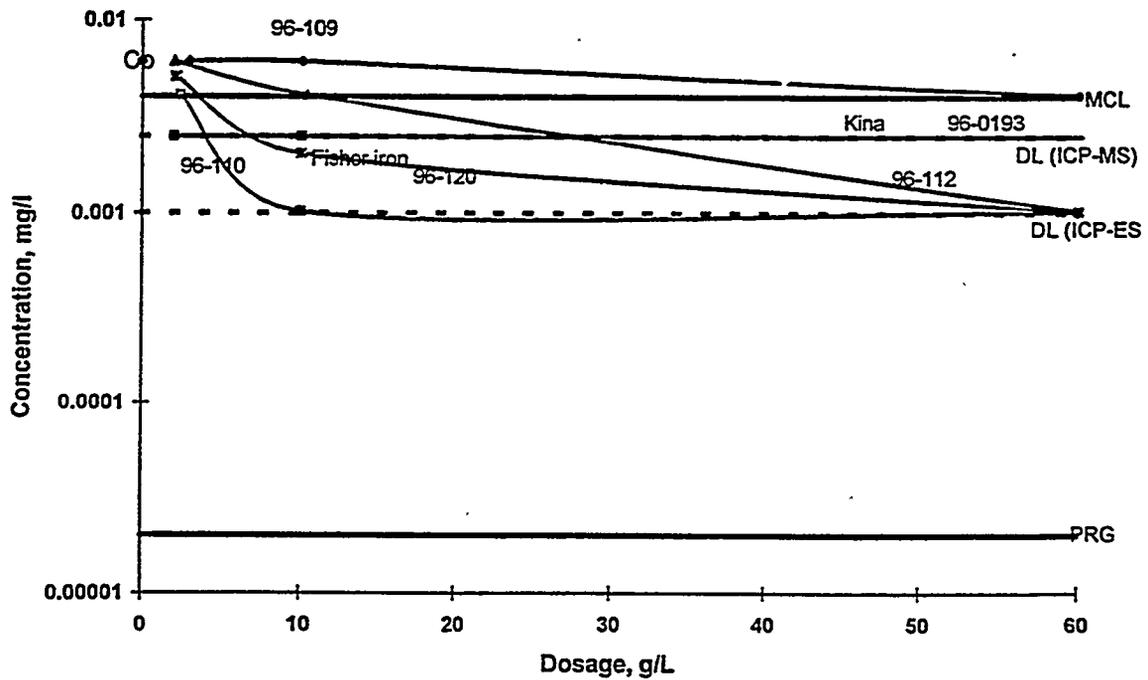
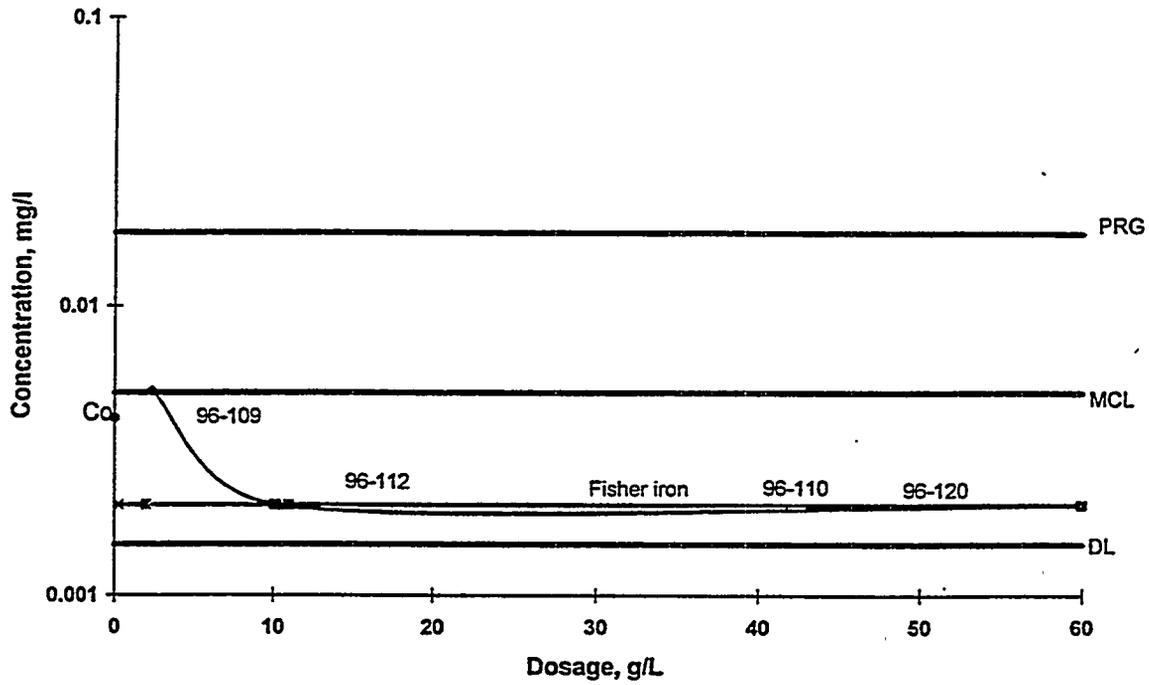


Fig. 5. Removal of Beryllium from NT-1 water.

REMOVAL OF Cd FROM WELL 087 WATER



8/27/96

REMOVAL OF Cd FROM NT-1 WATER

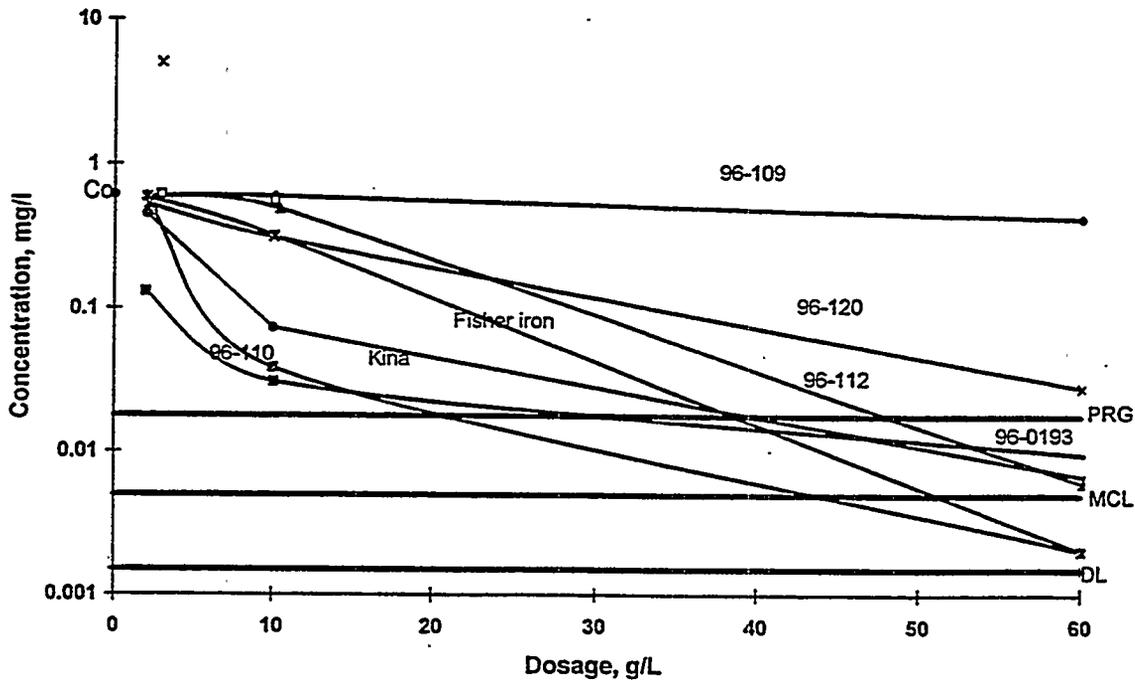
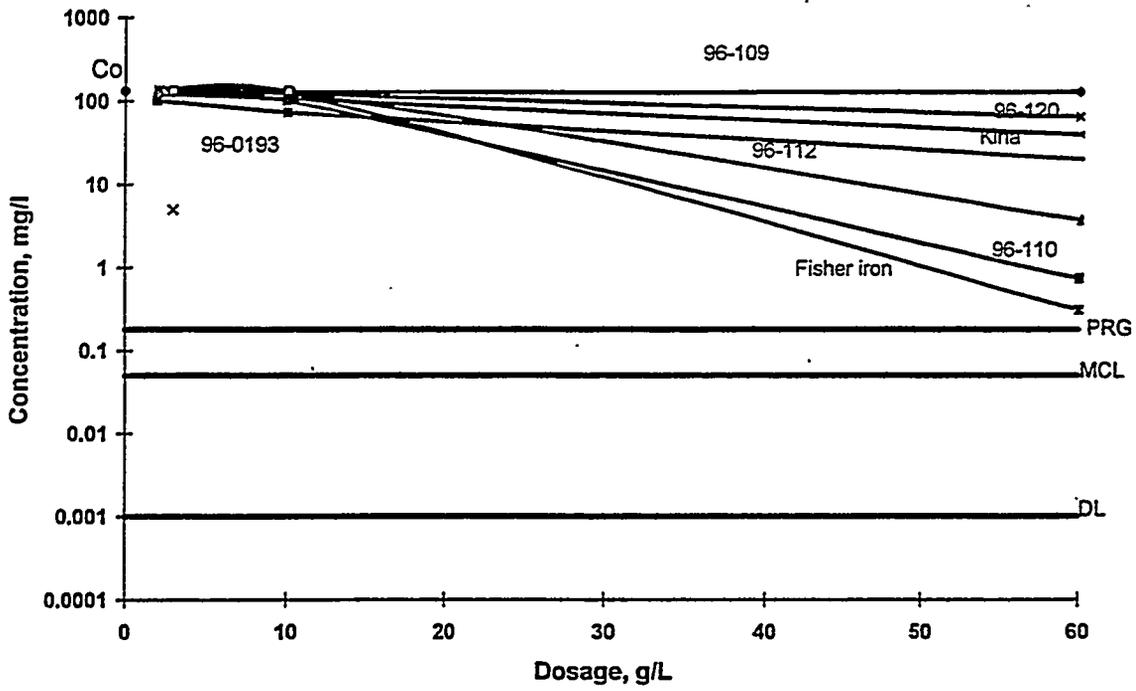


Fig. 6. Removal of Cd from Y-12 Waters.

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REMOVAL OF Mn FROM NT-1 WATER



8/27/96

REMOVAL OF Mn FROM WELL 087 WATER

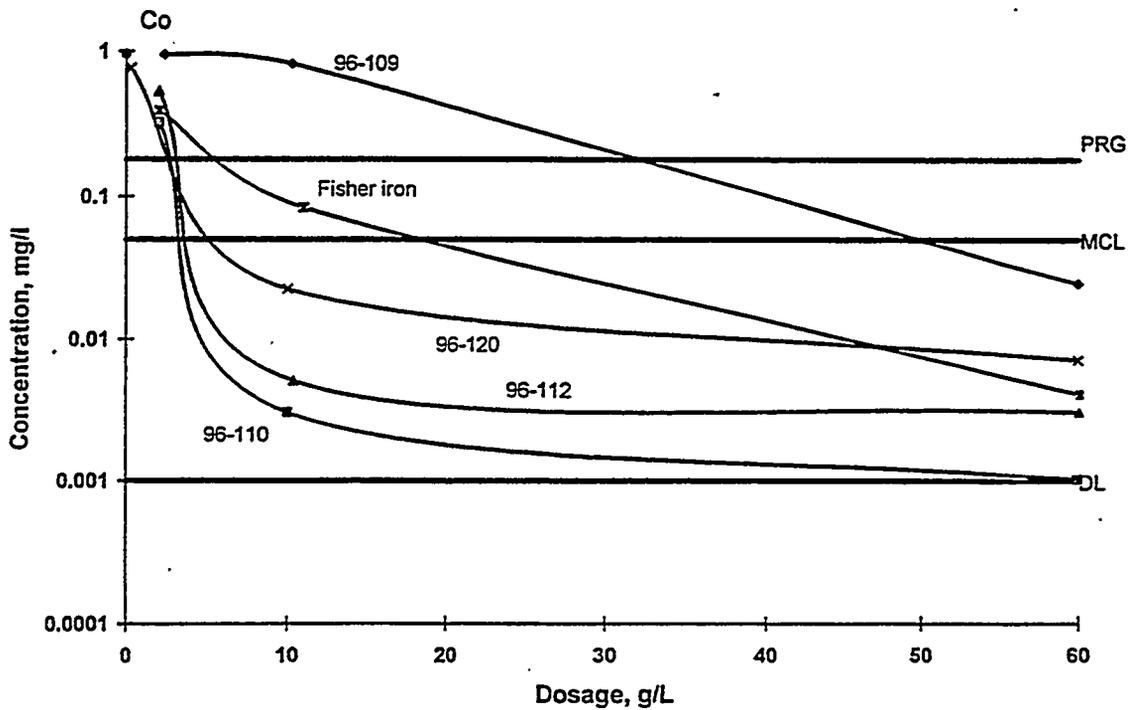
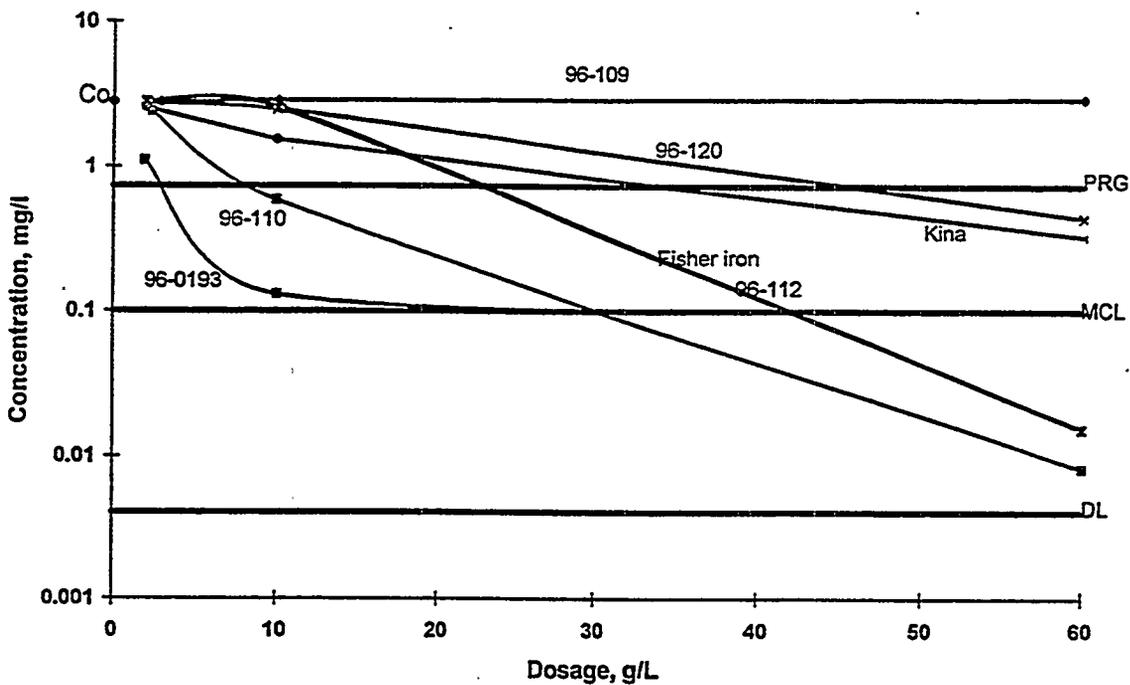


Fig. 7. Removal of Mn from Y-12 waters.

REMOVAL OF Ni FROM NT-1 WATER



Note: The results from all of the samples treated with Fisher iron were below the detection limit.

8/27/96

REMOVAL OF Ni FROM WELL 087 WATER

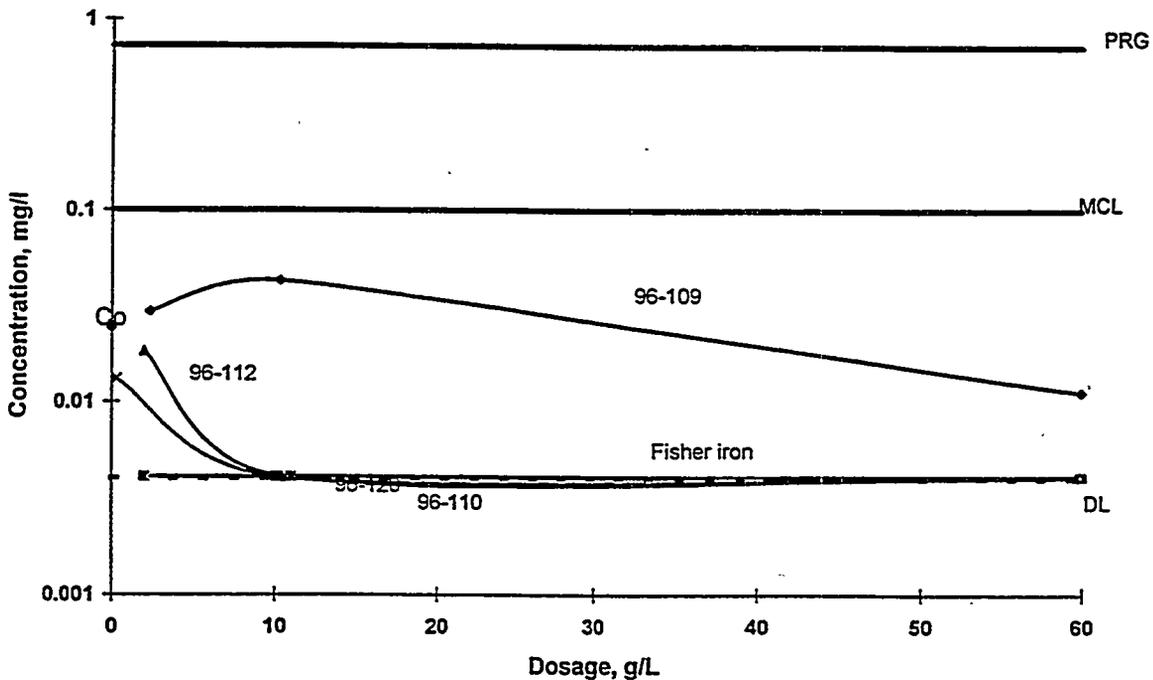
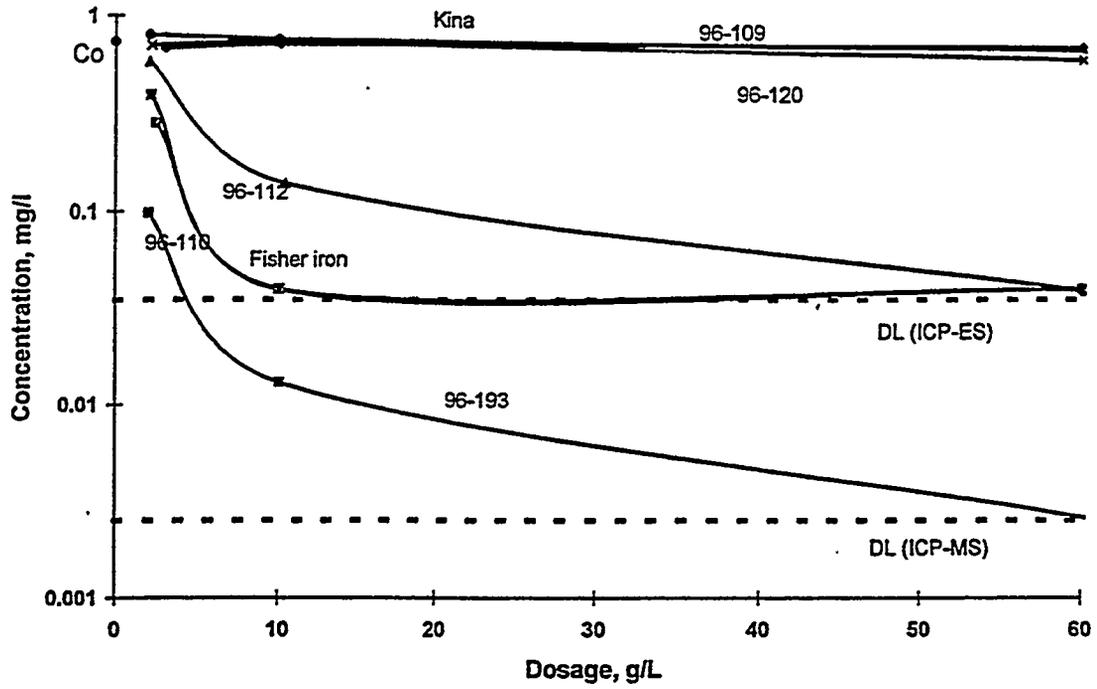


Fig. 8. Removal of Ni from Y-12 waters.

REMOVAL OF SPIKED U FROM NT-1 WATER



REMOVAL OF SPIKED U FROM WELL 087 WATER

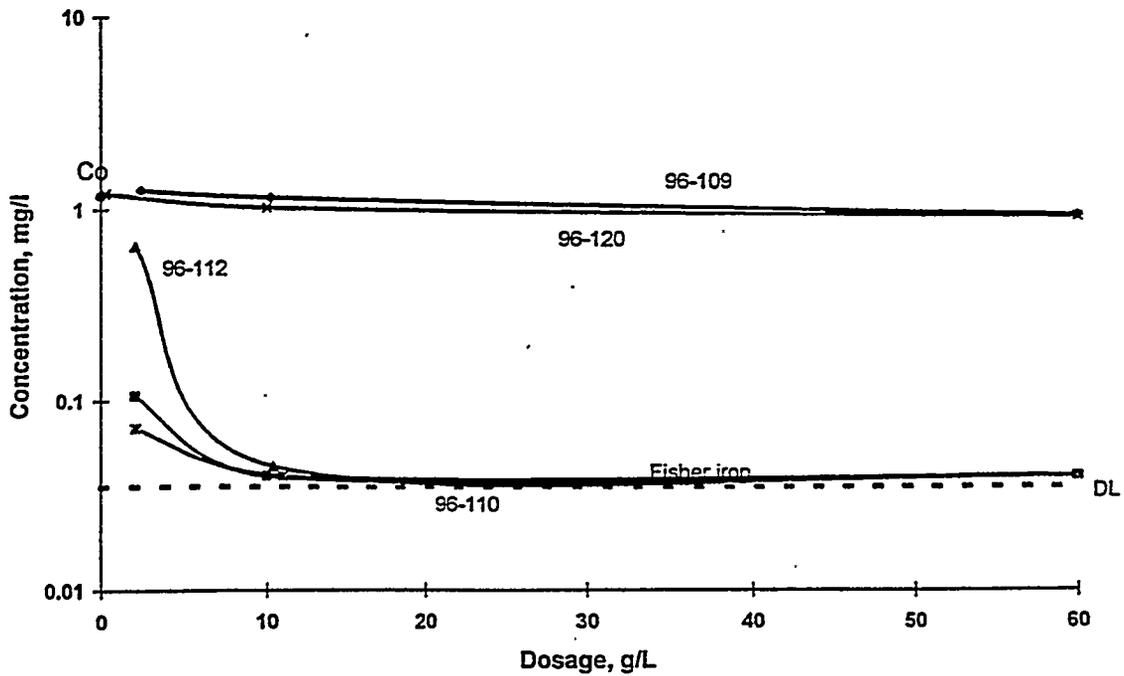
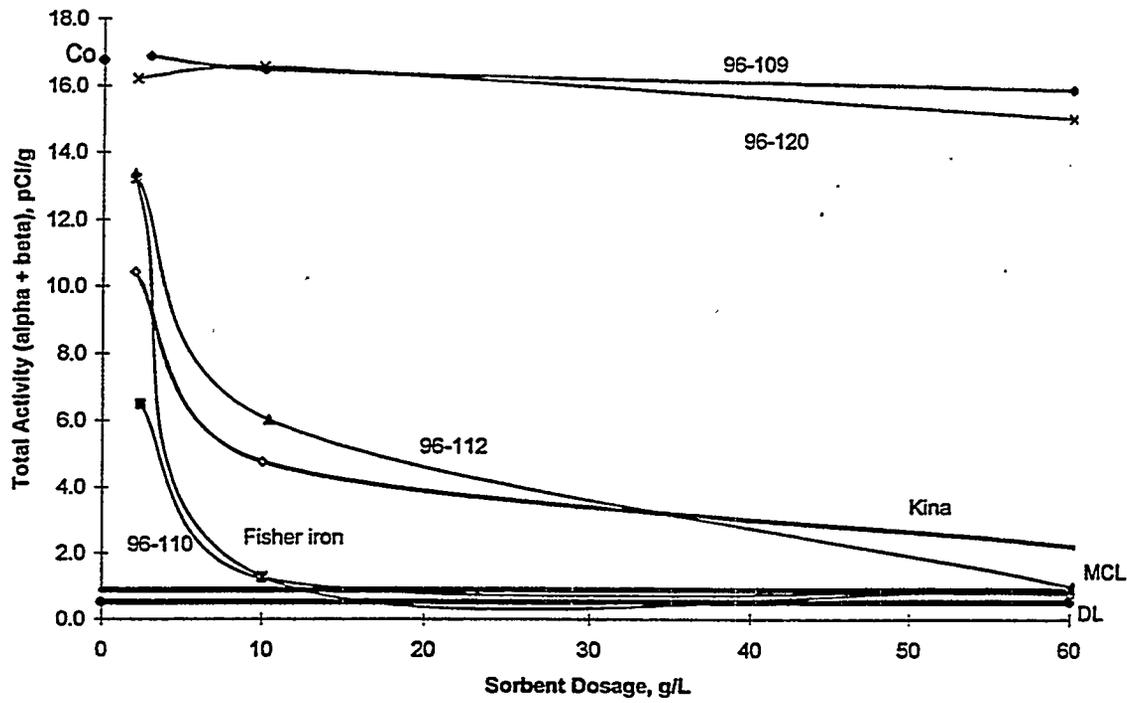


Fig. 9. Removal of spiked U from Y-12 waters.

REMOVAL OF RADIOACTIVITY FROM NT-1 WATER



8/27/96

REMOVAL OF RADIOACTIVITY FROM WELL 087 WATER

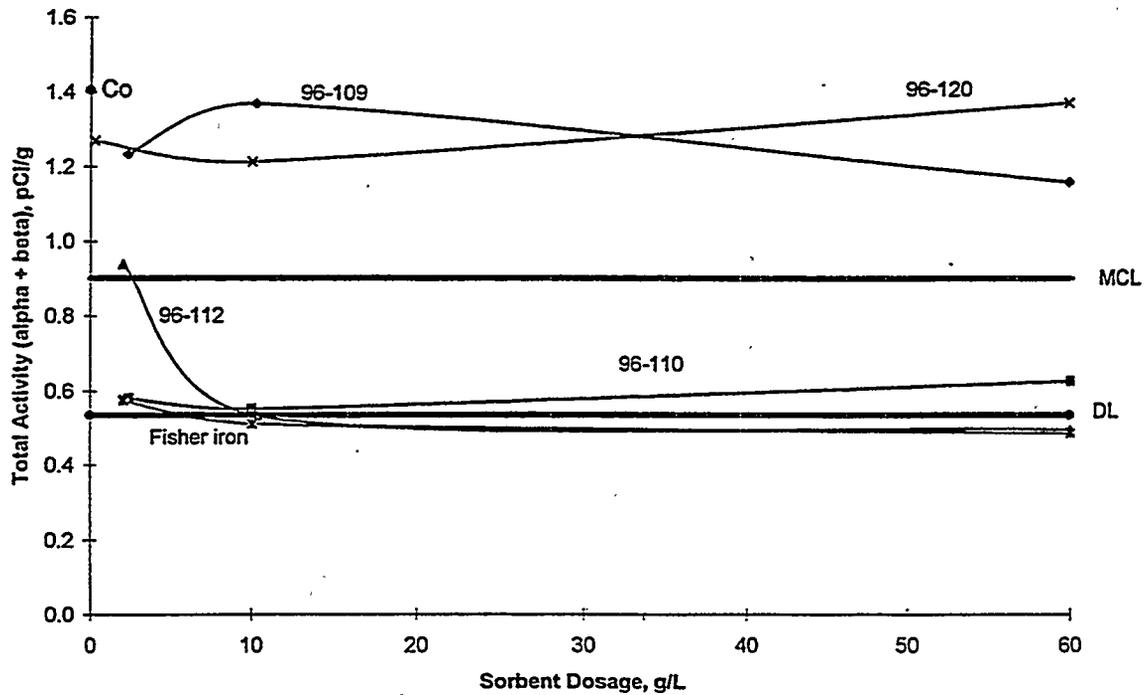


Fig. 10. Removal of radioactivity from Y-12 waters.

migration by precipitation as BaSO_4 (residual soluble Ba ~ 0.7 mg/L). In the NT-1 water (batch 2), addition of excess gypsum increased the Ca concentration from ~ 1800 mg/L to a value of ~ 2400 mg/L; this is an increase of ~ 15 mmol/L, in good agreement with the solubility of gypsum in water. This consumption of gypsum is equivalent to ~ 20 lb/1,000 gal treated.

4.1.4 Beryllium (Be) (Fig. 5; MCL = 0.004 mg/L)

Zero-valent iron products successfully remove Be, presumably by coprecipitation or sorption to ferric iron corrosion product or sorbent.

4.1.5 Cadmium (Cd) (Fig. 6; MCL = 0.005 mg/L, PRG = 0.018 mg/L)

Cadmium was not present at concentrations in excess of potential action levels in Well 087. Soluble cadmium in NT-1 water is removed by either zero-valent iron or sorbent containing iron oxide. This may be due to either reduction, precipitation, or sorption (EPRI RP2485-03).

4.1.6 Chromium (Cr) (MCL = 0.10 mg/L, PRG = 0.18 mg/L)

Chromium was not present at concentrations in excess of potential action levels in either water sample tested, therefore results are not illustrated.

4.1.7 Manganese (Mn) (Fig. 7; MCL = 0.05 mg/L; PRG = 0.18 mg/L)

Soluble manganese is removed by either zero-valent iron or sorbent containing iron oxide. However, the relatively high concentration of Mn in NT-1, relative to potential treatment goals, will require relatively high dosages of treatment material.

4.1.8 Mercury (Hg) (MCL = 0.002 mg/L, PRG = 0.011 mg/L)

Mercury was present at very low concentrations in the NT-1 water but was below the ICP detection limit in Well 087 water. Soluble mercury was readily removed by either zero-valent iron or sorbent containing iron oxide. Further investigations using mercury supplemented water are described in Section 5.1.

4.1.9 Nickel (Ni) (Fig. 8; MCL = 0.10 mg/L, PRG = 0.73 mg/L)

Soluble Ni in NT-1 water is removed by either zero-valent iron or sorbent containing iron oxide.

4.1.10 Uranium (U) (Fig. 9)

Uranium was not present in significant concentrations in the water samples as tested. For the data in Figs. 3–10, the water was supplemented with ~1 mg natural uranium per liter. Again, soluble uranium spiked into the water samples is removed by either zero-valent iron or sorbent containing iron oxide. Due to the interest in controlling off-site migration of uranium, we performed additional investigations and data interpretation, as described in section 5.2 of the report.

4.1.11 Total Radioactivity (Fig. 10)

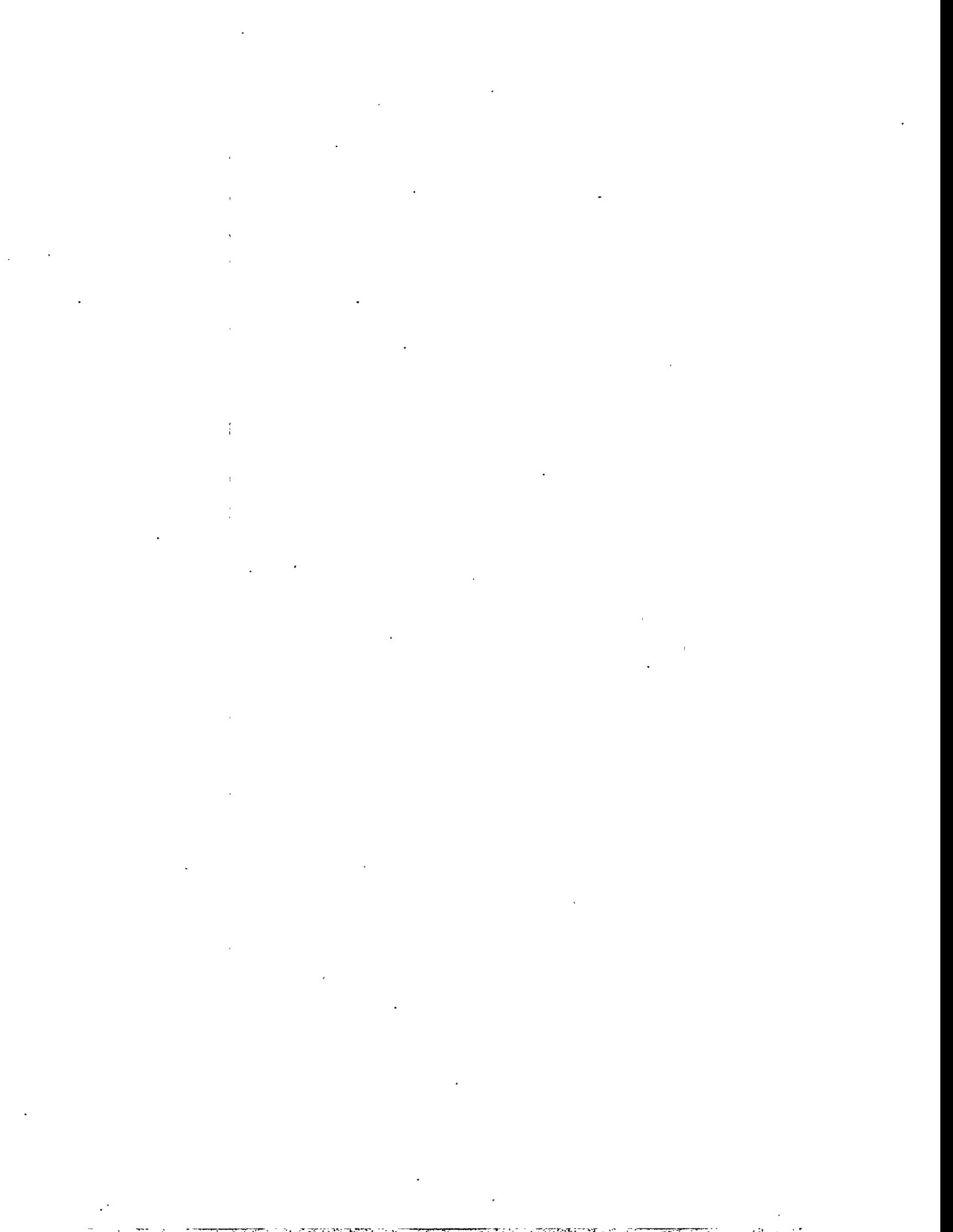
The total alpha and beta activity in solution was monitored using the Packard 2550 TR/AB liquid scintillation counter. Activity was dominated by the beta component, which in the NT-1 water is principally due to ^{99}Tc . For a remediation goal criterion, we selected the MCL value of 900 pCi/L total man-made beta activity (Bostick et al, K/TCD-1120). Of the inorganic materials tested, only those incorporating zero-valent iron were effective. Technetium in NT-1 water was removed by all zero-valent iron products, but the rate of removal was somewhat lower for the Cercona 112 iron aggregate. Literature reports indicate that magnetite and ferrous-iron minerals may remove soluble ^{99}Tc under

strictly anerobic conditions (Haines et al., 1987; Walton et al., 1986); however, we have found this effect to be minimal or at least kinetically slow in nitrogen-purged solution.

Activated carbon from various sources can sorb pertechnetate ion from aqueous solution (Ito and Yachidate, 1992). Gu and co-workers (1996) report that activated carbon is very effective in removing ^{99}Tc from contaminated groundwater. In Table 4, activated carbon (represented by Nucon Mersorb-3) is very effective for the removal of ^{99}Tc added to Well 087 water, as demonstrated by a large value for K_d . However, carbon is relatively ineffective for treatment of NT-1 water, or for Well 087 water supplemented to contain a nitrate ion concentration equivalent to that in the NT-1 water.

Table 4. Sorption of pertechnetate by Mersorb-3 granulated activated carbon (B.E.T. surface area = 767 m²/g)

Water System	Nitrate (mg/L)	Initial ^{99}Tc (pCi/L)	K_d (mL/g) at Nominal Carbon Dosage:		
			2.5 g/L	10.0 g/L	50 g/L
NT-1	12,400	22,500	433	417	377
Well 087 + ^{99}Tc	<1	34,600	38,400	10,700	10,000
Well 087 + ^{99}Tc + NaNO_3	12,400	35,600	382	342	256



5. FURTHER SCREENING STUDIES, WITH USE OF ISOTOPIC TRACERS

The sorption properties for mercury and uranium were further investigated by supplementing aliquots of Bear Creek Valley waters with a gamma-emitting isotopic tracer of the respective metal ion. This method allows relatively rapid and accurate determination of the fate of the metal over a wide range of concentrations.

In preliminary investigations, we assessed the effectiveness of selected solid reagents for the removal of soluble metal ion. The initial test solutions were ~1,000 mg U/L (in the form of natural uranyl nitrate solution) and ~5 mg Hg/L (in the form of ^{203}Hg -traced HgCl_2 spiked in Well 087 water). Results are summarized in Table 5. Removal of

Table 5. Preliminary testing of Cercona foam products[(bead form, -12/+20 mesh (nominal sorbent dosage ~1 mg/mL for U series, ~1.5-3.8 mg/mL for Hg series)]

Sample code	Description (Cercona)	Single-Point Kd (mL/g)	
		Uranium (1005 mg-U/L as Uranyl Nitrate)	Mercury (5mg-Hg/L as HgCl_2 , in Well 087 water)
MSD-96-109	Magnetite pellets	20	2,060
MSD-96-110	~98% Fe	290	107,000
MSD-96-111	Fe pellets, fired in 7% H_2	44	41,000
MSD-96-112	~98% Fe	47	72,000
MSD-96-113	~94% Fe oxide, balance aluminosilicate, unfired	28	8,000
MSD-96-114	~94% Fe, ~5% aluminosilicate, some carbon	42	92,000
MSD-96-115	~92% Fe	47	57,000
MSD-96-116	Fe foam aggregate	150	93,000
MSD-96-118	Zeolite + 20% FeOOH	34	6,900
MSD-96-119	Zeolite + ~50% iron	86	74,000
MSD-96-020	Zeolite + ~10% Fe pyrite	34	14,000
Iron filings	Fisher I-57, ~40 mesh	120	92,000
Fe_3O_4	Magnetite (Alfa Products)		740
FeOOH	Goethite (NOAH Chemicals)		830
Fe_2O_3	Hematite (Alfa Products)		320

uranium was relatively modest in this concentrated solution; however, media containing zero-valent iron (e.g., Fisher I-57, and ceramic foam or aggregates incorporating elemental iron) were relatively effective for the removal of either U(VI) or Hg(II), as judged by the criterion of a large computed value for conditional K_d at a relatively low reagent dose. The media containing zero-valent iron removed soluble mercury ($C_o = 5$ mg/L) to a residual level of ~ 0.035 mg/L, comparable to the solubility of liquid Hg^0 in water (0.02–0.03 mg/L at 20 °C; Bodek, 1988). In low ionic strength medium (Well 087 water), stable oxides of iron were also effective for the removal of soluble mercury, presumably by sorption or ion exchange.

5.1 SORPTION OF MERCURY

Multidosage testing of selected sorbents for removal of soluble mercury (traced with ^{203}Hg) is presented in Fig. 11 (for Well 087 water) and Fig. 12 (for NT-1 water).

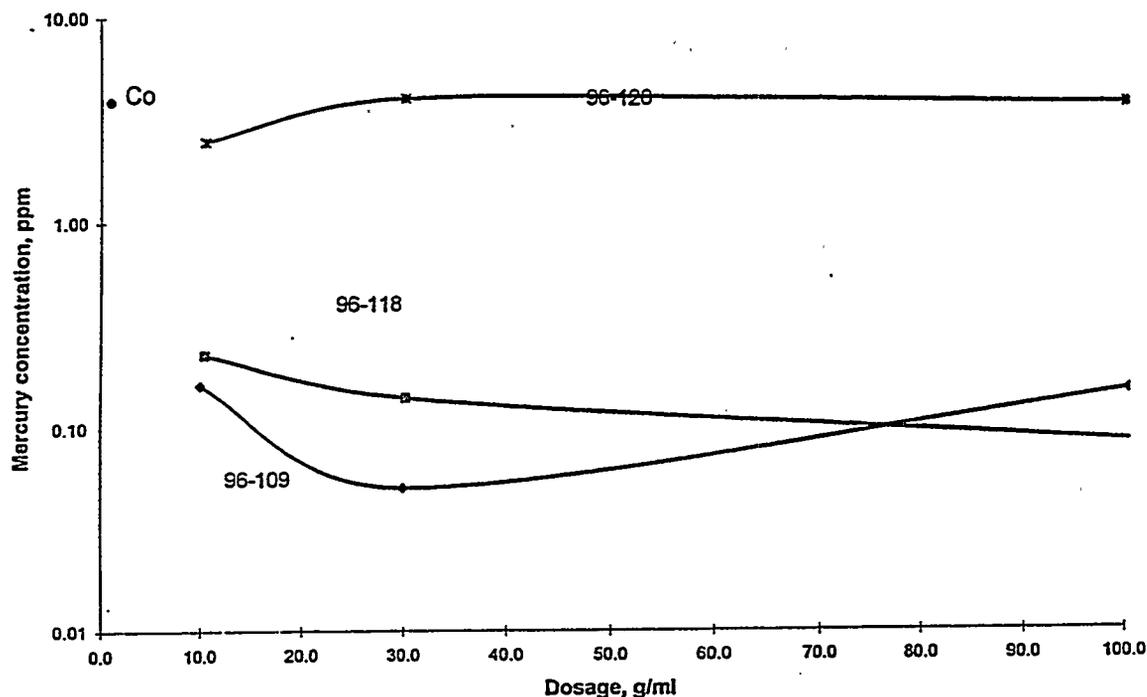


Fig. 11. Removal of Mercury from Well 087 water.

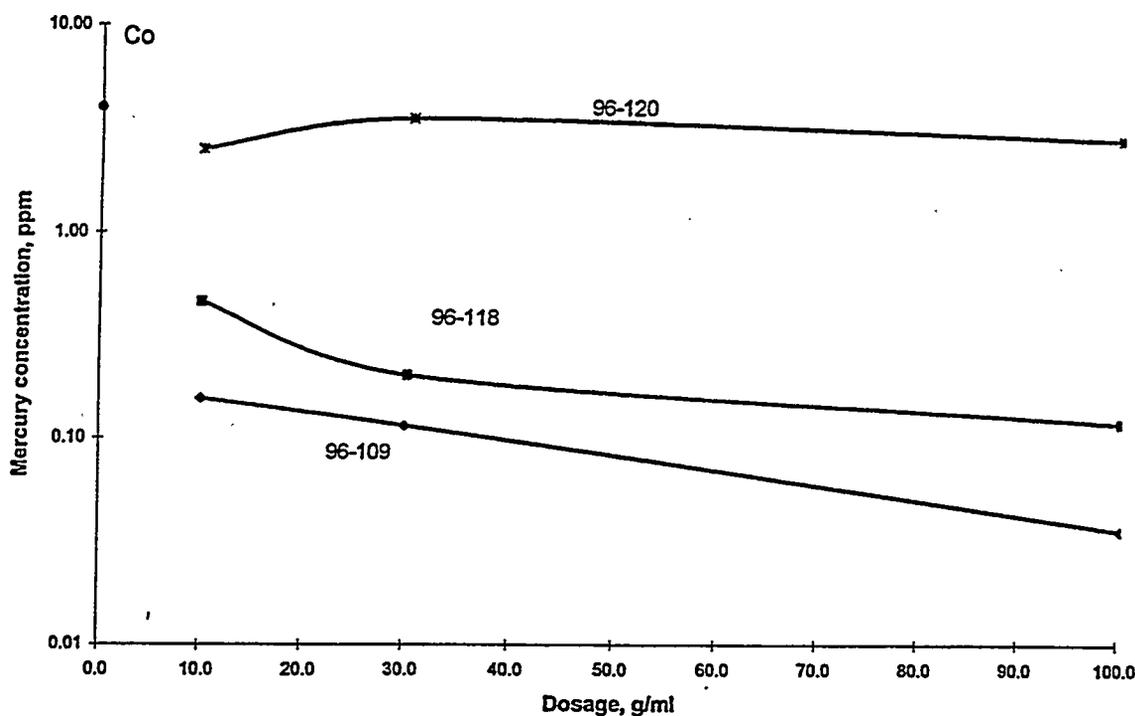


Fig. 12. Removal of Mercury from NT-1 water.

Pelletized iron oxides, especially magnetite (96-109) and goethite (96-118) were effective sorbents for soluble mercury in both water systems. Material 96-109 gave dose-dependent K_d values of $\sim 1,000$ – $2,500$ mL/g in these water systems.

5.2 SORPTION OF URANIUM

Cantrell et al. (1995) report that iron metal is especially effective for scavenging uranium from aqueous solution. The mechanism for this effect (i.e., reduction or sorption) was not established. Multidosage testing of selected solid reagents for removal of soluble uranium ($C_0 \sim 8$ mg/L, traced with ^{233}U) is presented in Fig. 13 (for Well 087 water) and Fig. 14 (for NT-1 water).

Media containing zero-valent iron are shown to be particularly effective for removal of soluble uranium, with residual concentrations in the Well 087 water of less than 10 ng/mL (i.e., <10 ppb) at modest dosages. However, the value for the conditional K_d decreases, and the solution pH value increases (due to corrosion), at the higher dosages

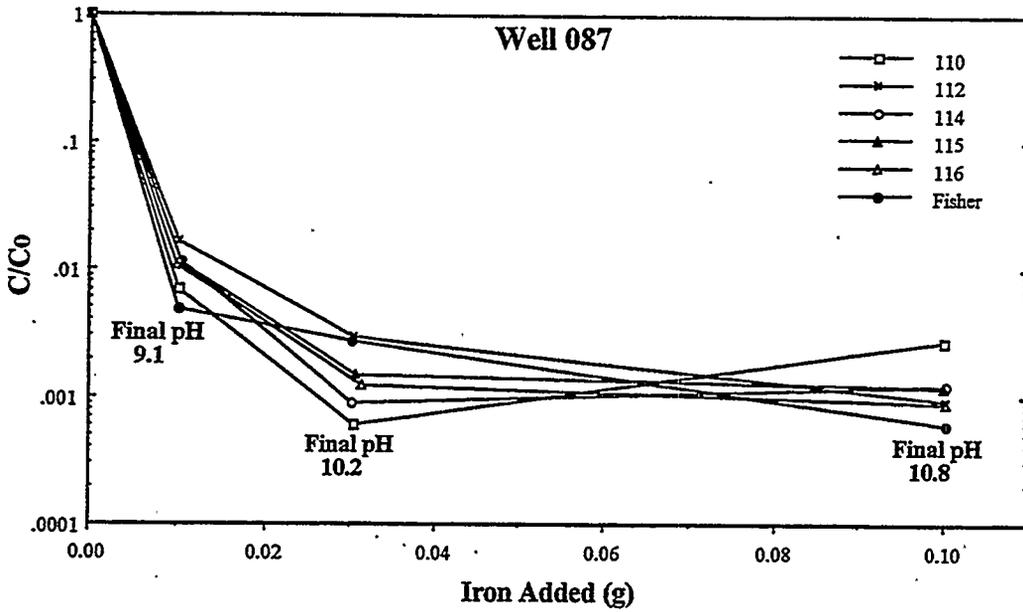


Fig. 13. Uranium removal by zero-valent iron products from 10 ml of ²³³U-spiked Well 087 water.

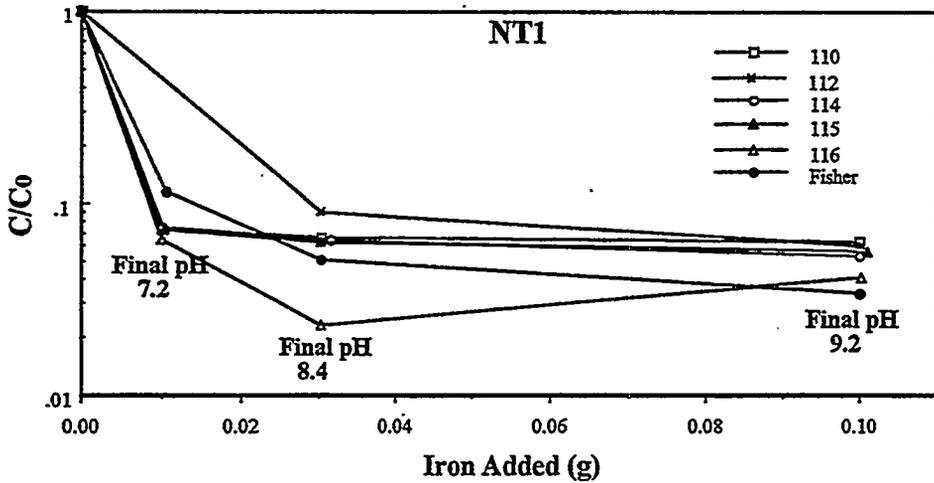


Fig. 14 Uranium removal by zero-valent iron products from 10 ml of ²³³U-spiked NT-1 water.

of iron reagent. These effects are illustrated in Fig. 15 for pelletized zero-valent iron (96-110) and a so-called bimetallic iron product (96-193). The latter product contains ~20 wt% high-silicon iron grit additive. These products were tested in as-received and pre-corroded condition. The pre-corroded ("pre-aged") condition was produced by presoaking the pellets in aerobic 0.1 mol/L NaNO_3 solution for 94 hours; the conditioned pellets were collected on a stainless steel sieve, rinsed with distilled water to remove loosely-adherent corrosion product, then rinsed with acetone and allowed to air-dry before use. The pellets and ^{233}U -traced NT-1 water ($C_0 = 6.9 \text{ mg-U/L}$) were contacted by shaking for 4 hours in sealed vials containing ~60 vol. % air headspace (i.e., aerobic conditions). As illustrated in Fig. 15, the iron products were similar in their ability to remove soluble uranium. Pre-corrosion of the pellets did not greatly affect uranium-removal performance, although removal of soluble uranium is somewhat lower for the pre-corroded material, at least for low solid-to-liquid ratios. In similar experiments, Bostick et al. (K/TCD-1120), showed that pre-aging ASTM A-518 high-silicon iron in nitrate medium greatly diminished the ability of this material to reduce Tc(VII). Fig. 16 illustrates the increase in solution pH value that occurs concurrently with the removal of soluble uranium.

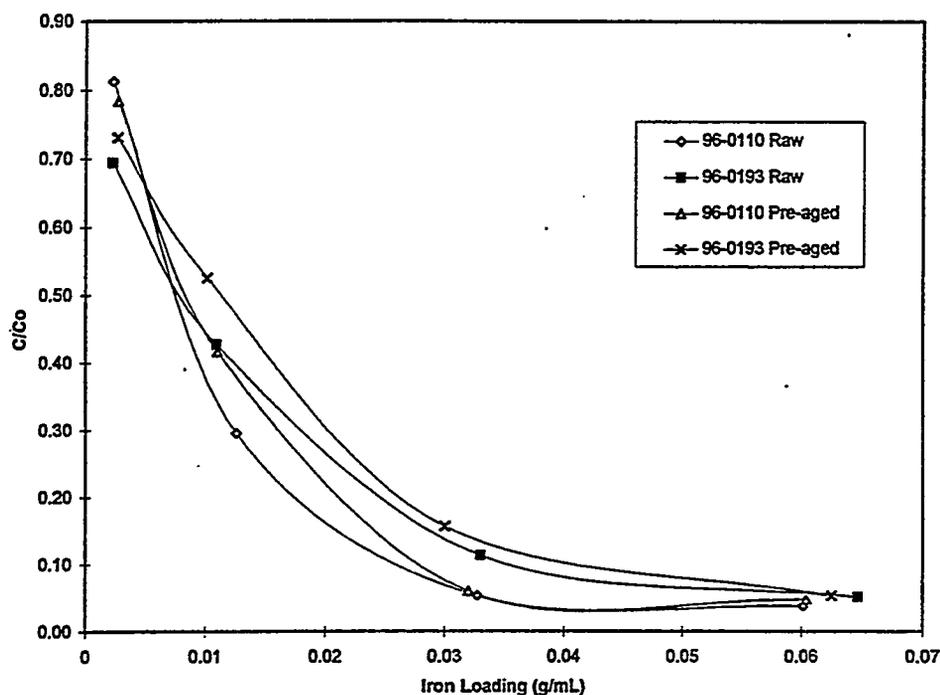


Fig. 15. Removal of soluble uranium ($C_0 = 6.9 \text{ mg-U/L}$) with use of as-received and pre-corroded iron products. See text for experimental detail.

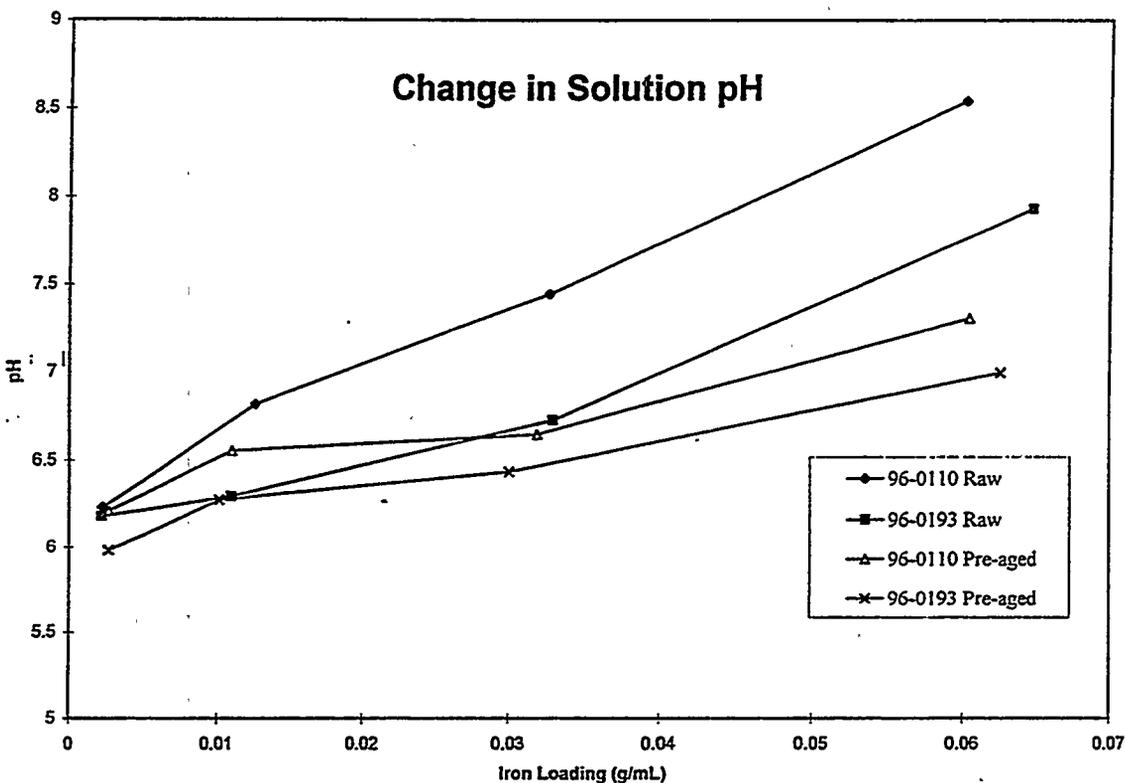


Fig. 16. Solution pH values after contacting test solution with iron products.

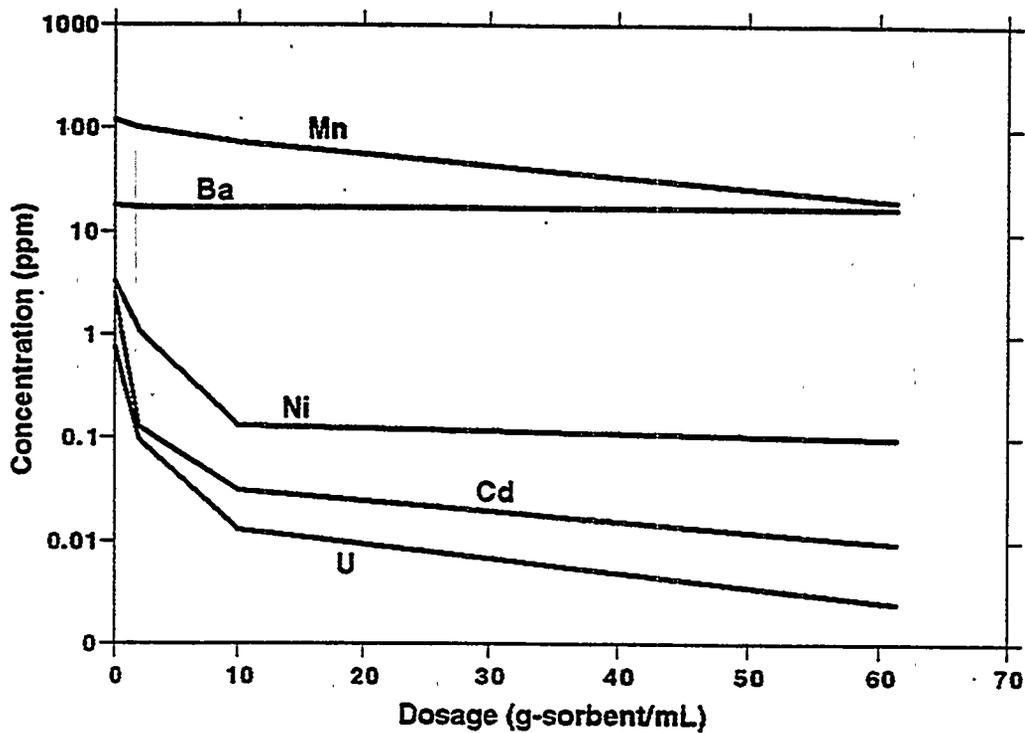


Fig. 17. Removal of metal ions in NT-1 water using Cercona bimetallic iron (96-193).

Pre-aging of the treatment media did appear to decrease the net corrosion rate somewhat, as evidenced by smaller pH excursions for a given solid-to-liquid ratio. The simultaneous removal of uranium and other priority metals from spiked NT-1 water, using as received 96-193, is illustrated in Fig. 17.

High surface area crystalline iron oxide media [hematite (Fe_2O_3), magnetite (Fe_3O_4), and goethite (FeOOH)], analogs to iron corrosion products, are shown to be effective sorbents for U(VI) in low-ionic strength Well 087 water. However, pelletized forms of the iron oxides [magnetite (96-109), goethite (96-118), and mixed oxides (96-113)] were significantly less effective than their fine-powder counterparts. This likely reflects a diminished accessible surface area for the pelletized material.

Figs. 13–15 indicate that, at a given dosage level, uranium was removed by all of the zero-valent iron products with near equal effectiveness. However, increasing the iron dosage did not substantially increase the amount of uranium removal. This is largely due to an increase in pH with increasing amounts of iron added, as indicated in Figs. 13, 14, and 16. High pH leads to the formation of an iron hydroxide film that passivates the iron surfaces and greatly reduces the reaction rate.

The rate of uranium removal by zero-valent iron can be characterized by the half-life of uranium in solution (i.e., the time required to reduce the dissolved uranium concentration to half of its initial value. Assuming a first order removal mechanism (i.e., the rate of removal is proportional to the amount in solution), the half-life for soluble uranium can be calculated from

$$t_{1/2} = \frac{\ln (1/2) * t}{\ln (C/C_0)} \quad (11)$$

where

$t_{1/2}$ = half-life,

t = elapsed reaction time,

C = solution concentration at time = t , and

C_0 = initial solution concentration.

The effect of surface passivation on the uranium removal rate by zero-valent iron is illustrated in Figs. 18 and 19 for the low dose iron samples in NT-1 water and Well 087 water, respectively. As shown in Fig. 20, the half-life for uranium measured during days 2–30 is more than a factor of 20 greater than the half-life measured over the first day of reaction. *This result indicates that treatment systems using zero-valent iron may decline in effectiveness over time due to passivation of the iron surfaces.*

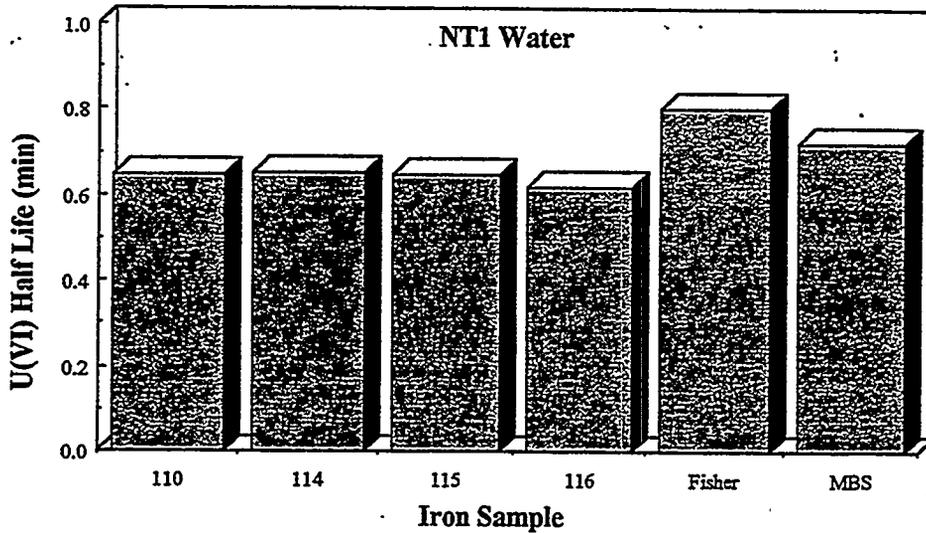


Fig. 18. Half-Life for uranium removal from solution by zero-valent iron products in NT-1 water.

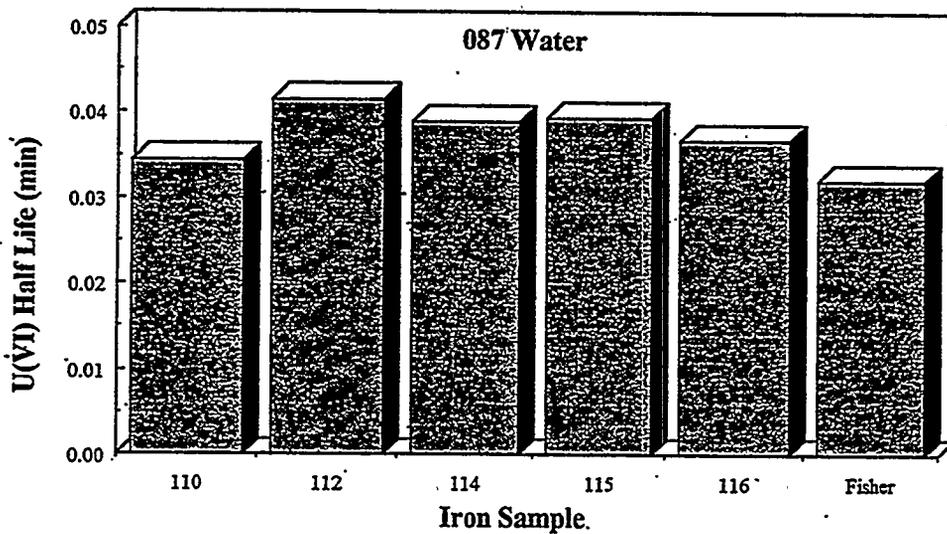


Fig. 19. Half-Life for uranium removal from solution by zero-valent iron products in Well 087 water.

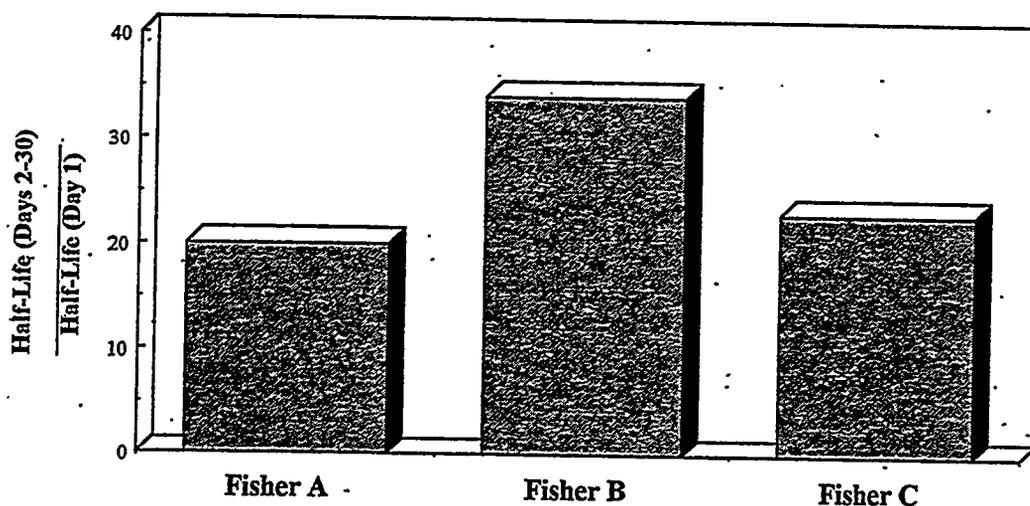


Fig. 20. Decline in uranium removal rate by Fisher iron due to surface passivation in NT-1 water.

Comparison of the uranium solution half-lives in Figs. 18 and 19 indicate that *removal of uranium by zero-valent iron occurs more rapidly in the more dilute Well 087 water compared to the higher ionic strength NT-1 water.* The effect of ionic strength on uranium removal rates was investigated in batch experiments in which a single iron coupon was placed in 500 ml of a de-aerated uranium solution. Fig. 21 compares rates of uranium removal in waters of differing composition and indicates that iron may lose its effectiveness for uranium removal in waters of high ionic strength. *This result indicates that treatment systems using zero-valent iron may be ineffective over the long-term in high ionic strength groundwaters.* The mechanism for removal of aqueous uranyl (UO_2^{+2}) species by zero-valent iron includes reduction to the sparingly soluble

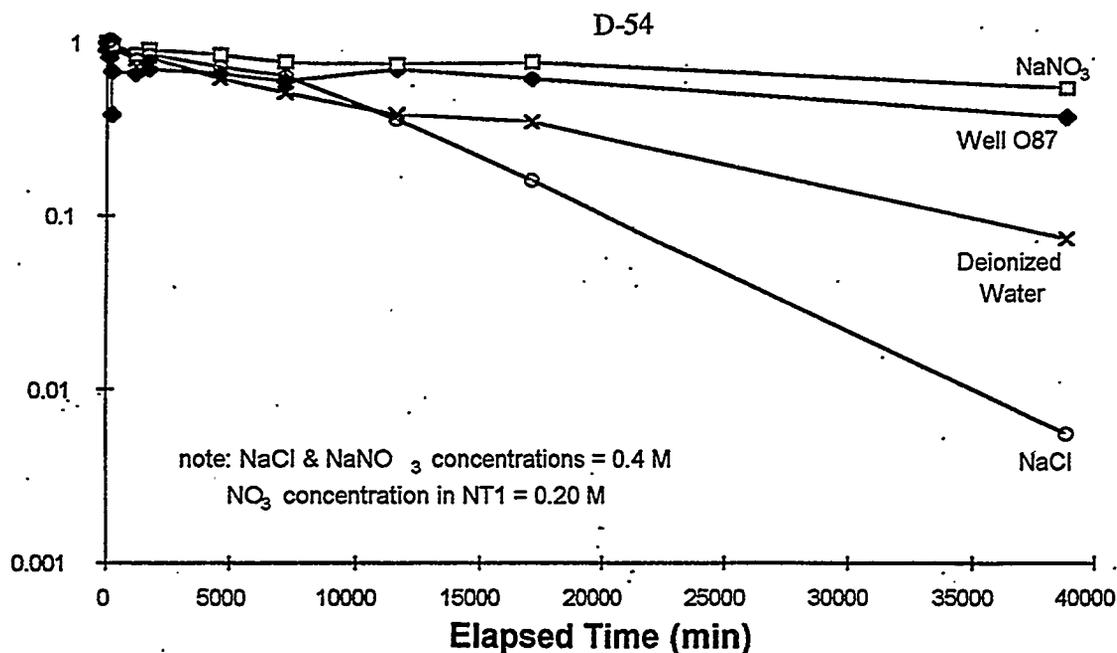


Fig. 21. Uranium removal by a single iron coupon in 500 ml of U^{233} spiked solutions of varying ionic strength under anaerobic conditions. The test solution contains an initial total U concentration of ~ 927 mg/L as uranyl nitrate.

uraninite (UO_2) species, adsorption of uranyl ion (UO_2^{+2}) onto iron corrosion products, and coprecipitation in either the U(IV) or U(VI) valence states with other redox active metals. Experiments with iron coupons in 1005 mg/L U(VI) solutions as uranyl nitrate indicated that the majority of the added uranyl ion was adsorbed onto the corrosion product slough after one day of reaction. When analyzed by scanning electron microscopy (SEM), the iron coupons were found to have a several micron (1–3 μm) thick uranium/iron oxide layer loosely adhered to the iron surface. Initial investigations on the valence state speciation of uranium bound to the iron surface, using X-ray photoelectron spectroscopy (XPS), suggested that the uranium had been reduced to U(IV); however, subsequent investigations have indicated that this was an instrumental artifact [i.e., the X-ray beam interacts with the iron coupon to induce the uranium reduction (Fiedor, unpublished results)]. Under the conditions of testing (using aerobic solution), sorption of U(VI) by the iron oxide corrosion product appears to be the predominant mechanism for the removal of soluble uranium. The adherent oxide layer may reduce the reactivity of the iron surfaces as the thickness of the layer builds. Fig. 18 indicates that the rate of uranium removal declines with time, even when the solution pH does not increase to values that would passivate the surface (cf. Fig. 1).

5.3 SORPTION EDGE PROFILES

Precipitated (oxy)hydroxides of metals such as iron, aluminum, and manganese—and many minerals containing these elements—are important reactive surfaces for the removal of inorganic contaminants from aqueous solution. For example, migration of U(VI) is greatly retarded by sorption to mineral phases in soil and sediment (Langmuir, 1978; Giblin et al., 1981; Koss, 1988; Maiti et al., 1989; Hakanen and Lindberg, 1992; Tricknor, 1994). Removal efficiencies for ^{203}Hg and ^{233}U from traced Bear Creek Valley groundwaters, as a function of solution pH, are presented in Figs. 22 and 23, respectively. The sorbent tested (at a nominal dosage of ~ 700 mg/L) is dried

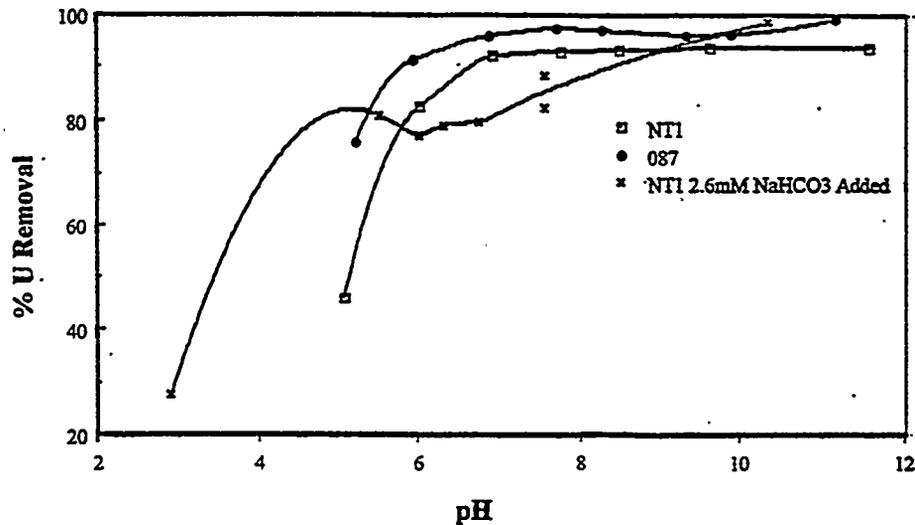


Fig. 22. Effect of pH and carbonate on uranium sorption by ferrihydrite.

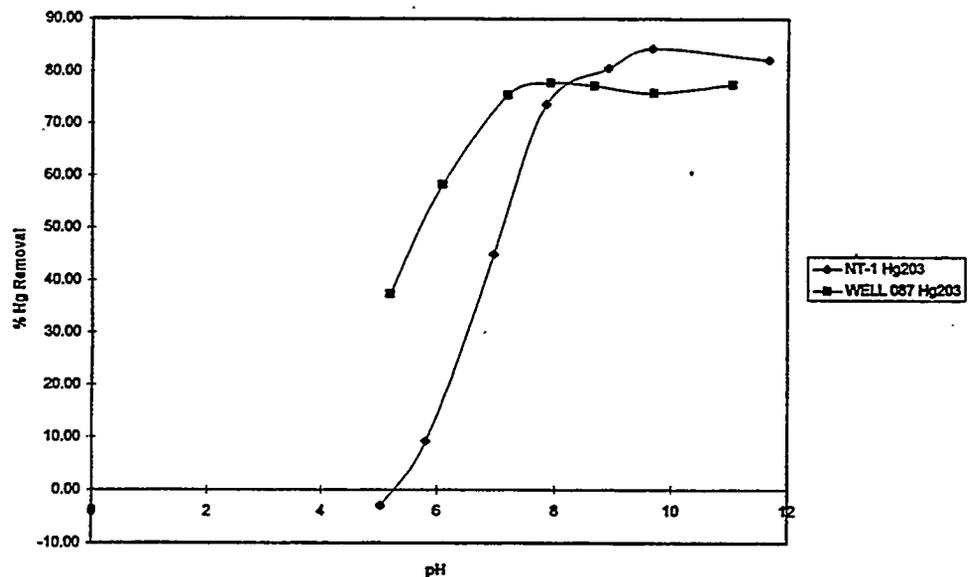


Fig. 23. Removal of mercury versus pH for NT-1 and Well 087.

hydrous ferric oxide (HFO), or ferrihydrate ($\text{Fe}(\text{OH})_3 \cdot x\text{H}_2\text{O}$) prepared by hydrolysis of ferric chloride solution. This material (MSD-96-191), aged ~1.3 years when tested, is largely amorphous, with some crystalline hematite and poorly crystallized goethite components; it is used here to represent sloughed iron corrosion product. The sorption profiles with this material indicate that both uranium and mercury are effectively removed at elevated pH values. Similar sorption profiles for uranyl ion on ferric oxyhydroxides have been reported by Hsi and Langmuir (1985); these authors note that addition of bicarbonate ion to the test system results in formation of soluble anionic complexes (e.g., uranyl carbonate and hydroxy-carbonate species, with $\text{UO}_2(\text{CO}_3)_3^{4-}$ prevailing in more alkaline solution). Although ferrihydrate is above its pzc in alkaline waters (pzc ~8) (Giblin et al., 1981) and thus carries a net negative charge, negatively charged uranyl species readily adsorb onto ferrihydrate as shown in Fig. 22.

Addition of bicarbonate to the NT-1 water to replicate the natural alkalinity of the two groundwaters (~3 mmol/L bicarbonate) had only minor effects on uranyl adsorption; the sorption at lower pH values was improved somewhat, due to formation of strong anionic species. However, in the bicarbonate amended water, adsorption of uranyl carbonates [likely $\text{UO}_2(\text{CO}_3)_3^{4-}$] caused colloidal dispersion of the ferrihydrate in the high pH sample. At pH >10, the ferrihydrate floc remained suspended after several hours of quiescent settling. In contrast, the ferrihydrate readily settled to the bottom of the reaction vials in all other samples. *This result indicates that uranium may adhere to iron corrosion products and may be transported from the reaction zone in colloidal form.*

Uranium transport in colloidal form may be especially significant if aqueous uranyl species are removed from solution by coprecipitation with other redox active metals. Fig. 21 depicts data for an experiment in which an iron coupon was placed in anoxic ^{233}U -spiked NT-1 water. Although some uranium was removed from solution, the mechanism of removal was not reduction to uraninite. Instead, the uranium formed a yellow powder at the bottom of the bottle. XPS analysis indicates that this powder contains uranium in the U(VI) valence state. Because the water in this experiment was filtered prior to use, the settled particles are either iron corrosion products (however, in these anaerobic experiments minimal rusting of the iron coupons was observed), or other redox active metals precipitated by the reducing conditions generated by the iron coupon.

5.4 ADSORBENTS

The effectiveness of an adsorbent material for removing a particular species from solution is best characterized by the *packed bed capacity*. The packed bed capacity is the maximum loading of the adsorbent, expressed in the number of bed volumes which may be treated before the adsorbent is saturated with the adsorbate. This is not the breakthrough volume since the bed continues to adsorb after breakthrough until the bed capacity is reached. The packed bed capacity differs from the breakthrough volume due to both mass transfer kinetics and fluid mechanical dispersion.

The packed bed capacity is a function of the influent contaminant concentration, and may be calculated from isotherm parameters determined from batch experiments. In contrast, the breakthrough volume cannot be determined *a priori* from batch experiments since it depends on the flow rate (which affects mass transfer kinetics), the grain size distribution of the packing material, the homogeneity of the bed packing, and the viscosity of the fluid. The packed bed capacity (or retardation factor) may be determined from

$$R_f = \left[1 + K_d \frac{\rho_b}{\theta} \right] \quad (12)$$

where

R_f = [= maximum number of bed volumes which can be treated] [-],

ρ_b = packed bed density [= mass of dry adsorbent per empty bed volume] [g/ml],

θ = total void fraction of the packed bed [-], and

K_d = slope of the adsorption isotherm.

Adsorption isotherms on most of the adsorbents tested were nonlinear; thus, K_d values are a function of concentration. Therefore, as shown by Eqs. 8 and 12, the packed bed capacity will also be a function of concentration. In some instances, the adsorption isotherms increased with decreasing equilibrium concentration, as illustrated in Fig. 24 for uranium adsorption on crystalline magnetite. For this material, the bed capacity will decrease with increasing influent concentration.

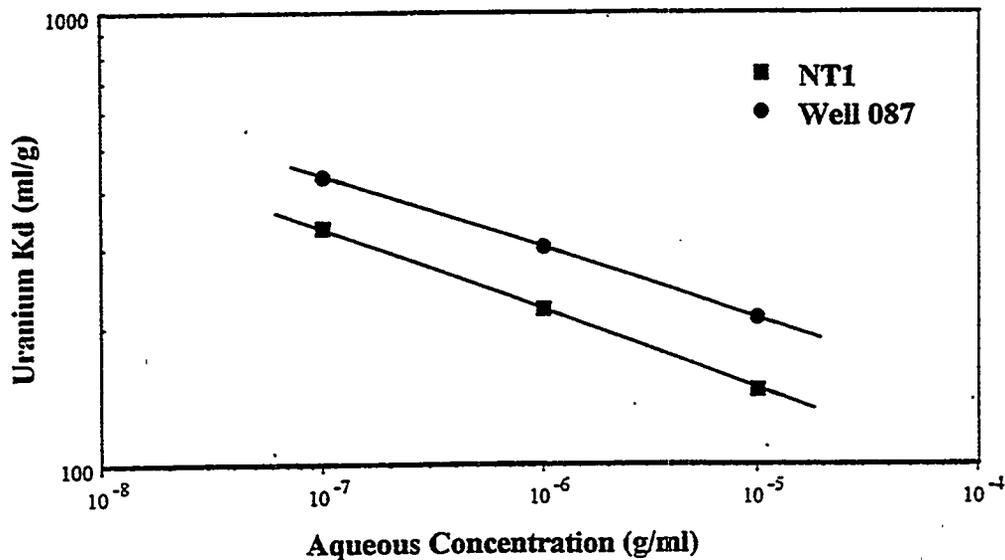


Fig. 24. Effect of equilibrium uranium concentration on apparent K_d for adsorption by crystalline magnetite in NT-1 and Well 087 waters.

The packed bed capacities presented in Figs. 25 and 26 were calculated using Eq. 10 with the parameter values listed in Table 6. The conditional K_d values listed in Table 6 were estimated at 1 mg/L aqueous uranium concentration from isotherms determined from batch testing. The isotherm parameters used to extrapolate the experimental data to 1 mg/L were based on least squares regressions to either the Freundlich or linear isotherm models. An estimate of 40% intergranular porosity was assumed for all materials except for the peat moss, where a porosity of 75% was used (McKay, 1996). The values for bed density were either measured, estimated based upon material similarities, or obtained from the literature.

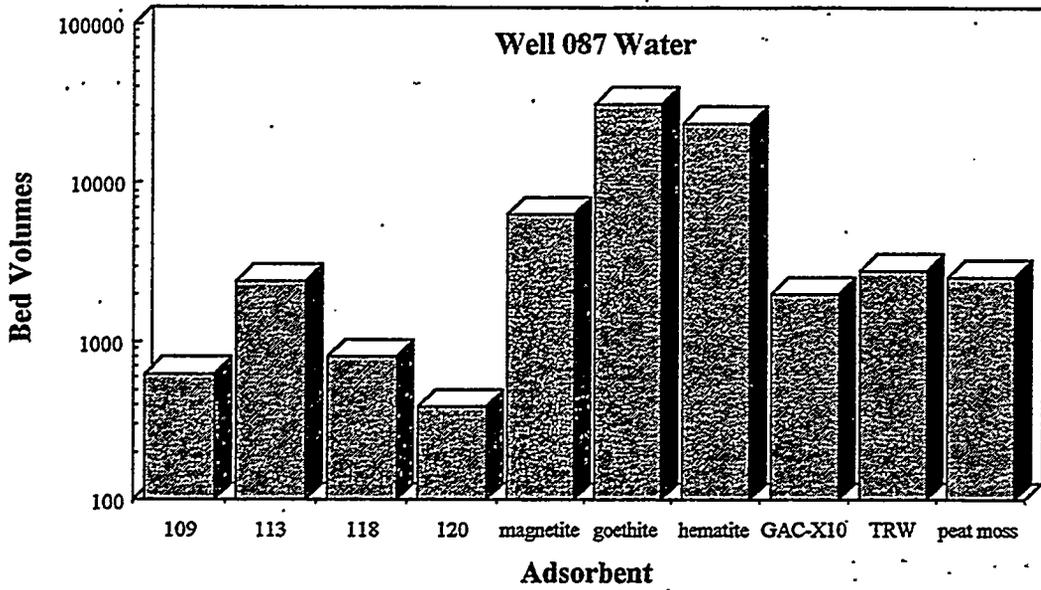


Fig. 25. Bed capacities for uranium adsorption in Well 087 water.

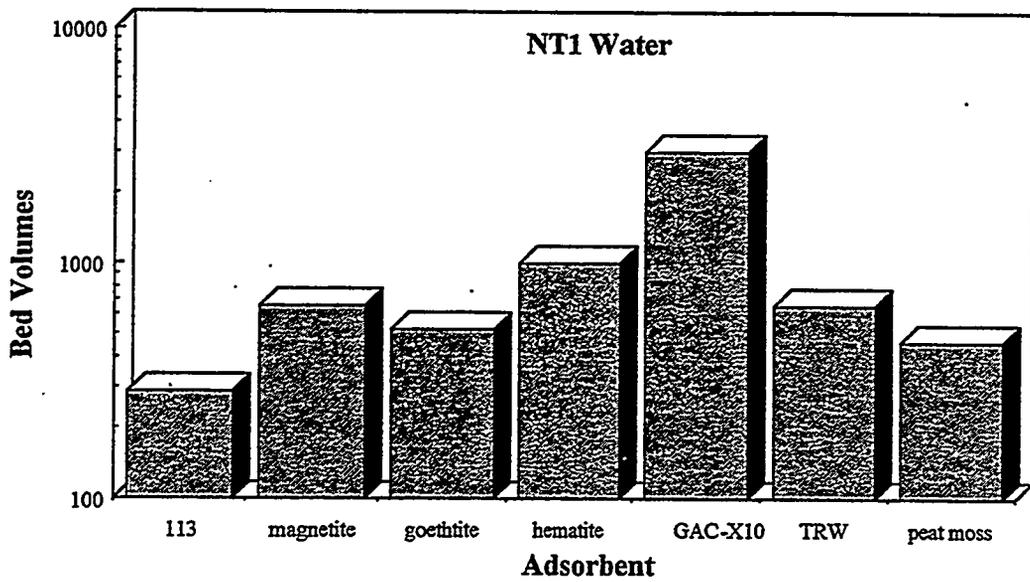


Fig. 26. Bed capacities for uranium adsorption in NT-1 water.

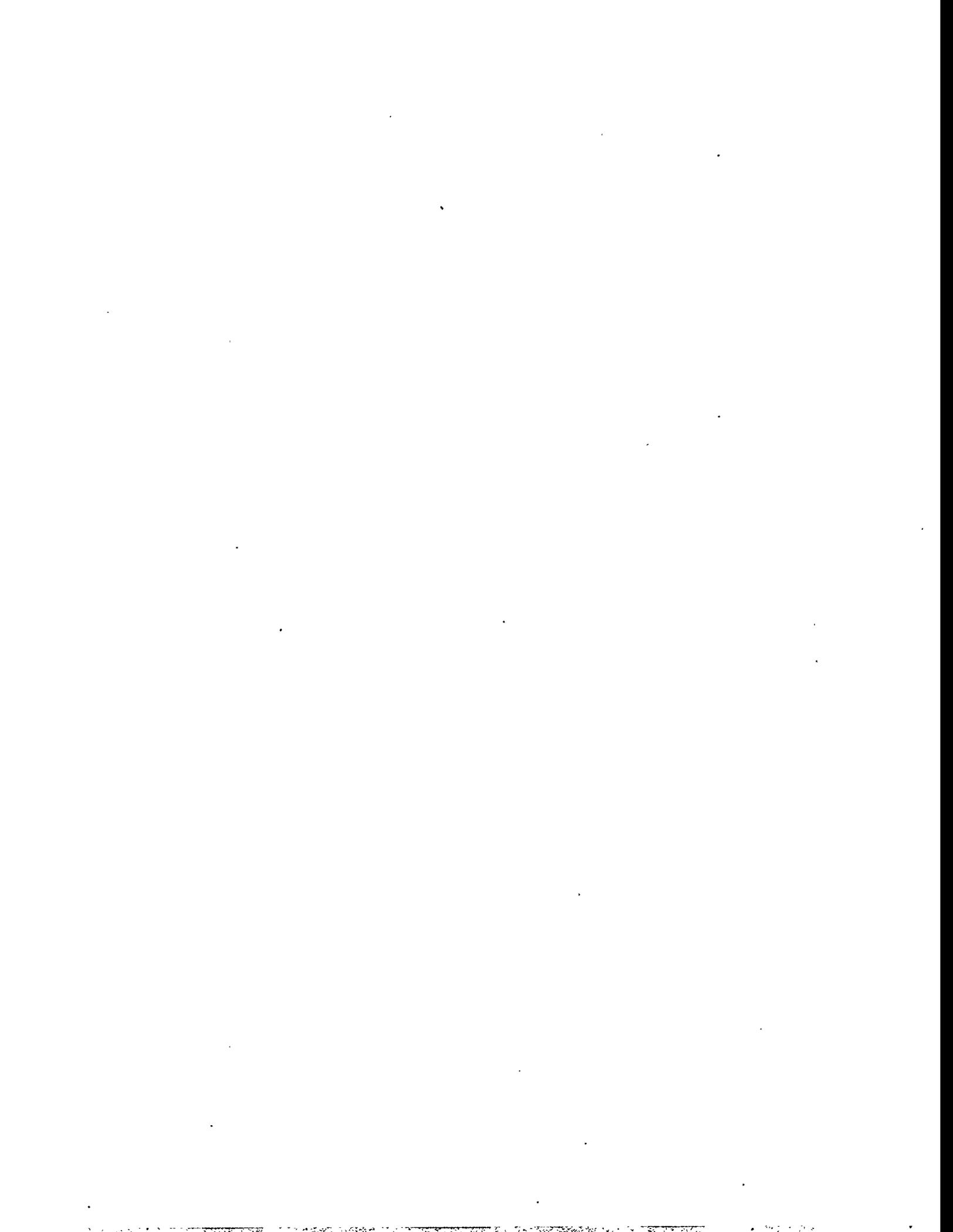
Table 6. Parameters used to evaluate bed capacities for uranium adsorption in Well 087 water

Adsorbent	K_d ml/g @ 1×10^{-6} g/ml	Bulk density (g/ml)	$\rho\theta$ (g/ml)	Retardation factor	Intergran porosity
109	29.2	1.36	3.4	100	0.4
175	55	1.36	3.4	188	0.4
Cercofoam	114	1.36	3.4	389	0.4
113	85	1.27	3.2	271	0.4
118	64	0.86	2.2	139	0.4
120	16.7	0.94	2.4	40	0.4
magnetite	324	1.2	3.0	973	0.4
goethite	1264	1.0	2.5	3161	0.4
hematite	953	1.0	2.5	2384	0.4
GAC-Mersorb	303	0.56	1.4	425	0.4
GAC X-10	1400	0.56	1.4	1961	0.4
TRW	2560	0.56	1.4	3585	0.4
Peat Moss	5000	0.22	0.3	1501	0.75

Table 7. Parameters used to evaluate bed capacities for uranium adsorption in NT-1 water

Adsorbent	K_d ml/g @ 1×10^{-6} g/ml	Bulk density (g/ml)	$\rho\theta$ (g/ml)	Retardation factor	Intergran porosity
113	90	1.9	4.7	420	0.4
Magnetite	221	1.9	4.7	1029	0.4
Goethite	210	1.5	3.9	810	0.4
Hematite	403	1.8	4.6	1851	0.4
GAC Mersorb	84	0.5	1.2	106	0.4
TRW	600	0.5	1.2	751	0.4
Peat Moss	900	0.22	0.3	271	0.75

Chapter 6 has been removed because of potentially patentable subject matter that is pending patent disclosure.



7. SUMMARY AND CONCLUSIONS

7.1 ZERO-VALENT IRON

- Zero-valent Iron is shown to be very effective for the removal of soluble radionuclides (TcO_4^- , UO_2^{+2}) and toxic metals from Bear Creek Valley waters. The following observations affect its utility.

7.2 REACTIVITY OF IRON IS COUPLED TO ITS CORROSION

- The corrosion process contributes electrons for reductive reactions, and iron-containing corrosion products for sorption.
- Corrosion by air is minimized under anaerobic conditions and at elevated pH values (i.e., $\text{pH} > 10$).

In batch testing, pH increases due to substrate corrosion, decreasing the effectiveness of the substrate. This decrease in reactivity (at pH values > 9.5) is likely due to surface passivation.

Batch-testing in a closed vessel allows the accumulation of the hydroxyl ion corrosion product (cf. text Eqs. 1 and 2); whereas, under favorable circumstances, it can be diluted and transported out of the reaction zone under conditions of dynamic flow.

- For soluble uranyl ion, a principle contaminant of potential concern, the predominant removal process appears to be sorption to iron corrosion products; transport of these sorbed products must be controlled.

At near-neutral and moderately alkaline pH values, the ferrous iron corrosion product may oxidize to ferric ion, hydrolyze, and be removed from solution by polymerization/flocculation and precipitation; this process is analogous to iron co-precipitation using ferric salts. Minimization of possible dispersion of metals sorbed on the floc may require a clear well or settling basin, or mechanical filtration. Secondary waste (sludge or filter medium) may be mixed hazardous and radiologically contaminated. If the

solution pH is allowed to exceed a value of ~10 in high nitrate medium (such as NT-1 water), the floc may be destabilized and fail to settle, enhancing the possibility of metal transport as colloidal particulate.

7.3 STABLE IRON OXIDES AS SORBENTS

- Iron oxides are demonstrated to be effective sorbents for uranium and other metal contaminants, such as mercuric ion.
- The oxide material must be pelletized or foamed to be useful for water remediation.

Pelletized, foamed, or granular material is required to permit useful hydraulic conductivity in a packed bed or permeable reactive barrier. However, agglomeration of the oxide particles may severely decrease the available sorptive surface area, requiring the use of larger quantities of material in an engineered system. Theis et al. (1994) have similarly formed high surface area granular agglomerates (~0.5 mm diameter) of iron oxide (goethite, FeOOH), in a proprietary binder, and demonstrated the material for the removal of Cd and Cr from aqueous solution in batch reactors and packed columns. They report that batch testing consistently gave lower estimates for the total sorptive capacities than the dynamic flow estimates, which range from 1.1 mg/g for Cd to 3.3 mg/g for CrO₄. These loadings are modest, however, compared to the potential contaminant removal by cementation reaction; Bostick et al. (K/TSO-7) used steel wool under dynamic flow conditions to remove >1g soluble mercury (as mercuric ion in saline solution) per gram of original steel substrate before column breakthrough.

Either iron or iron oxide product would be suitable for use in the Well 087 system. The most effective use of zero-valent iron may be to intermix the medium with either an inert (e.g., sand) or reactive (e.g., pelletized iron oxide) matrix; this would allow separation of the individual iron particles, so that they would not cement together and plug flow (due to the volume increase from rust formation) and perhaps would allow for better dilution of the hydroxyl ion reaction product (minimizing the self-passivation of the iron substrate). This may also promote filtration or settling of the corrosion product fine particulate. The corrosion 'slough' has the potential to redisperse sorbed contaminant.

The pH increase that accompanies iron corrosion could potentially enhance the sorption of cationic contaminants on pelletized iron oxide medium.

The NT-1 system, with a higher concentration of total metals and nitrate ion, is a greater challenge, perhaps requiring the use of multiple approaches. For example, the stream could first be treated with stable iron oxide, configured in a retrievable form; this would remove the bulk of the heavy metal contaminants. Next, zero-valent iron could be used to remove residual heavy metals, including ^{99}Tc (which requires reduction); some halogenated organic compounds would also be treated, although these reactions are kinetically slow, compared to redox reactions. Barium is not appreciably removed by either iron or iron oxide, and may require the use of gypsum as a precipitating agent. Finally, the solution, detoxified by removal of heavy metals, could be treated with biological agents to reduce the high concentration of nitrate ion. This sequence of treatments would reduce the probability of loss of sorbed metals by colloidal iron corrosion product and would greatly reduce the water toxicity for biological treatment (and reduce the loading of toxic and radiologic metals in the biological treatment residuals).

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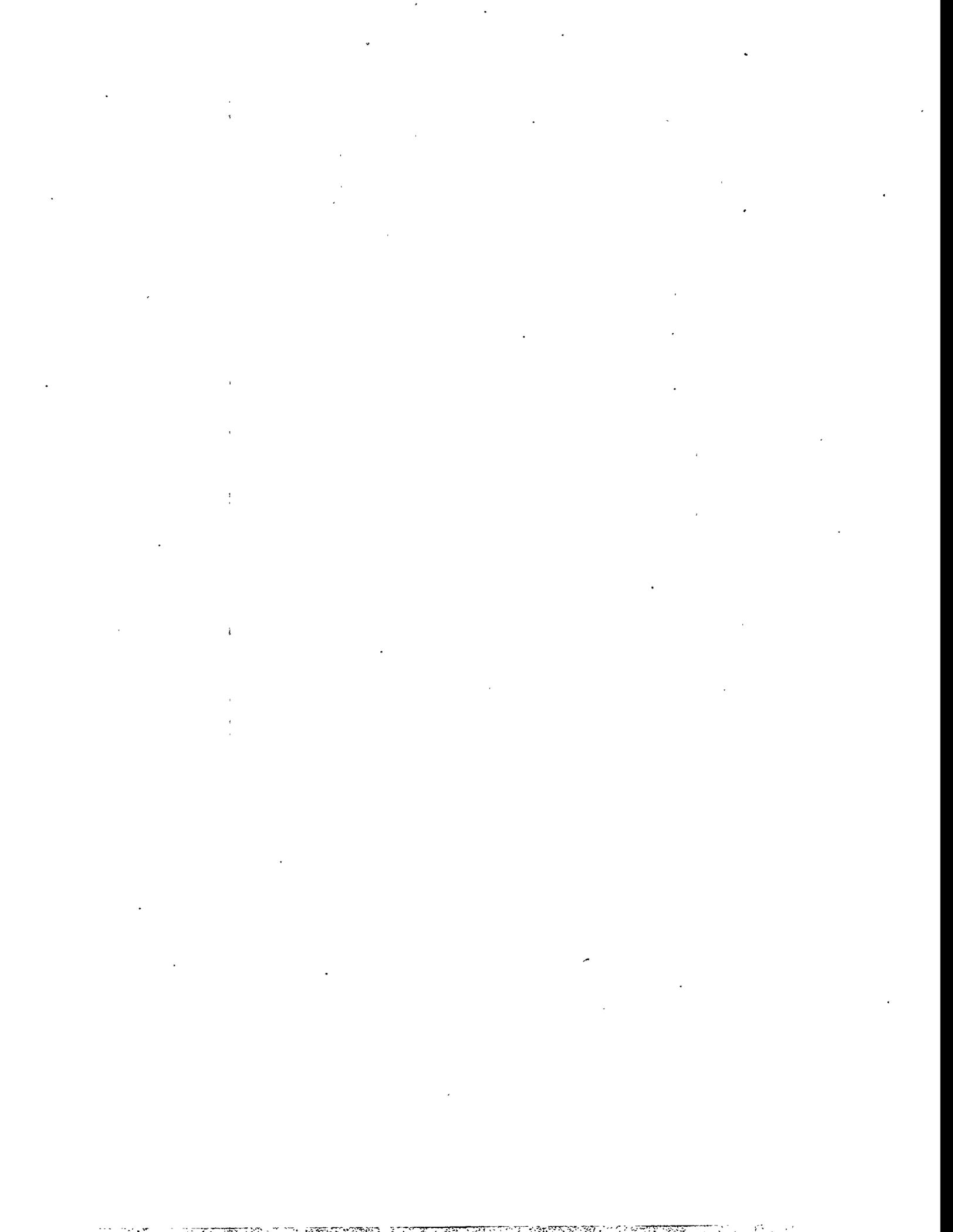
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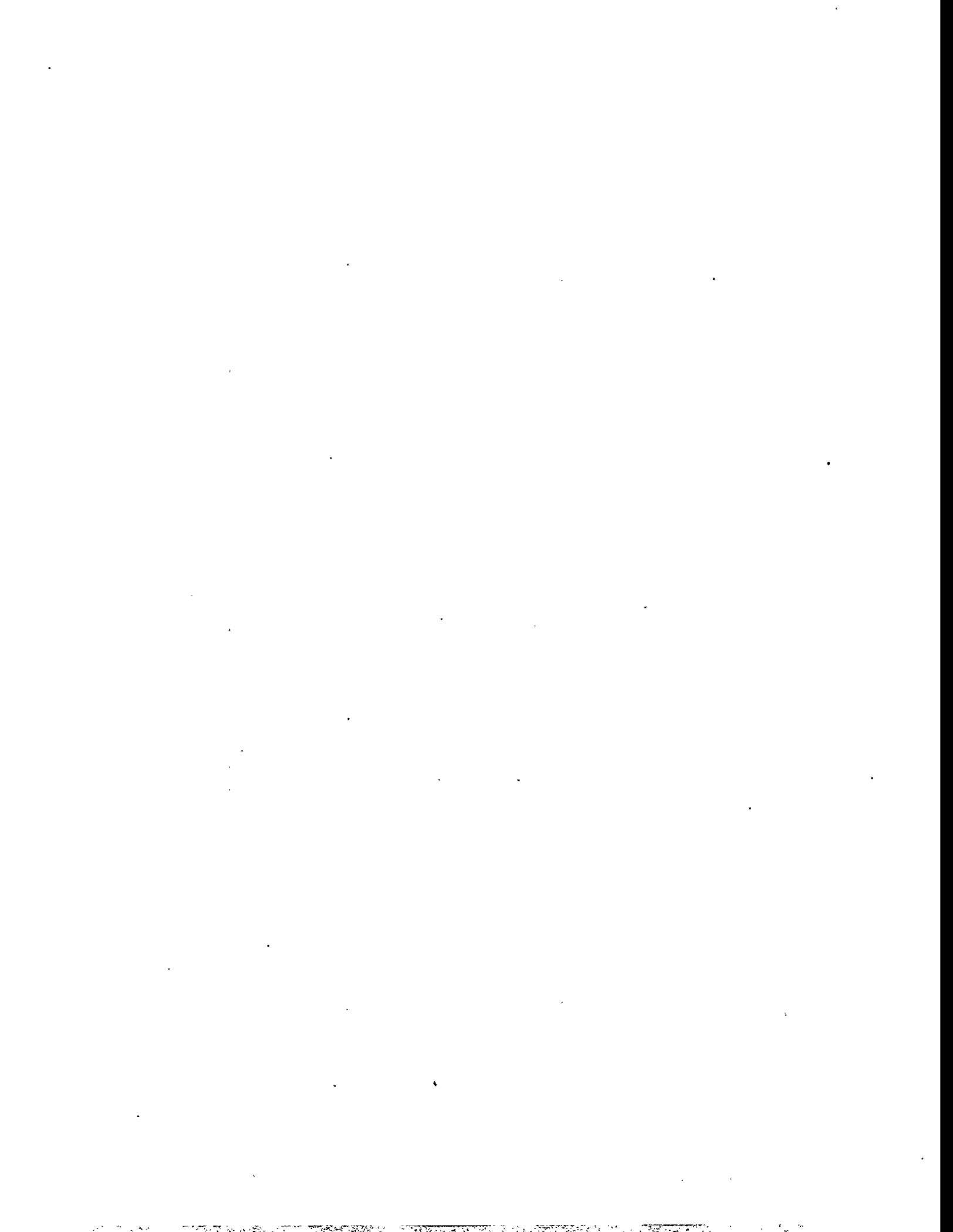
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APPENDIX E

**CONSTRUCTED WETLAND TECHNOLOGY FOR LOWERING
THE CONCENTRATIONS OF NITRATE AND URANIUM IN WATER**



Bear Creek Valley Characterization Area Technology Demonstration Project

**CONSTRUCTED WETLAND TECHNOLOGY FOR LOWERING
THE CONCENTRATIONS OF NITRATE AND URANIUM IN WATER**

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EXECUTIVE SUMMARY

Various studies have shown that microbial denitrification processes in wetlands can lower the concentrations of nitrate-nitrogen ($\text{NO}_3\text{-N}$) in water. Wetlands are also known to be excellent "sinks" for many metals, which may precipitate from solution in response to microbial changes in redox conditions. Because wetlands are essentially passive "solar powered" self-sustaining systems with diverse useful contaminant-removing or contaminant-transforming properties, properly engineered wetland systems might be developed to provide a cost-effective method for reducing the concentrations of nitrate and uranium in water. Our study explored this possibility.

Three replicate constructed wetland cells were deployed near SS-4, a nitrate- and uranium-contaminated tributary to Bear Creek, on the west end of the U.S. Department of Energy's Oak Ridge Y-12 Plant in Oak Ridge, Tennessee. Solar-powered pumps were used to supply each of these wetlands with water from this tributary, at a flow rate of approximately 200 mL per minute per wetland. Twice weekly for seven consecutive weeks, samples of water entering and exiting the wetlands were collected and analyzed for concentrations of $\text{NO}_3\text{-N}$, ammonium-N, and total uranium. We then imposed a "feeding" treatment on each wetland cell: a 2% mixture of corn-steep liquor was dripped steadily into the upstream end of each cell at a low flow rate by use of a simple gravity-flow system. This was done to encourage growth of subsurface microbes that could increase the rate of denitrification. Twice weekly for five consecutive weeks after organic matter addition had started, we collected samples of water entering and exiting the wetlands and analyzed them for $\text{NO}_3\text{-N}$, ammonium-N, and total uranium. On almost every sampling date, both before and after organic matter addition had started, water entering and exiting the wetlands was also analyzed for pH, conductivity, and water temperature. The results of these analyses were examined by analysis of variance (ANOVA), primarily to test for the effects of organic-matter addition. A preliminary mass-balance estimate of nitrogen (dissolved organic N and dissolved inorganic N species) was conducted near the end of the study to estimate overall efficacy of the wetlands for nitrogen removal.

The following findings are of significance. First, the solar-powered pump system operated reliably; however, the water lines between the stream and the pumps clogged frequently, requiring daily maintenance. Flow stoppages caused an inability to determine the mass of water treated at any given time. Second, most of the plant species that were put into the wetlands at the start of the study grew vigorously and appeared healthy. Third, $\text{NO}_3\text{-N}$ removal by the wetlands before organic-matter addition started was low (on average, about 2.8 mg/L, compared to an average concentration of 22.9 mg/L in the inflowing water). However, the apparent efficiency of nitrogen removal by the wetlands increased dramatically after organic-matter addition had started (to 16.85 mg/L, compared to an average concentration of 30.7 mg/L in the inflowing water). The mass-balance estimate for N indicated a loss rate of about 26% for all N entering the systems, probably primarily by denitrification. The mass-balance estimate also showed that the organic-matter mixture used to stimulate denitrification contained a significant amount of nitrogen. Thus, it is reasonable to suppose that use of an organic-matter mixture containing a higher ratio of carbon to nitrogen would further increase the rate of denitrification in a wetland environment. Fourth, the efficiency of uranium removal by the wetlands was moderately high, both before and after organic matter was added (46.3% and 31.3%, respectively). The mean delta (or upstream-to-downstream difference in concentration) for total uranium was 61.15 $\mu\text{g/L}$ before organic-matter addition started, and 49.6 $\mu\text{g/L}$ after organic-matter addition started. We noted only slight upstream-to-downstream effects on pH.

We conclude that constructed wetland systems could be built to significantly lower levels of nitrate and uranium in water from SS-4. Issues that might need to be addressed as this project moves to a field-scale demonstration include: (1) the potential effects of season (e.g., cold-weather periods) on processes that might reduce efficiency of $\text{NO}_3\text{-N}$ removal at some times of the year; (2) selection of a low-cost organic-matter supplement, with a low nitrogen content, to maximize rates of denitrification; and (3) a better understanding of processes that control the uptake and/or release of uranium from wetland substrates.

1. INTRODUCTION

Constructed wetlands can be designed to biodegrade or transform diverse organic and inorganic pollutants in wastewaters, including various forms of nitrogen (Gumpton, Isenhardt, and Fisher 1993; Sharma and Ahler 1990; Good and Patrick 1987; Watson et al. 1989; Kadlec and Knight 1996). We used a replicated system to test whether an engineered wetland system might be used to help lower the concentrations of nitrate-nitrogen and uranium in water that now enters Bear Creek via a north-flowing tributary referred to as SS-4.

2. MATERIALS AND METHODS

2.1 WETLAND SYSTEM DESIGN

The demonstration involved use of a system comprised of three wetland cells, plus a set of solar-powered peristaltic pumps to deliver water (see Fig. 1). Each wetland cell was 207 cm long, 52 cm deep, and 56 cm wide with a volume of approximately 600 litres; the cells contained pea-gravel (quartz stone; approximately 1 cm median diameter) to a depth of approximately 42 cm (range: 40.7 to 43.2 cm). A screen was placed vertically near the end of each cell to hold back the gravel substrate, thereby forming a small reservoir both at the upstream and downstream end of each cell. Each wetland cell drained from the bottom of the downstream end through a slotted 1.5-inch diameter polyvinyl chloride (PVC) pipe placed across the width of the trough. The height of the water within each cell was controlled by use of a standpipe fitted with a swivel union connection. During operation, the water level was about 2.5 cm beneath the surface of the gravel: thus, the systems were operated as subsurface flow "rock reed" wetlands.

Each wetland cell was initially planted with about 40 wetland plants belonging to six species. The species were: *Eleocharis* spp. (spike rush), *Glyceria striata* (nerve mannagrass), *Scirpus validus* (soft-stem bulrush), *Scirpus cyprinus* (wool grass), *Scirpus pungens* (common three-square), and *Sparganium eurycarpum* (giant bur-reed).

Three peristaltic pumps (Masterflex[®], with Quick-Load heads size 7021-22) were used to deliver water to the wetland cells directly from SS-4. The pumps were powered by eight 55-watt solar panels (1' by 4'; Siemens Model MC55) wired in parallel to a 12-volt, 30-amp photovoltaic controller (Morningstar model ProStar-30). Ten 12-volt deep-cycle marine batteries wired in parallel were connected to the battery-charger terminals on the controller. Each pump had a built-in rate-controller to regulate the pumping rate of water.

Water used to "feed" the wetlands was pumped from SS-4 to the upstream end of each cell at an average flow rate of 200 mL per minute. Water exiting the wetland cells was allowed to flow back to SS-4, downstream from where water was taken to "feed" the cells, by gravity through a garden hose. Based on the designed flow rate of 200 mL per minute, the average residence time of water in the wetland cells was 17.2 hours. Due to small differences in the amount of gravel in the cells, the residence times for the three cells varied slightly: it was 16.3 hours for Cell 1, 17.3 hours for Cell 2, and 18.1 hours for Cell 3.

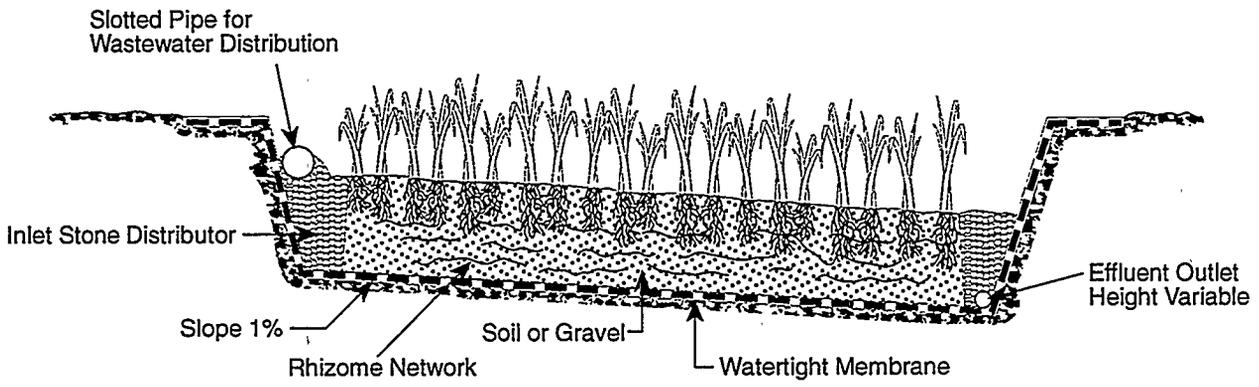


Fig. 1. Constructed wetlands test reactor.

2.2 WETLAND SYSTEM OPERATION

The hardware for the wetland system was in place and operational, with plants planted and water flowing, by the end of May 1996. The sampling design was simple: about twice weekly, water samples were taken from the inlet and outfall of each wetland cell. Two sets of samples from each location were filtered on each sampling date. One set of these samples, filtered through Syrifil-MF (0.45-um pore-size) filters, was analyzed for nitrate and ammonium, using colorimetric procedures, with a Trax 8000 autoanalyzer; the other set was filtered through Whatman GF/F (glass fiber) filters before being analyzed for total uranium, by kinetic phosphorescence (ASTM method D5174). The nitrate and ammonium measurements were made at Oak Ridge National Laboratory; the uranium measurements were made by ThermoNutech (Oak Ridge, Tennessee). On most sampling dates, water entering and exiting each wetland cell was also analyzed for pH, water temperature, and conductivity.

Wetlands plants can assimilate nitrate, but the major route of nitrate loss in wetlands is more often due to denitrification, a process wherein nitrate is converted to N_2 by microbes. Denitrification can occur when the rate of catabolic metabolism by heterotrophic bacteria exceeds the supply rate of oxygen, which serves as the preferred terminal acceptor of electrons in aerobic conditions (Wetzel 1983; Rich and Wetzel 1978). If bacterial metabolism outstrips the rate of oxygen supply, anaerobic metabolic pathways dominate and nitrate becomes the next "preferred acceptor," in terms of redox potential. When all oxygen and nitrate has been consumed, continued anaerobic catabolism can use sulfate as an acceptor, which results in the production of reduced sulfur compounds (e.g., H_2S). These considerations suggest that wetlands can be encouraged to denitrify more rapidly by controlled additions of a labile organic material, particularly if the added material has a low ratio of nitrogen to carbon. To test this idea, we began drip-wise addition of a labile organic solution near the upstream end of each wetland cell on August 18. The material used as a substrate was Staley's corn steeped liquor (Staley's Inc., Loudon, Tennessee). This material was diluted to 1% full strength in distilled water, and diluted mixture was dripped from a 10-L reservoir into the upstream end of each cell via gravity flow through microbore tubing. For the first week, the mixture was added to each cell separately at a rate of approximately 2.5 mL per minute. Thereafter, the rate was increased to approximately 5 mL per minute, by use of larger-diameter microbore tubing.

3. RESULTS

3.1 GENERAL OPERATIONAL CONSIDERATIONS

We assessed operation of the wetlands both subjectively and quantitatively. Subjectively, the following aspects seemed positive. First, the experimental design itself appeared to be rigorous enough to address initial questions about feasibility of this technology for lowering concentrations of nitrate in water at SS-4, despite limitations outlined below. Second, few of the plants that were originally planted into the wetland cells died, and all of those that survived grew vigorously. Thus, by the end of the experiment, each cell contained much healthy appearing vegetation. Third, the solar-powered aspect of the water-delivery system worked reliably, but line clogging increased the maintenance effort and prohibited calculation of water

mass treated. Fourth, the organic-amendment treatment system, although not perfectly quantitative, operated fairly consistently, such that we had some confidence that we could block the results of the experiment into a "before-addition" phase and a "post-addition" phase. Most values for nitrate, ammonium, and uranium were well above detection limits, which permitted the use of the use of simple and robust statistical methods to analyze the data.

3.2 DATA ANALYSIS

In this study, nitrate nitrogen ($\text{NO}_3\text{-N}$) and total uranium were the two contaminants of greatest interest. To determine the effect of wetland passage on nitrate and uranium concentrations, and to estimate the influence of added organic matter on wetland processes influencing the uptake or transformation of these contaminants, we first computed the upstream-to-downstream difference for each parameter on each sampling date. This computation involved simple subtraction. For example, if the concentration of total uranium in water entering a wetland cell was $103 \mu\text{g/L}$ and the concentration of total uranium in water exiting that wetland cell was $72 \mu\text{g/L}$, the difference in total uranium for that cell on that sampling date was $103 - 72$, or $31 \mu\text{g/L}$. These differences—upstream concentration, minus downstream concentration, for each wetland cell on each sampling date—are referred to hereafter as "deltas", for each parameter of interest. After computing parameter deltas, we then compared the mean deltas for various parameters (including nitrate and uranium) for sampling dates before organic-matter addition to the mean deltas for these materials for sampling dates after organic matter addition, by use of analysis of variance (ANOVA). In this analysis, we had 42 observations (14 sampling dates, and 3 replicate deltas per date) for conditions before organic addition started, and 30 observations (10 sampling dates, and 3 replicate deltas per date) for each parameter of interest. Conductivity, pH, and water temperature measurements were not made on the first sampling date, so the number of observations included in the analysis were not identical for all parameters.

3.3 EFFECTS ON NITRATE AND AMMONIUM

Mean concentrations of $\text{NO}_3\text{-N}$ in water entering and exiting the wetland cells are shown in Fig. 1. Before organic matter addition started, nitrate deltas for the wetlands were low but positive (Fig. 2). Although the removal efficiency of nitrate by the wetlands was not great, it was consistent: the mean concentrations of $\text{NO}_3\text{-N}$ in water exiting the wetlands were lower than for water entering the wetlands on 11 of the first 14 sampling dates. The computation method for estimating loss, through use of deltas, makes no correction for water lost by evapotranspiration. Thus, the actual nitrate delta for water passing through the wetlands was undoubtedly greater than the apparent nitrate delta.

Before organic addition started, the mean delta for $\text{NO}_3\text{-N}$ was 2.85 mg/L ($N = 42$ observations); after organic addition started, the mean delta for $\text{NO}_3\text{-N}$ after was 16.85 mg/L ($N = 30$ observations). The difference between these two sets of deltas was large and statistically significant ($R^2 = 0.365$; $p = 0.0001$) (Table 1). Thus, even cursory inspection of the data indicated that denitrification could be "driven" by adding labile organic matter, as we had speculated.

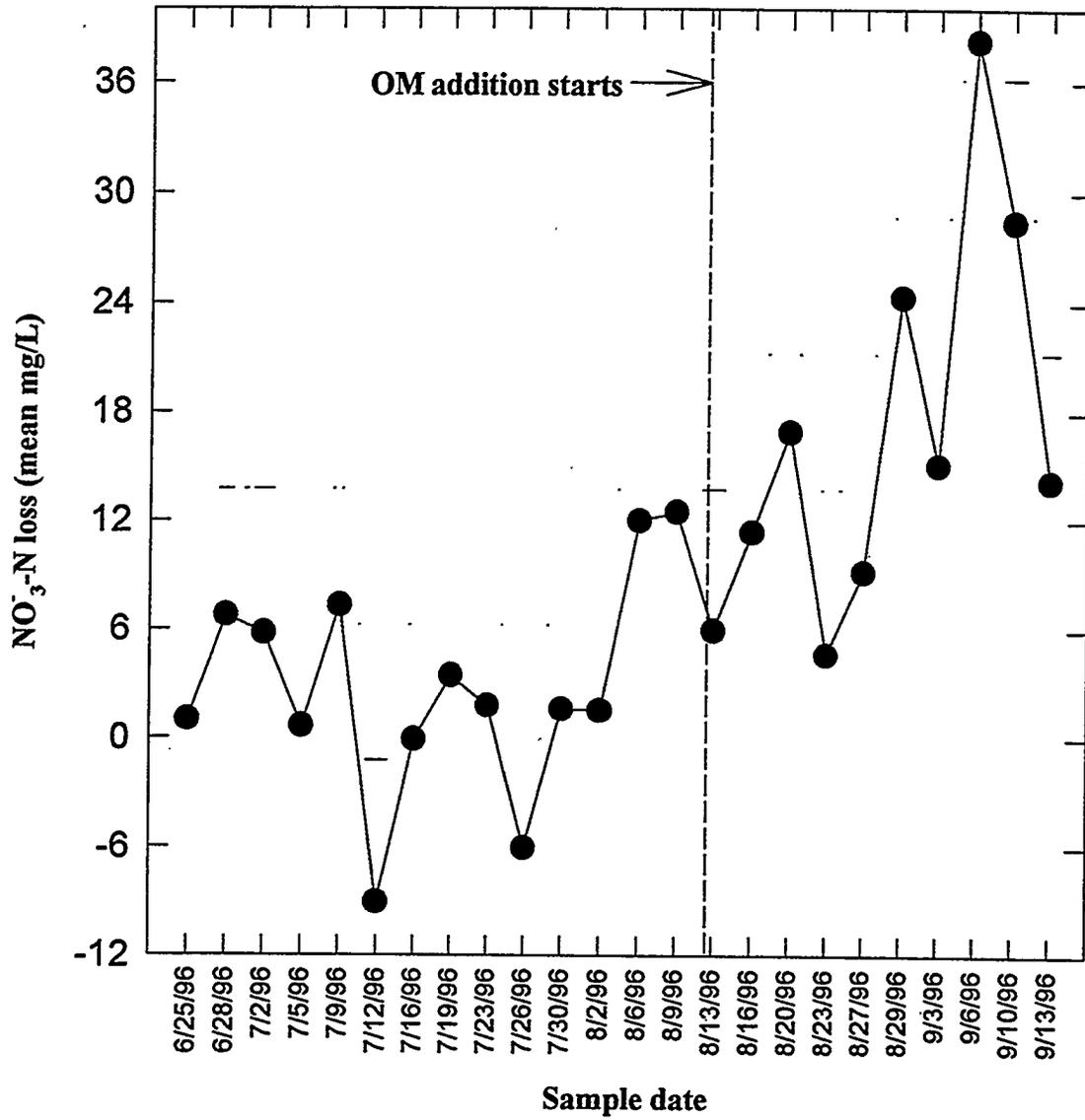


Fig. 2. Nitrate removal (mean: influent minus effluent) by constructed wetlands.

Table 1. Analysis of variance results for nitrate mean deltas, for sampling dates before and after organic matter additions to constructed wetland cells. R^2 (the proportion of variation explained) for the effect of organic-matter addition (before versus after) on nitrate mean delta was 0.365.

Source	DF	Sum of Squares	F value	Prob. > F
Model	1	3443.97	40.29	0.0001
Error	70	5983.03		
Corrected total	71	9427.00		

The actual rate of denitrification in the wetlands could have been substantially greater than the apparent rates of denitrification, if (1) the organic matter used to "feed" the wetland cells contained high concentrations of nitrogen, or (2) concentrations of dissolved organic nitrogen (DON) in water exiting the wetlands exceeded DON concentrations entering the wetlands. These possibilities are of potential significance to this demonstration project for two reasons. First, a large fraction of the total concentration nitrogen (excluding N_2) in natural-water systems can be due to DON (Wetzel 1983; Rich and Wetzel 1978). Second, many DON compounds are efficiently converted to inorganic form [e.g., dissolved inorganic nitrogen species (DIN), such as N_2 , NH_4^+ , or NO_3^-], or vice versa, by aerobic and anaerobic microbes. Thus, strong and compelling evidence about denitrification rates in these wetlands would require the need to develop a more rigorous consideration of nitrogen mass-balance issues.

As a first step in this direction, we collected three samples on September 20. One of these samples was a filtered composite sample of water being pumped into the three wetland cells; another was a filtered composite sample of water exiting the three wetland cells; and the third was an unfiltered aliquot of the organic matter mixture being drip-fed into the wetland cells. Each of these samples was analyzed for NH_4 -N, NO_3 -N, and DON. The DON analysis involved measuring the DIN concentration of each sample (i.e., NH_4 -N plus NO_3 -N), then photochemically oxidizing the sample (by UV light plus potassium persulfate), and reanalyzing the digestate for DIN. While the conversion efficiency for DON to DIN is undoubtedly less than 100%, the method does appear to yield generally reliable results (P.J. Mulholland, Environmental Sciences Division, personal communication).

The concentrations of NH_4 -N, NO_3 -N and DON for the three samples described above are shown in Table 2. The feed-rate of the organic-matter mixture to the wetland cells was approximately 5 mL per minute, and the flow of water into (and out of) the wetlands was approximately 200 mL per minute. Thus, the concentrations of NH_4 -N, NO_3 -N, and DON in the wetland cells directly contributed by the organic-matter mixture were computed to be about 6 mg/L, 0.01 mg/L, and 1.84 mg/L, respectively. The total concentration of N entering the wetlands (DIN plus DON in inflowing water, plus DIN and DON from the organic-matter mixture, added to a final concentration of 2.5%) was approximately 50.6 mg/L, and the total concentration of N exiting the wetlands (DIN plus DON) 37.0 mg/L. Thus, from this rudimentary single mass-balance estimate, denitrification and plant-uptake processes within the wetlands appeared to lower total N levels by about 26%.

Table 2. Concentrations (mg/L) of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and dissolved organic nitrogen (DON) in organic-matter mixture used to "feed" constructed wetland cells, and in composite samples of water entering and exiting the wetland cells. The organic matter mixture was added, at 2.5% of full strength, downstream of the "inflowing water" sampling site.

Substrate analyzed	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	DON
Organic matter mixture	247	<0.5	73.6
Inflowing water	1.6	34.9	6.1
Outflowing water	0.1	31.5	5.4

The mean concentration of $\text{NH}_4\text{-N}$ entering the wetlands before organic matter addition started was about 3 $\mu\text{g N/L}$, and the mean concentration of ammonium exiting the wetlands, before organic matter was added, was about 60.5 $\mu\text{g N/L}$. Thus, at least some of the nitrate entering the wetlands via water being added from SS-4 appeared to be converted to $\text{NH}_4\text{-N}$. The undiluted organic matter used to "feed" the wetland system contained a high concentration of $\text{NH}_4\text{-N}$ (about 247 mg/L; Table 2). When diluted to the concentration expected, based on drip-feed rate of the mixture, the expected concentration of $\text{NH}_4\text{-N}$ in water exiting the wetlands was >6 mg/L. However, the mean concentration of $\text{NH}_4\text{-N}$ in water exiting the wetlands, after organic-matter addition started, was only 2.32 mg/L. Thus, much of the $\text{NH}_4\text{-N}$ added with the organic-matter supplement must have volatilized, or been oxidized to nitrate, or been consumed by plants. Because many reactions and processes could (and probably did) account for losses in $\text{NH}_4\text{-N}$, it made no sense to analyze this constituent by ANOVA: the results would have been highly significant, statistically, and essentially meaningless, in terms of helping to understand processes of interest.

3.4 EFFECTS ON URANIUM

The removal efficiencies for uranium by the wetlands was moderately high both before and after organic matter was added (46.3% and 31.3%, respectively) (cf. Fig. 3). The mean delta for uranium before organic matter addition started was 61.15 $\mu\text{g/L}$, and the mean delta for uranium after organic matter addition began was 49.6 $\mu\text{g/L}$. This difference was not statistically significant (Table 3). Thus, the wetlands did a moderately good job at lowering the concentration of total uranium, and organic matter addition did not greatly alter this tendency. The lack of much effect of organic matter addition on uranium uptake was particularly striking, given the strong effect of organic matter addition on $\text{NO}_3\text{-N}$ (Fig. 4).

Table 3. Analysis of variance results for uranium deltas, for sampling dates before and after organic matter additions to constructed wetland cells. R^2 for the effect of organic-matter addition was 0.022.

Source	DF	Sum of Squares	F value	Prob. > F
Model	1	2323.8	1.60	0.210
Error	70	101776.4		
Corrected total	71	9427.00		

3.5 EFFECTS ON FIELD MEASUREMENTS

Twice each week during the test period, influent and effluent samples from each cell were analyzed for pH, specific conductivity, and temperature. The results are described as averages of the three cells and are shown in Table 4. Influent pH values were always slightly higher than neutral, with average values ranging between 7.31 and 7.76 standard units. Effluent was always lower than the corresponding influent sample, with values ranging between 6.75 and 7.3. The difference in pH mean deltas between influent and effluent before and after organic carbon addition (0.27 before addition, and 0.60 after addition) was statistically significant, by ANOVA (Table 5). It is reasonable to suspect that the slight tendency towards acidification attributed to the addition of organic matter could have also accounted for a lower efficiency of uranium removal. This may not be an issue in a longer term test since the need for supplemental organic carbon would diminish in a mature system. Overall, the slight decrease in pH was not considered a detriment since all values remained within a generally neutral range.

Temperature was slightly higher in effluent samples compared to influent samples (by approximately 0.5 degrees). This is attributed to the increased exposure of water to the atmosphere, and is not considered an effect of treatment.

Specific conductivity declined slightly with treatment (Table 4). Effluent values only exceeded corresponding influent values in six of the 23 sampling events. There was no apparent trend in these observations. The overall average influent conductivity was 0.651m (check units). Effluent values averaged 0.628, approximately 5% lower than the average influent value.

Table 4. Mean values for wetland testing field measurements

EVENT	Mean Values for Cells A, B & C					
	<i>pH</i> Inf	<i>pH</i> Eff	<i>COND.</i> Inf	<i>COND.</i> Eff	<i>TEMP.</i> Inf	<i>TEMP.</i> Eff
1	7.62	7.17	0.575	0.534	27.3	29.9
2	7.50	7.23	0.673	0.601	23.8	24.9
3	7.64	7.26	0.641	0.614	22.8	22.0
4	7.58	7.19	0.688	0.353	23.3	24.2
5	7.58	7.30	0.561	0.698	22.8	21.6
6	7.20	7.29	0.564	0.547	22.1	22.9
7	7.44	7.16	0.604	0.555	24.1	24.4
8	7.48	7.22	0.750	0.709	25.4	24.7
9	7.49	7.20	0.554	0.688	25.0	22.6
10	7.48	7.22	0.750	0.709	25.4	24.7
11	7.31	7.16	0.394	0.353	20.9	21.8
12	7.47	7.25	0.579	0.443	24.7	29.9
13	7.49	7.07	0.707	0.636	21.5	23.0
14	7.44	6.75	0.504	0.719	20.5	21.9
15	7.49	7.12	0.617	0.579	23.3	22.9
16	7.59	7.05	0.722	0.678	25.7	26.2
17	7.60	7.02	0.725	0.711	24.8	24.3
18	7.34	6.82	0.263	0.272	20.2	21.4
19	7.69	7.03	0.772	0.799	23.3	22.6
20	7.67	7.02	0.755	0.759	22.6	22.9
21	7.76	7.21	0.953	0.839	23.5	27.3
22	7.67	6.92	0.795	0.876	21.0	22.1
23	7.73	7.00	0.818	0.781	17.8	17.8
END	7.53	7.12	0.651	0.628	23.1	23.7

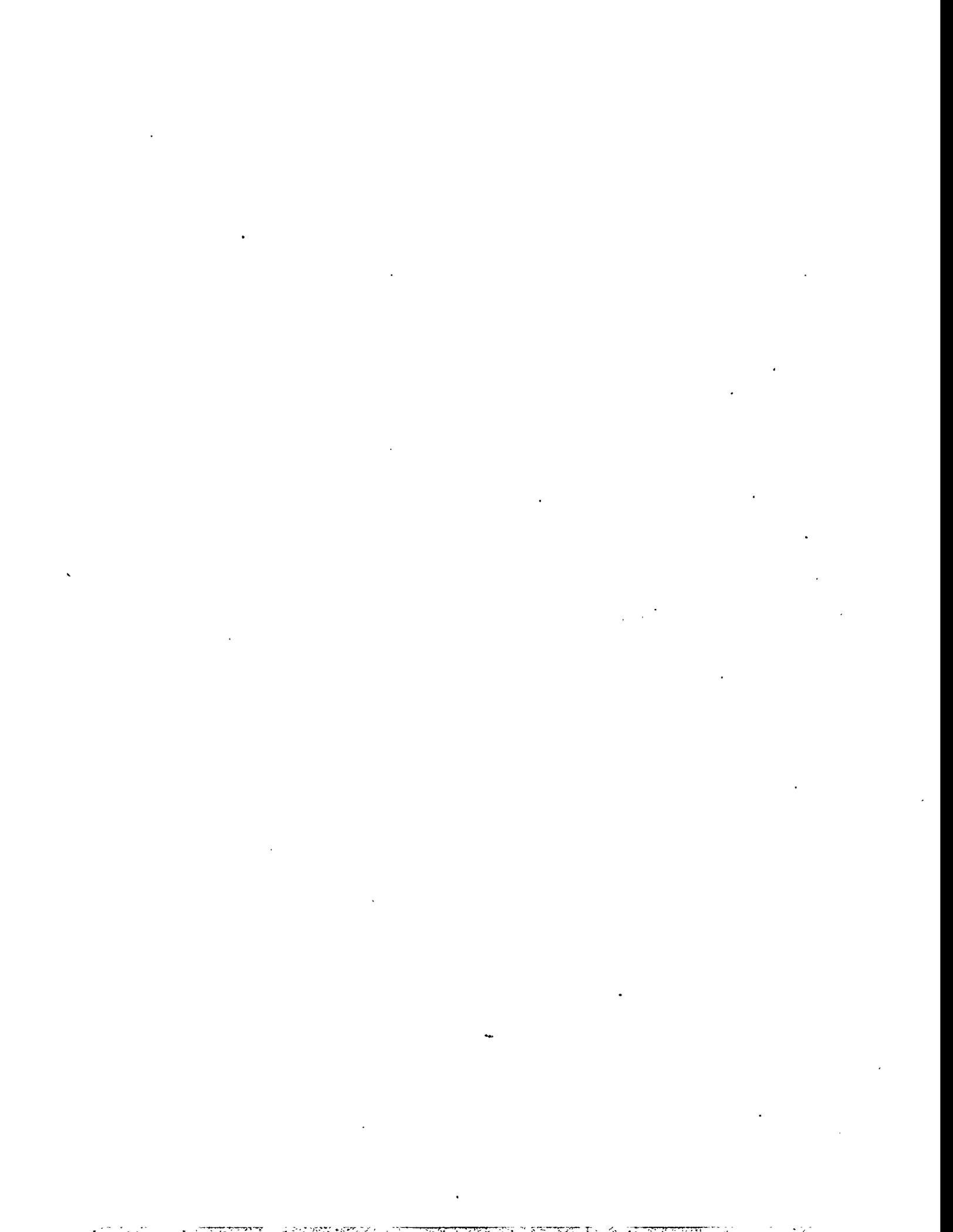
Table 5. Analysis of variance results for pH deltas, for sampling dates before and after organic matter additions to constructed wetland cells. R^2 for the effect of organic-matter addition was 0.483.

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APPENDIX F

**BEAR CREEK VALLEY TREATABILITY STUDY
METAL REMOVAL USING ALGAL MATS**

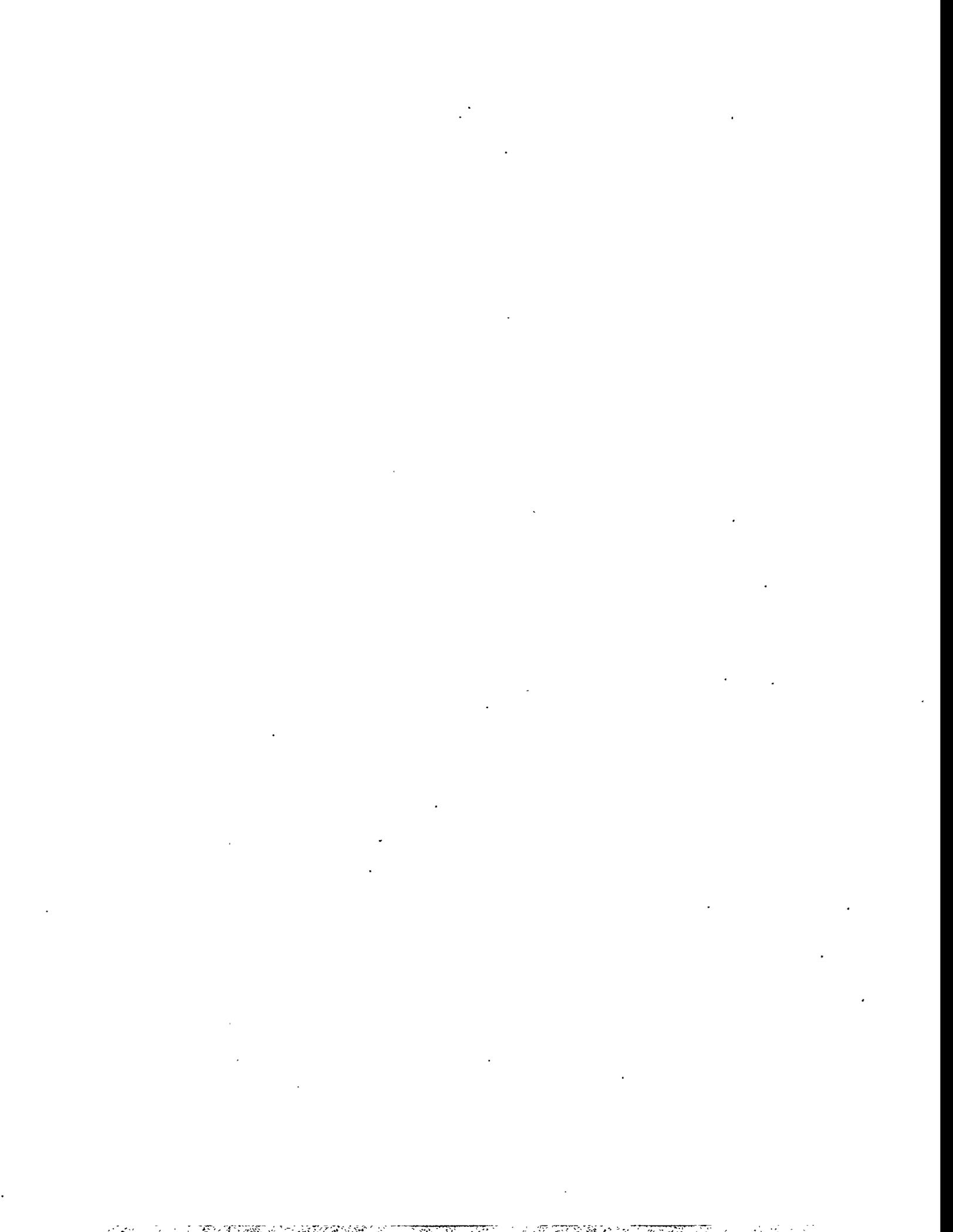


**BEAR CREEK VALLEY TECHNOLOGY DEMONSTRATION
METAL REMOVAL USING ALGAL MATS**

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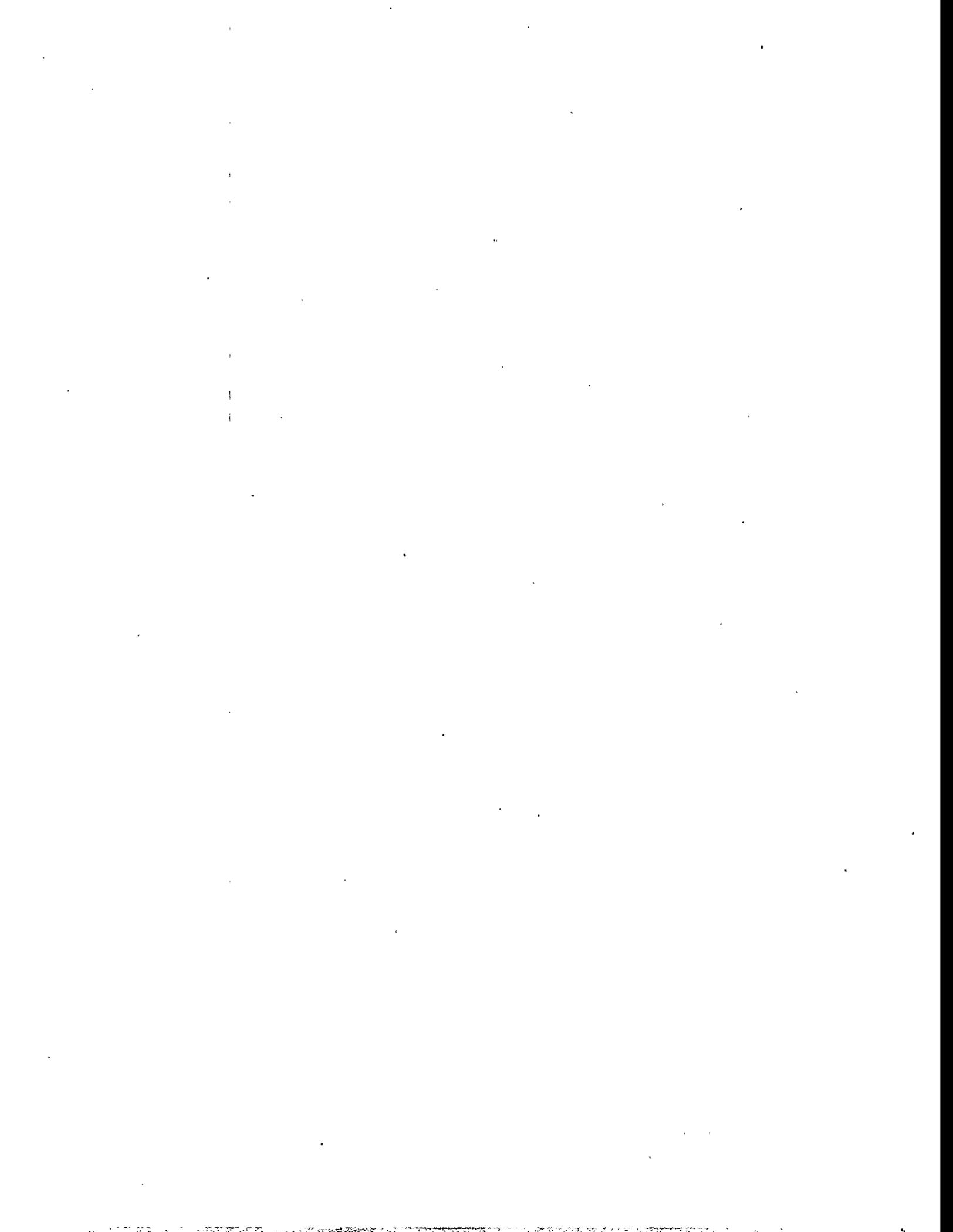
SAIC Project No. 01-380-07-6663



EXECUTIVE SUMMARY

The Bear Creek Valley Technology Demonstration is designed to evaluate technologies that have the potential to provide low cost, low operation and maintenance in situ treatment of surface water and groundwater within the Bear Creek Valley (BCV) characterization area (CA). Contaminants of concern include uranium and nitrate as well as additional metals. Different areas of BCV CA have vastly different characteristics. Phase I of this three phase demonstration was planned to screen pertinent technologies using site water that may be improved through treatment with that medium.

This report describes Phase I screening results obtained from testing algal mats technology. Algal mats are complex communities of bacteria and blue-green algae that are fixed to an inert substrate such as glass wool. The community provides a self-regenerating matrix of oxidizing and reducing conditions to degrade organic contaminants and accumulate metals. These attributes and their low maintenance requirements make mats treatment applicable to BCV surface water.



1. INTRODUCTION

Algal mats are self-sustaining communities of bacteria, protozoa, and blue-green algae impregnated in an inert permeable substrate. The algae are photosynthetic, producing an oxidative environment and additional carbohydrates (algal mass). Within the mat structure, bacteria colonize in small niches, feeding on the algal biomass and producing anaerobic or reducing conditions. This balance of redox conditions renders the mats system capable of many different treatment functions to remove contaminants from water. The mats require very little nutrition, generally gaining all requirements from the sun and target water once the mats are established. The entire system represents a low operations and maintenance alternative for water treatment. However, due to the biotic and photosynthetic nature of the mats, they are not suitable for a subsurface trench application. For this reason, mats technology will be considered for a surface application.

2. OBJECTIVE

The purpose of this study is to demonstrate the general performance of the mats with actual site water. Because the mats are living material, batch systems do not represent the capacity of the system. The systems are best suited to a continuous flow design. The goal of the tests is to understand the capacity of the mats to remove metals (including uranium), reduce nitrate, and sustain growth under site conditions in a continuous flow mode of operation.

3. APPROACH

During August and September 1996, two pilot-scale mats reactors were tested under a protective, translucent structure placed at the Oak Ridge Y-12 West End Treatment Facility (Fig. 1—all figures are at end of appendix). One reactor received water from SS-4 tributary, the other received water from NT-1 surface water. Performance was based on the change in contaminant concentrations between influent and effluent as well as visual observations of mats viability. Water was delivered to the reactor by gravity flow from a 12-gal storage container. Influent and effluent samples were collected twice weekly, and whenever the storage container was refilled. Each reactor was maintained for 4 weeks between mid-August and mid-September 1996.

For each sample collected, pH, specific conductivity, and temperature were measured using a Horiba U-10 water analyzer, which was calibrated each day according to manufacturer's specifications. Samples for metals and nitrate analysis were filtered and delivered to Y-12 Analytical Services. Metals were analyzed by inductively coupled plasma (EPA method 6010) and by plasma mass spectrometry (EPA method 200.8). Nitrate analyses were completed by Environmental Sciences Division laboratory professionals using a Technicon Traac 800 (Technicon Instruments Corporation, Tarrytown, New York). The instrument method 818-87T, which is based on a copper-cadmium reductor cell, was the standard operating procedure.

4. RESULTS

4.1 SS-4 REACTOR

Approximately 40 gal of water from SS-4 was treated within the 4-week test period. Field data for pH, specific conductivity, and temperature are provided in Table 1 (all tables are at the end of appendix). Influent pH values ranged from 6.87 to 7.36. Effluent values were always higher than the corresponding influent value, with a range of 7.88 to 8.64. Effluent pH does not represent a hazard to biota, but since the trend consistently increased over time, it may be a consideration for Phase II testing.

Conductivity measurements from influent samples ranged from 0.715 to 0.950 mS/cm and from 0.454 to 0.744 mS/cm in effluent samples. This represents an average reduction of approximately 19% during reactor treatment. Changes based on samples collected on the same date ranged from 4 to 36% reduction in conductivity.

Temperature was consistently higher in the effluent compared to the influent due to increased exposure of water to the atmosphere during incubation within the reactor. Influent temperatures ranged from 21.5 to 27.9°C. Effluent temperature measurements ranged between 25.3 to 39.2°C.

4.1.1 Metals Removal

A comparison of influent and effluent streams produced a significant reduction in concentration of several metal species as a result of treatment by the mats reactor (Table 2). Concentrations of affected metals in influent and effluent samples are shown in Figs. 2 and 3. With very few exceptions, uranium, barium, magnesium, calcium, and strontium concentrations were lower in the effluent of the SS-4 reactor, compared to influent values. Removals efficiencies varied within a given metal's data set. To determine the overall percent removed, mean influent and effluent concentrations of metals removed from the water were calculated. These data are shown in Table 2. Average removal ranged from 25% (magnesium) to 93% (uranium).

To confirm that the loss of metals was due to uptake by the mats, samples of mats were also analyzed for metals species. These values were compared to another mat sample that had not been exposed to test water. The results are shown in Figs. 4 and 5. Each metal showed an increased concentration in the post-treatment biomass. It is interesting to note that, with the exception of uranium, the metals were present at detectable levels in the untreated mat sample.

4.1.2 Nitrate Reduction

Nitrate reduction is conducted by the anaerobic bacteria found within the mats. To some extent, nitrate uptake can also be a function of algal growth, although it is considered proportionally small compared to the bacterial impact. Nitrate concentrations are shown in Fig. 6. Comparing paired data, nitrate was consistently lower in the effluent, but not to the levels observed previously with similar mats reactors (personal communication). This may be due to an incomplete acclimation of denitrifying bacteria. It may also be attributable to a lack of

vigor in algae resulting from dormancy of the mats while they were stored for two months prior to treatment. This issue should be clarified in a longer term study prior to concluding the denitrifying capacity of the mats system.

4.2 NT-1 REACTOR

Approximately 30 gal of water were treated during the 4-week test period using NT-1 surface water collected from the vicinity of the piezometer installed near the Southeastern bank of NT-1 (SWP01). Field data for pH, conductivity, and temperature collected during the test are provided in Table 3. The range of influent pH values varied from 6.62 to 7.09. Effluent pH values ranged from 7.73 to 8.73. It is interesting to note that these ranges are remarkably similar to those cited for the SS-4 reactor, although this reactor produced both the highest and lowest values of all.

Conductivity measurements from influent samples ranged from 1.77 to 2.17 mS/cm, consistently rising as time continued. This is attributed mainly to the continued progression of NT-1 flow toward baseflow after a series of heavy rain events in late July. Effluent values also increased steadily with time, ranging from 1.25 to 2.00 mS/cm. The average reduction in conductivity of treated water was only 7%; the conductivity values of influent and effluent samples collected on the same date ranged between 0 and 29%.

Temperature measured in influent samples ranged between 23.9 and 29.4°C. Effluent temperature values were always higher, ranging from 24.4 to 36.1°C. As stated previously, this is due to increased exposure of the test cells to the summer heat in an unventilated greenhouse and is not attributable to treatment.

4.2.1 Metals Removal

The metals species present in NT-1 vary in type and concentration compared to SS-4. The mats were successful in removing several metal species from NT-1 test water. Among these target metals are aluminum, barium, calcium, cadmium, manganese, nickel, strontium, and uranium. Magnesium and thallium were marginally reduced in concentration due to the mats treatment. Figures 7 through 9 show the record of influent and effluent data for these metals. The mean influent and effluent values and resulting treatment efficiency (calculated as percentage of effluent concentration compared to influent concentration) are shown in Table 4.

Uptake of metals by the mats solids is shown in Figs. 10 and 11. These data clearly show that the metals removed from NT-1 water accumulated in the mats biomass.

4.2.2 Nitrate Removal

The record of nitrate concentrations in the influent and effluent of the NT-1 mats reactor is shown in Fig. 6. Similarly to the SS-4 reactor, nitrate removal was marginal, with effluent nitrate concentrations increasing throughout the test period. The lack of activity could be due to the loss of vigor in activity of the mats during the 2 months of storage prior to testing; however, this should be clarified with more extensive field testing before a valid conclusion about nitrate removal efficiency can be drawn.

5. SUMMARY

The algal mats treatment system meets all of the objectives described in the *BCV Technology Demonstration Action Plan*, with the exception of true subsurface treatment. The following items are key summary statements:

- The algal mats reactors were very easy to maintain, meeting the objective of a low operations and maintenance remedy to treat certain types of surface water contamination. The mats appeared to thrive during exposure to the contaminated test water samples, eliminating toxicity to algae and microbes comprising the mats system as a concern for operation.
- The mats showed promise as a treatment system to remove certain metals from contaminated surface water. Several metals were removed from the two test water samples (SS-4 and NT-1), including: aluminum, barium, calcium, cadmium, magnesium, manganese, nickel, strontium, thallium, and uranium. Based on influent and effluent mean concentrations, removal efficiencies as high as 98% were observed.
- Nitrate removal rates were much lower than expected based on other mat's performance data. This is attributed to the negative impact of reactor storage prior to treatment; however, the impact of dormancy should be clarified with an additional test to demonstrate higher denitrification rates.

6. RECOMMENDATIONS FOR PHASE II

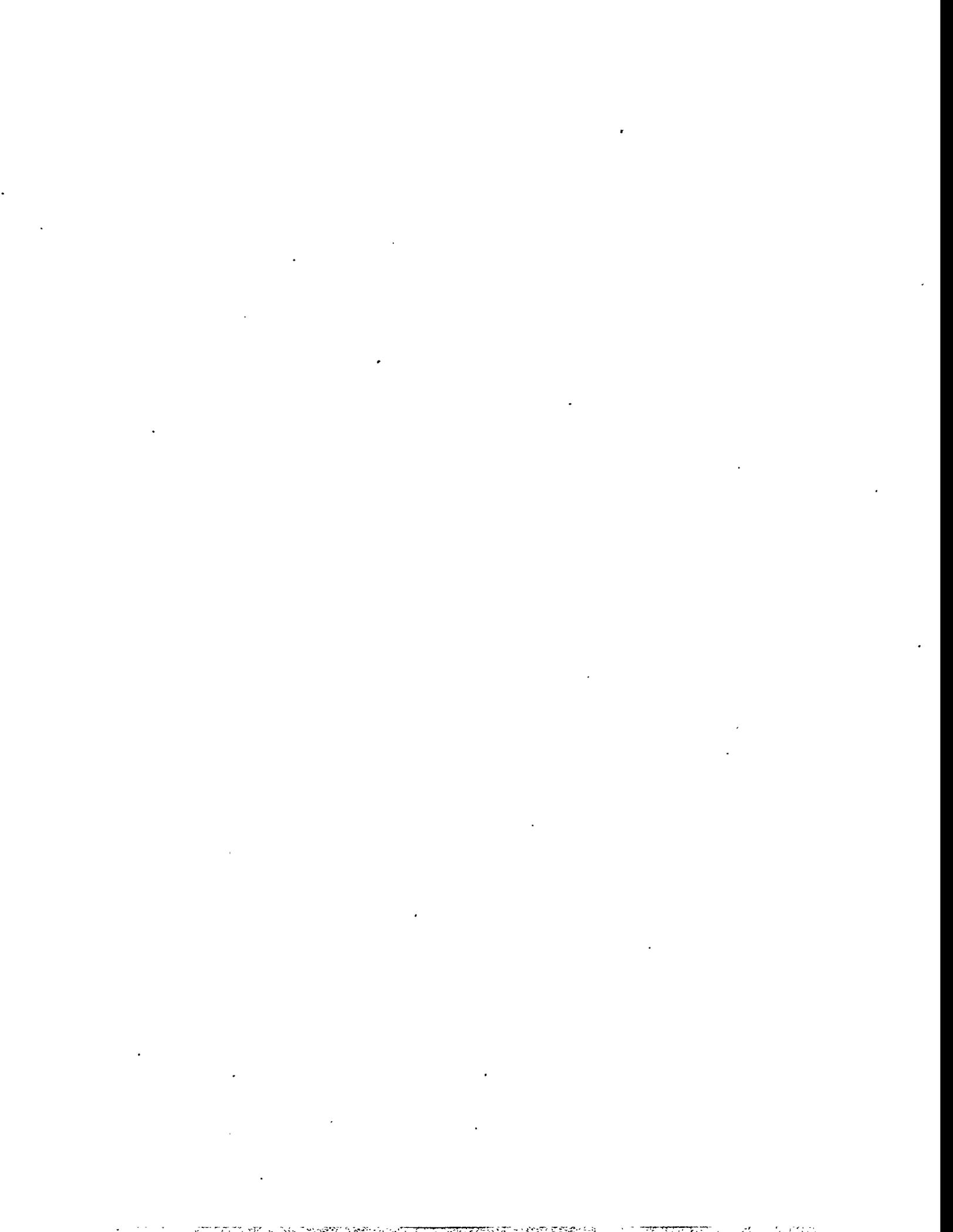
There are three main issues that should be clarified prior to implementing mats in a full-scale application:

Nitrate Reduction. A longer treatability study should be completed to understand fully acclimated nitrate reduction. The limited performance observed during Phase I may be temporary as the culture adjusts to the harsh conditions. It may also be possible that nitrate reduction will remain low due to toxicity effects. Much higher levels of nitrate reduction have been observed with this mats system; therefore, it is likely that the rate will increase with time.

Metal Binding Capacity. The mats system is thought to be self-regenerative, providing virtual infinite metal binding capacity. To approach quantification of this capacity, it is critical to document where the metals accumulate within the mat and at what rate they accumulate relative to the increase in biomass. This can be accomplished simultaneously with the nitrate reduction extended test.

Full-Scale Engineering. The baffle reactor design used in the Phase I test is adequate for controlled flow. However, other designs may provide better contact with the mats and have more capacity to handle fluctuating water flow. Further, if the mats are considered for in-stream placement, a different engineering design will be needed to address issues such as anchoring, biomass fixation, and stormflow. This task would be primarily a paper study, with the potential for prototype construction and testing.

FIGURES



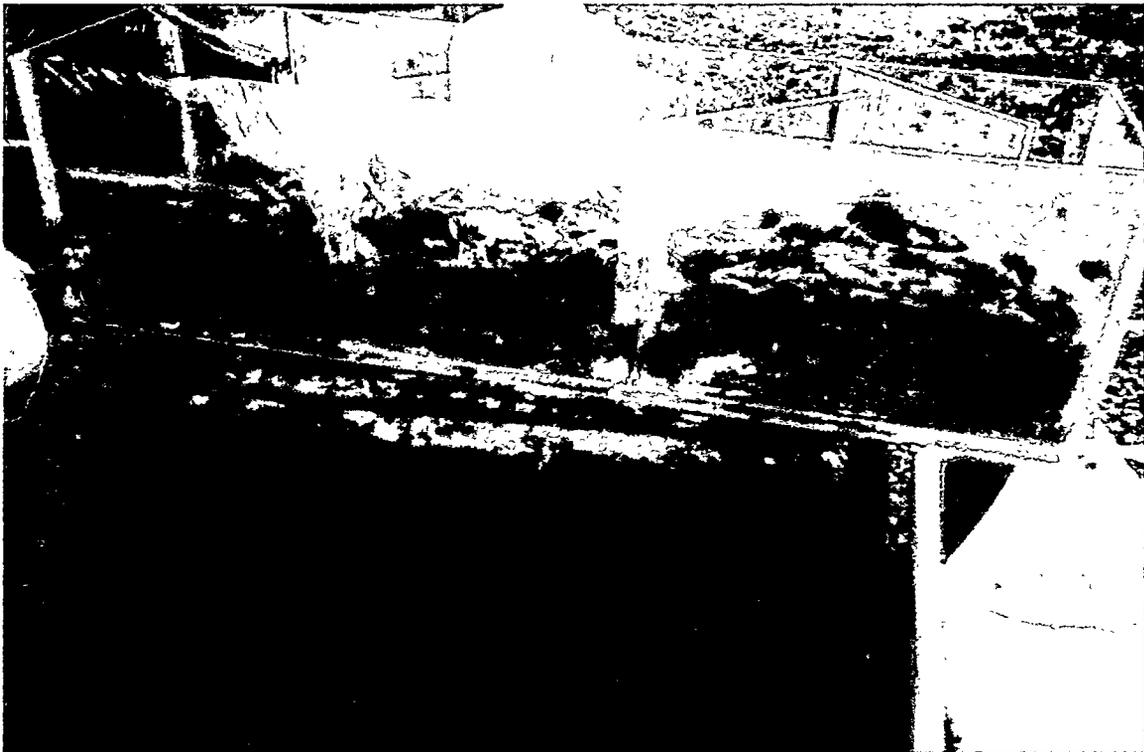


Fig. 1. Algal mats reactors.

Uranium

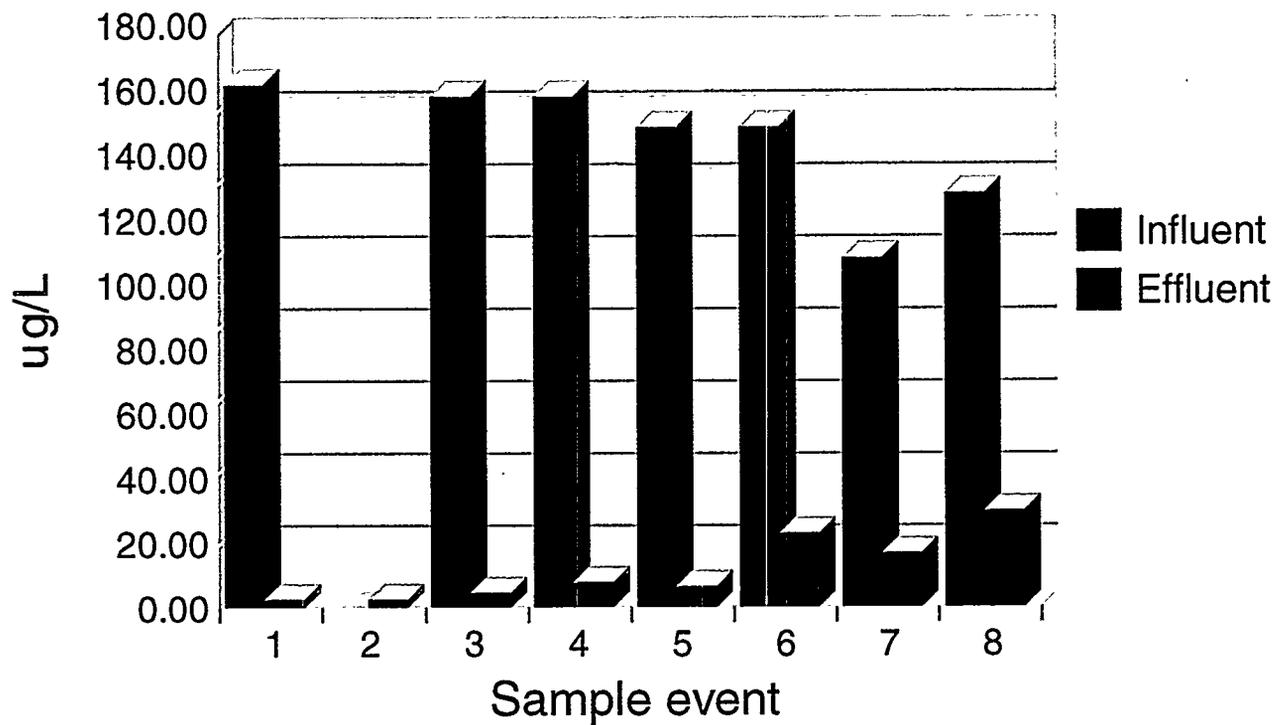


Fig. 2. Results of algal mat remediation on SS-4 water: uranium.

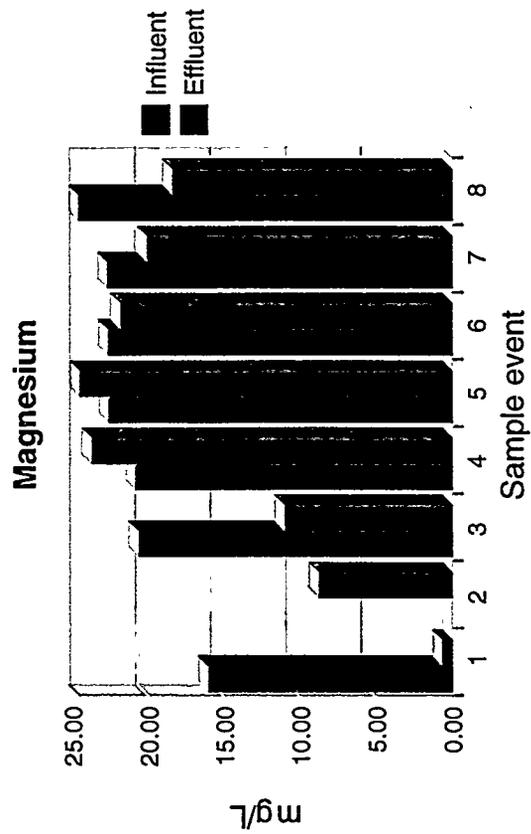
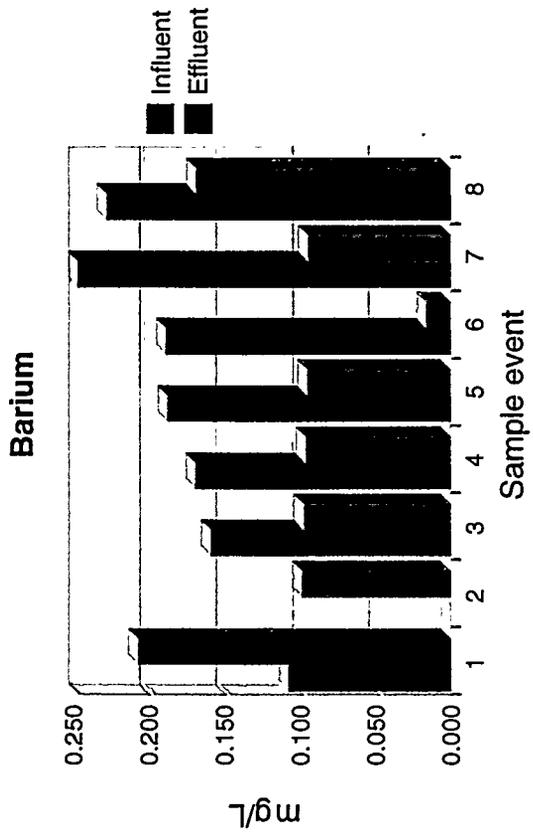
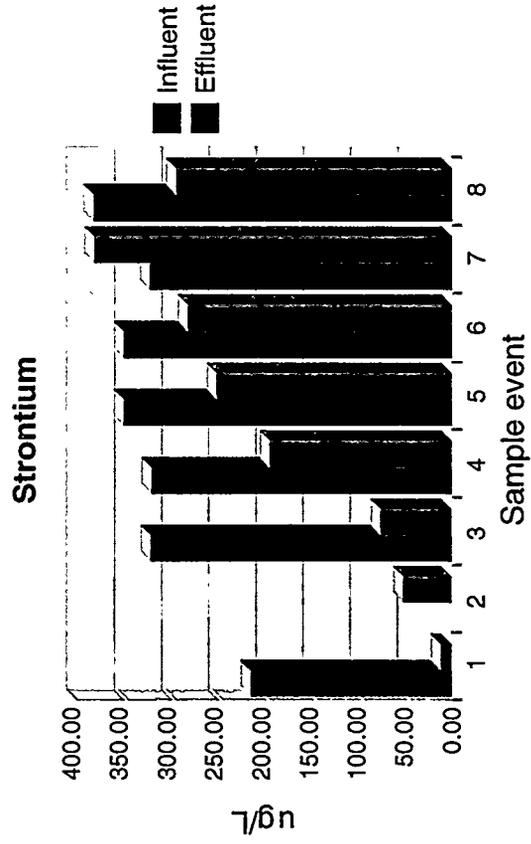
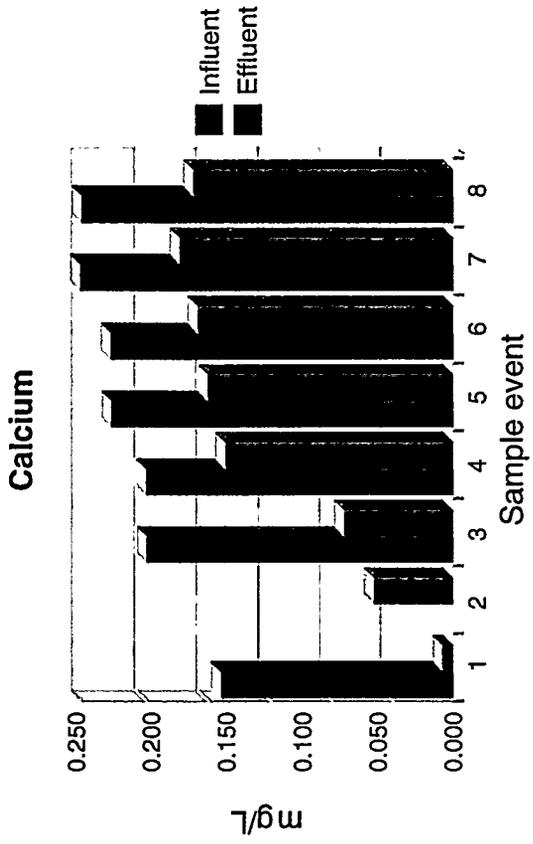


Fig. 3. Results of algal mat remediation on SS-4 water: barium, calcium, magnesium, and strontium.

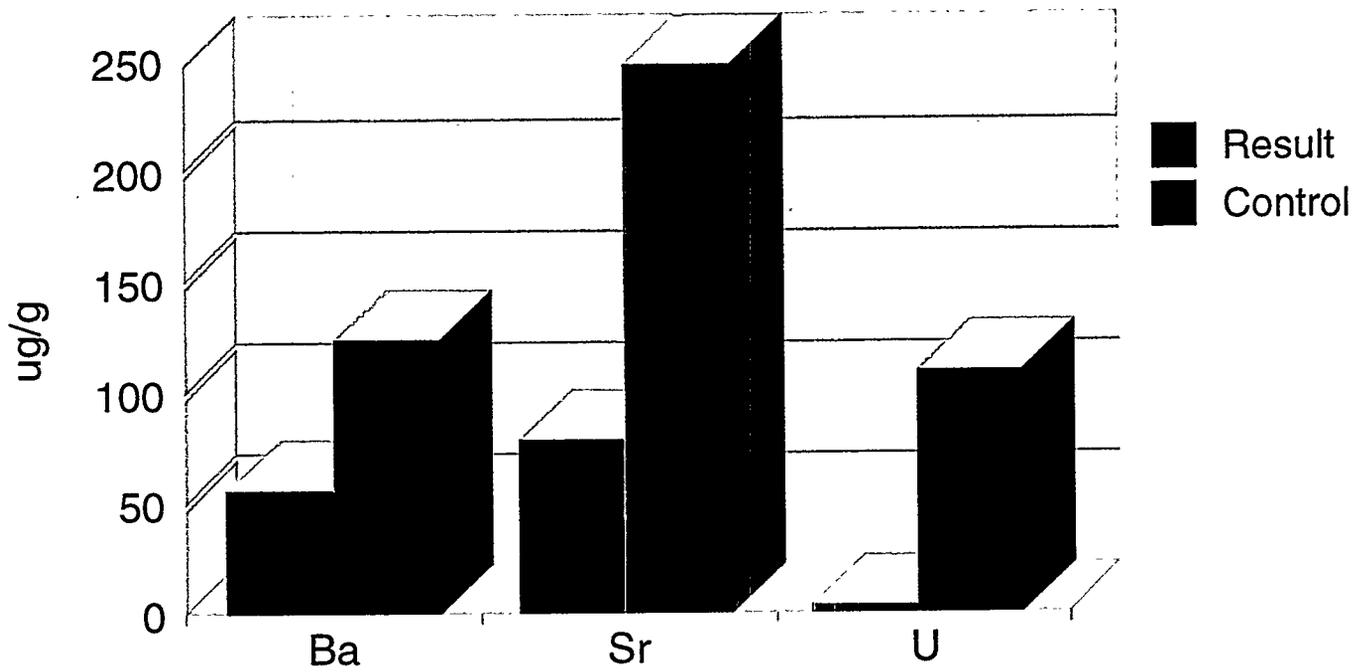


Fig. 4: Results of metal analysis on algal mats used to remediate SS-4 water: barium, strontium, and uranium.

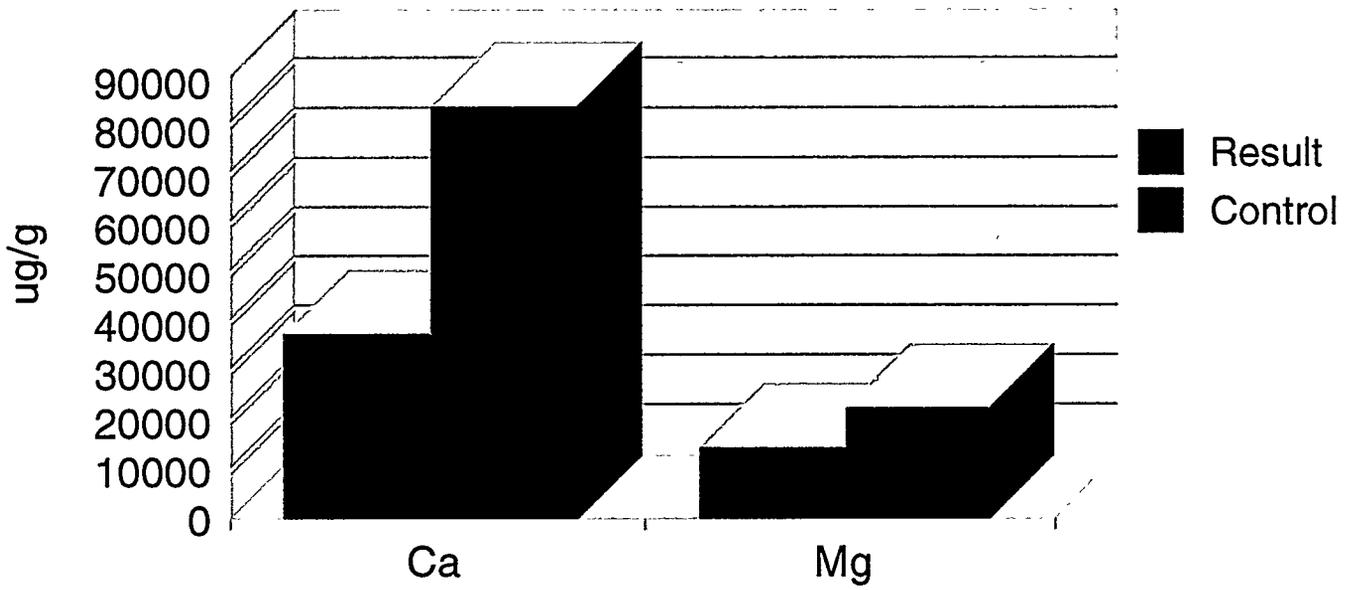


Fig. 5: Results of metal analysis on algal mats used to remediate SS-4 water: calcium and magnesium.

F-14

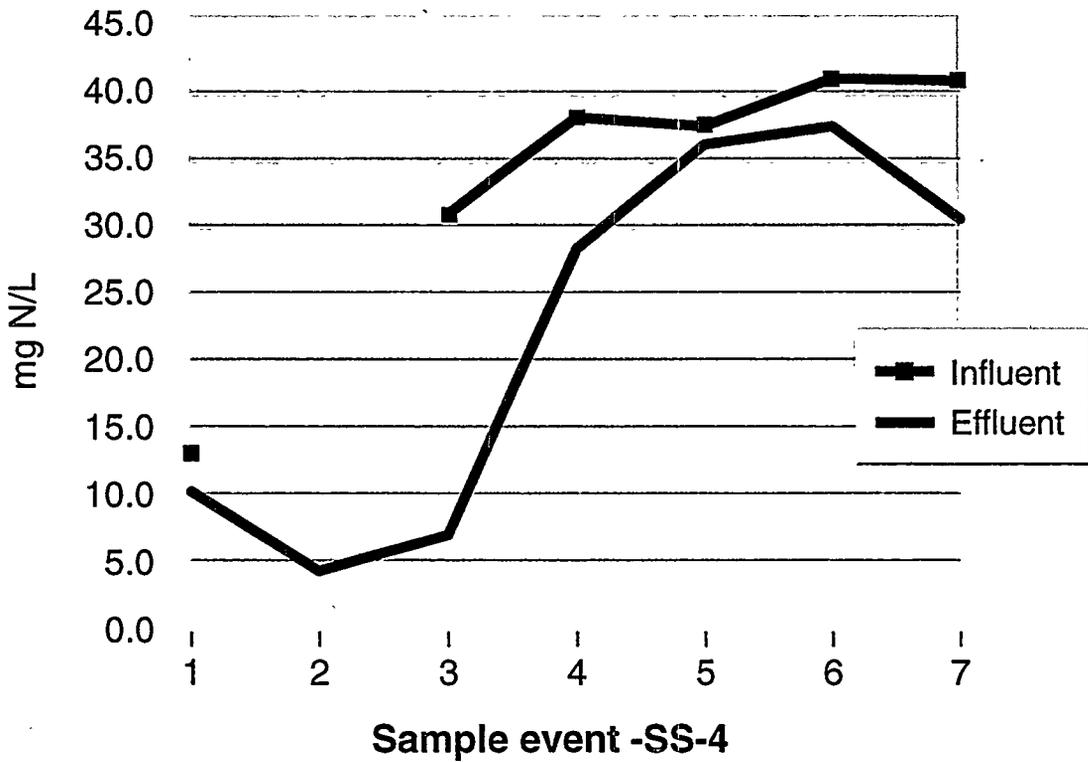
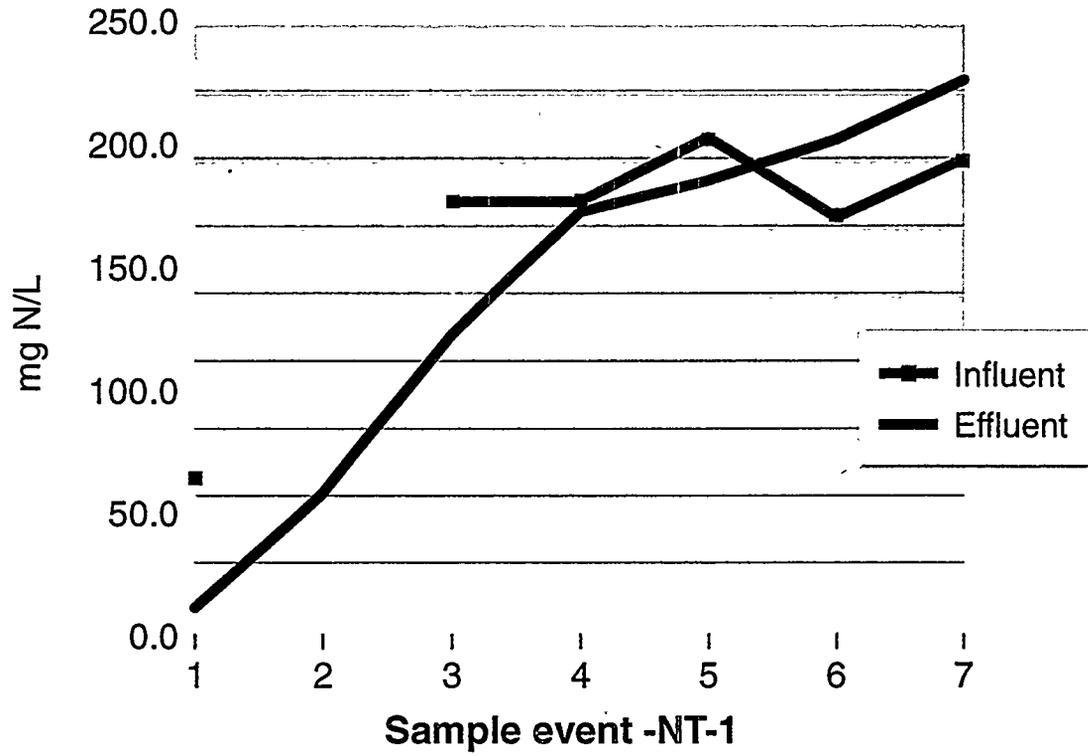


Fig. 6. Nitrate concentrations in influent and effluent samples of NT-1 (top) and SS-4 (bottom) water treated with mats.

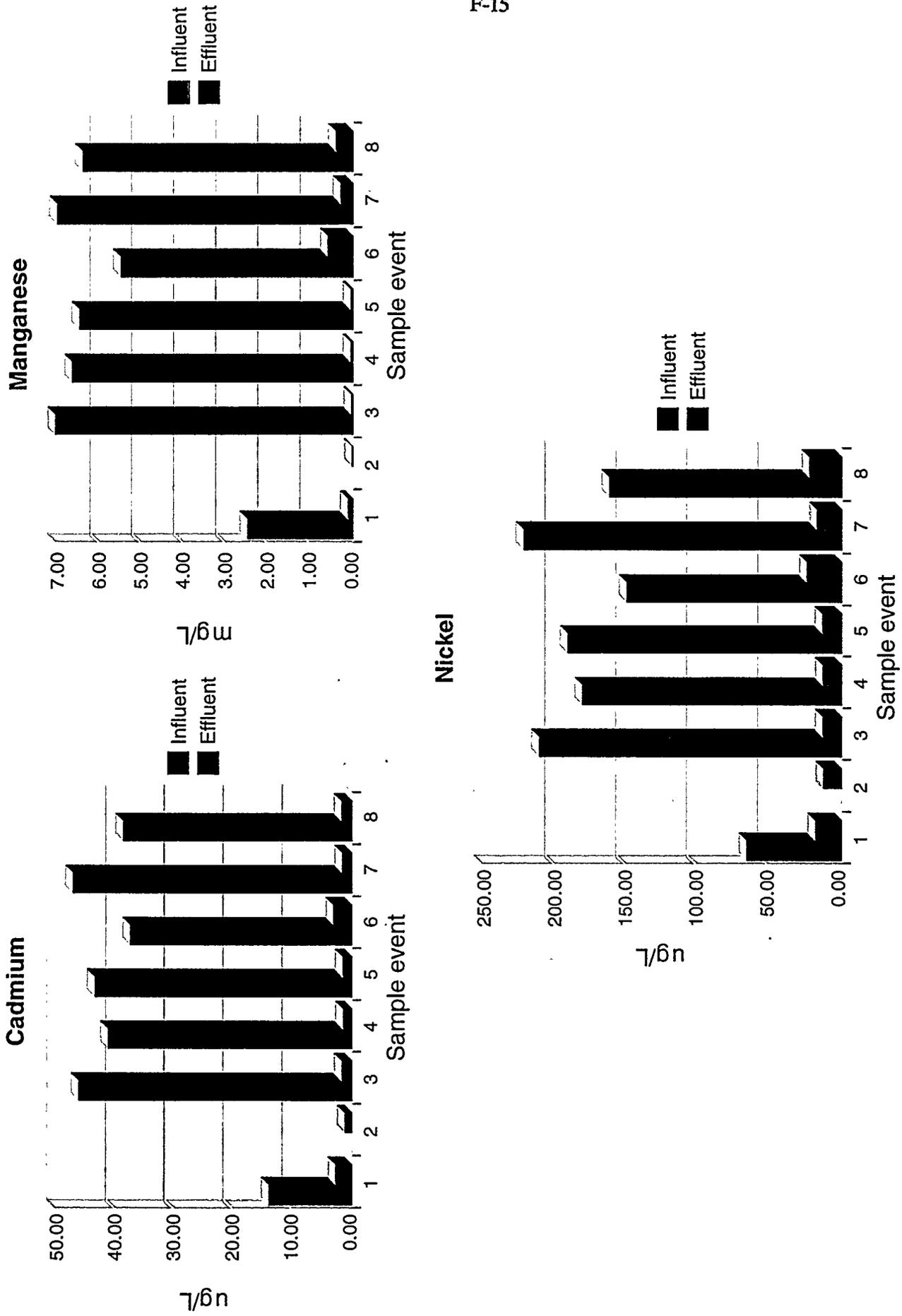


Fig. 7. Results of algal mat remediation on NT-1 water: cadmium, manganese, and nickel.

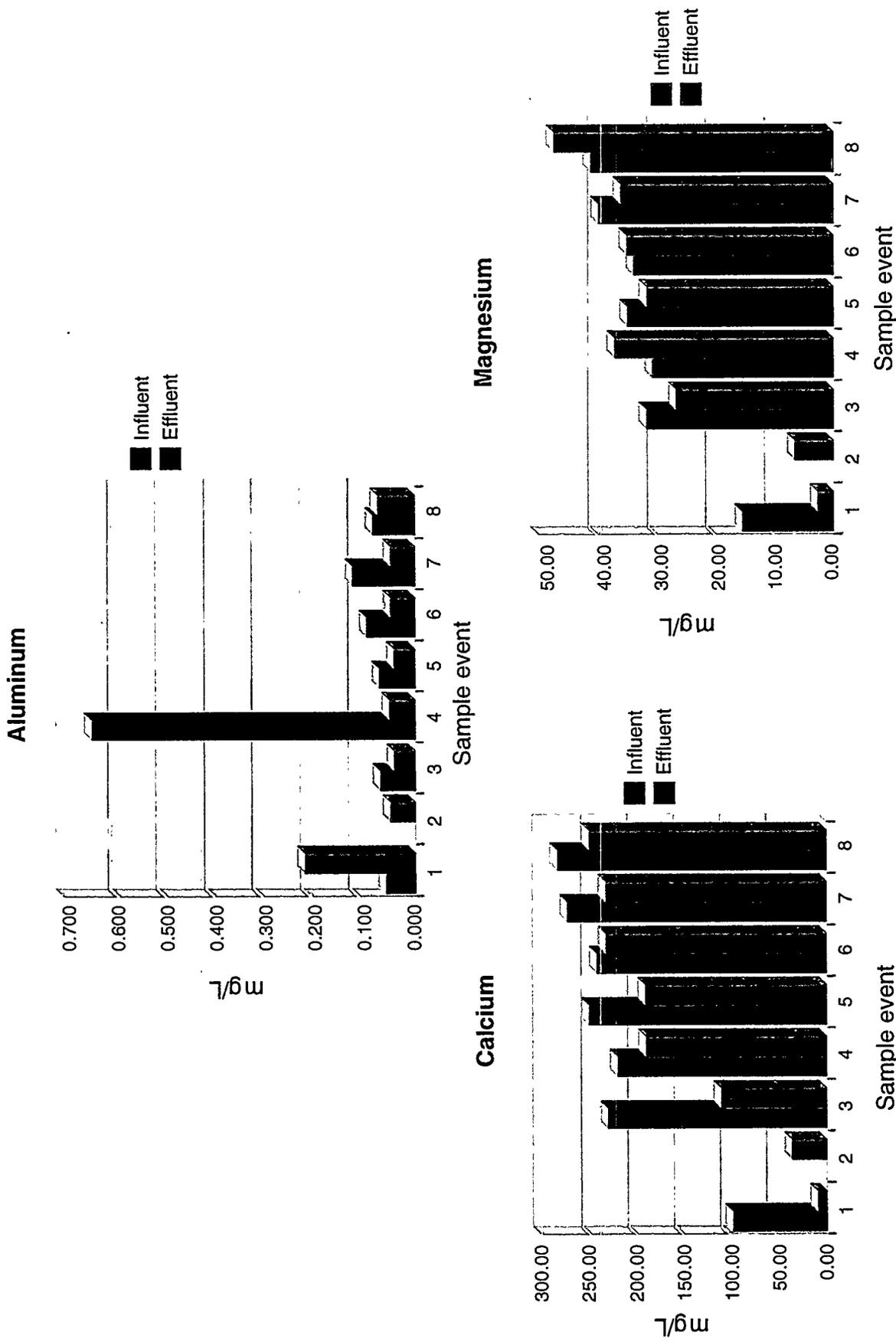


Fig. 8. Results of algal mat remediation on NT-1 water: aluminum, calcium, and magnesium.

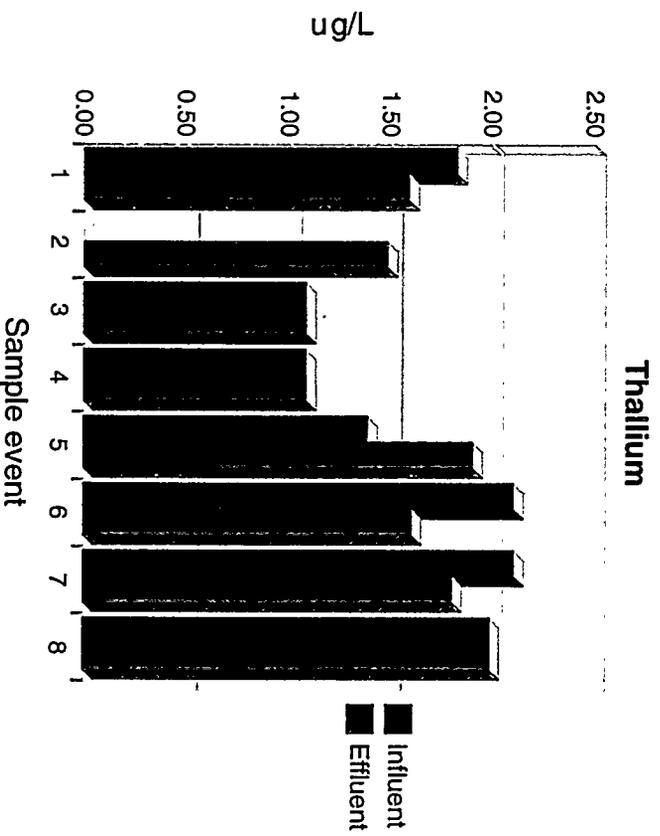
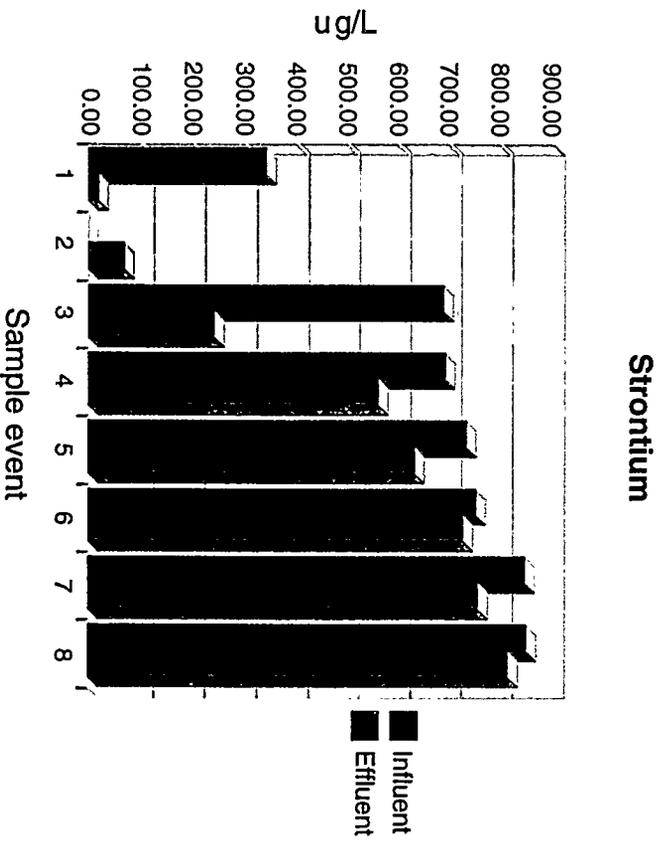
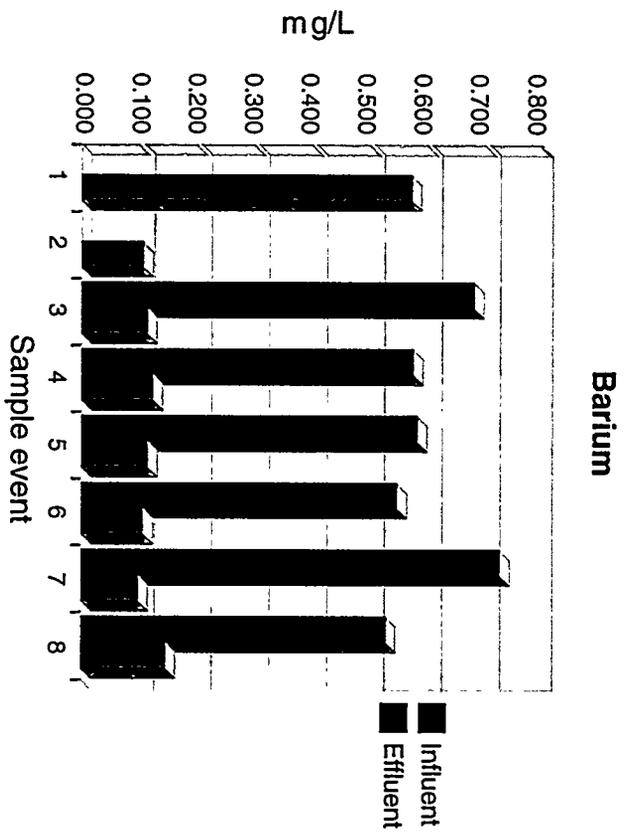


Fig. 9. Results of algal mat remediation on NT-1 water: barium, strontium, and thallium.

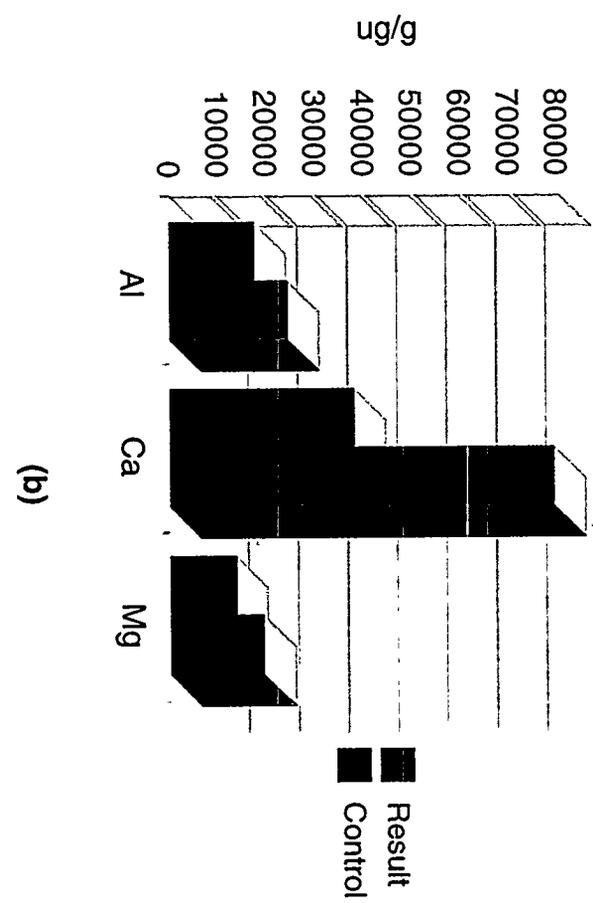
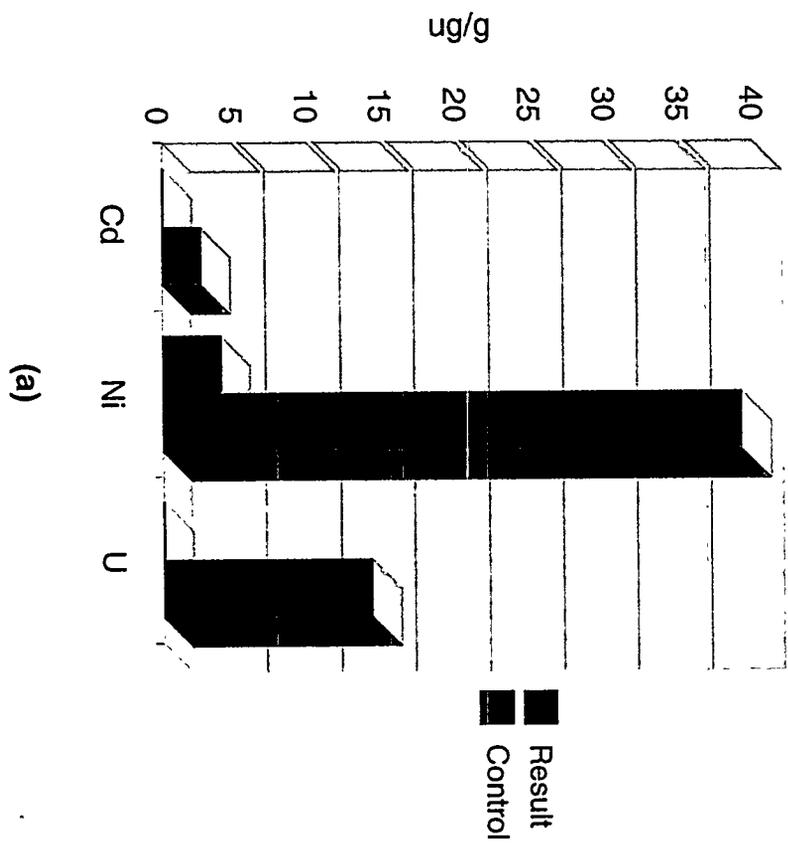


Fig. 10. Results of metal analysis on algal mats used to remediate NT-1 water: (a) cadmium, nickel, and uranium; (b) aluminum, calcium, and magnesium.

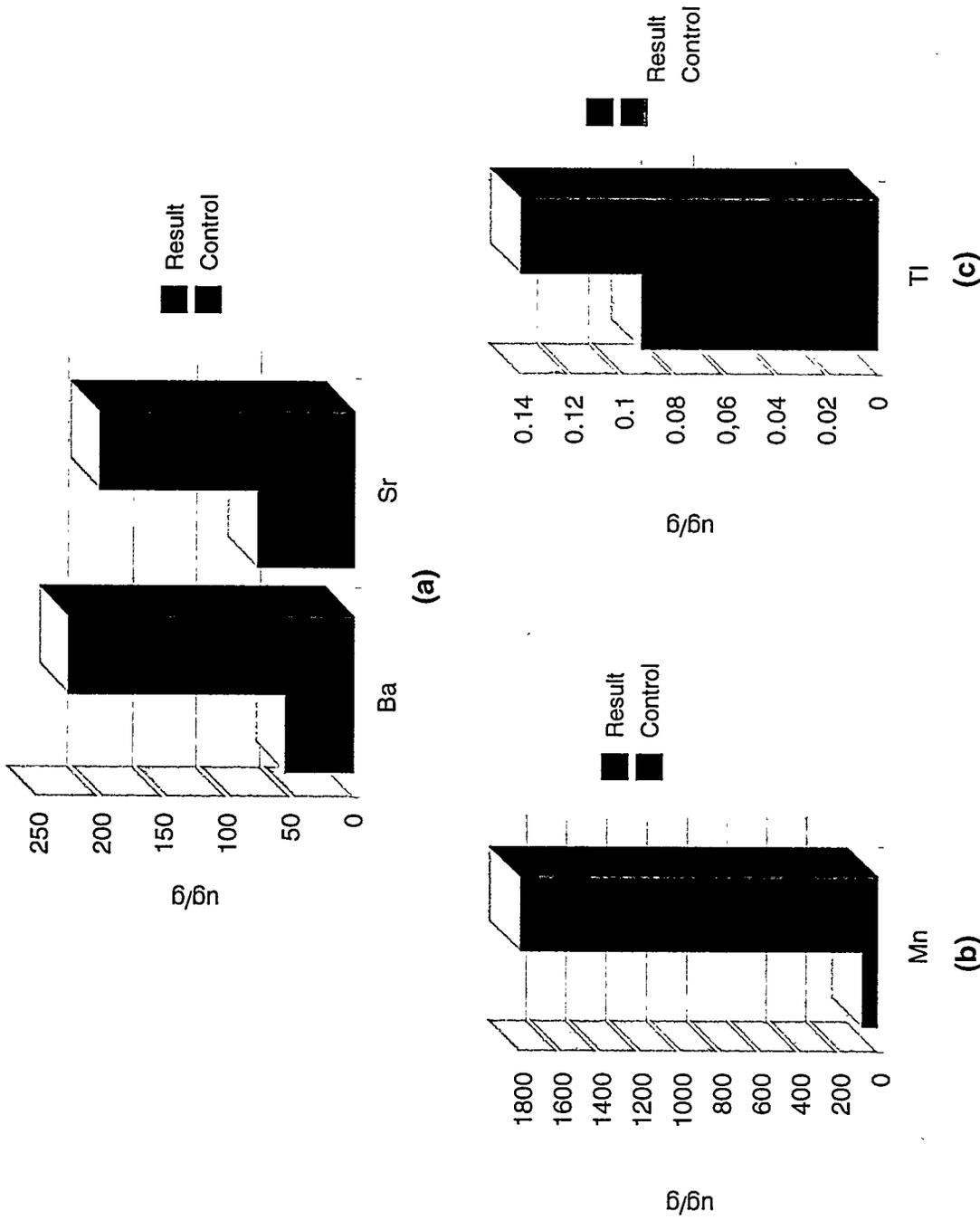


Fig. 11. Results of metal analysis on algal mats used to remediate NT-1 water: (a) barium and strontium, (b) manganese, and (c) thallium.

TABLES

Table 1. Field screening results of the SS-4 water treated by the algal mat method

Location	SS-4 INF	SS-4 EFF	SS-4 INF	SS-4 EFF	SS-4 INF	SS-4 EFF
Date	pH (su)	pH (su)	Cond. (mS/cm)	Cond. (mS/cm)	Temp (°C)	Temp (°C)
8-20-96	NR	8.64	NR	0.519	NR	32.60
8-23-96	7.19	8.59	0.715	0.454	26.60	28.40
8-27-96	6.87	7.88	0.818	0.683	21.50	27.70
8-30-96	7.23	8.01	0.779	0.731	27.90	32.10
9-3-96	7.36	8.04	0.788	0.741	24.70	26.90
9-6-96	7.16	8.19	0.950	0.744	24.40	39.20
9-11-96	7.34	8.36	0.930	0.699	23.90	25.30

Table 2. Mean influent and effluent concentrations of metals removed by mats treatment of SS-4 water

Metal	Mean influent concentration (ppb)	Mean effluent concentration (ppb)	Percent removal
Barium	186	111	40
Calcium	105	58	45
Magnesium	21,620	16,170	25
Manganese	9.5	5.1	46
Strontium	322	189	41
Uranium	146	11	93

Table 3. Field screening results of NT-1 water treated by the algal mat method

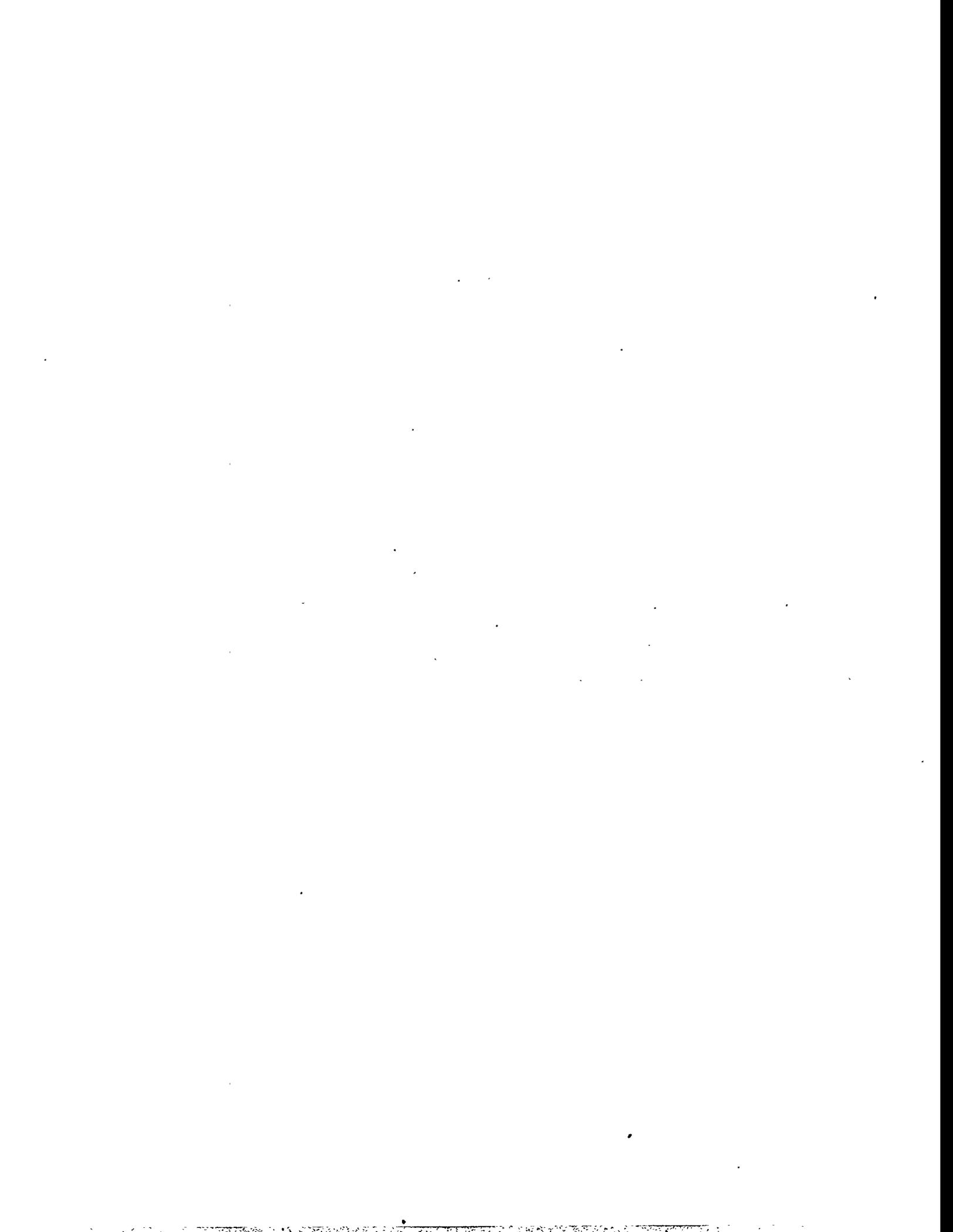
Location	NT-1 INF	NT-1 EFF	NT-1 INF	NT-1 EFF	NT-1 INF	NT-1 EFF
Date	pH (su)	pH (su)	Cond. (mS/cm)	Cond. (mS/cm)	Temp (°C)	Temp (°C)
8-20-96	NR	8.73	NR	NR	NR	NR
8-23-96	6.62	8.15	1.770	1.250	26.90	29.20
8-27-96	6.79	7.69	1.830	1.820	25.40	26.50
8-30-96	6.93	8.19	1.880	1.890	28.20	33.10
9-3-96	7.09	8.10	1.860	1.960	25.30	28.10
9-6-96	6.86	8.05	2.170	1.900	29.40	36.10
9-11-96	7.03	7.73	2.080	2.000	23.90	24.40

Table 4. Mean influent and effluent concentrations of metals removed by mats treatment of NT-1 surface water

Metal	Mean influent concentration (ppb)	Mean effluent concentration (ppb)	Percent removal
Aluminum	163	72	56
Barium	547	167	68
Calcium	227	156	31
Cadmium	38	1.5	96
Magnesium	32,670	27,960	14
Manganese	5,870	130	98
Nickel	168	15	91
Strontium	698	473	32
Thallium	1.66	1.58	5
Uranium	55.4	2.5	96

APPENDIX G

**BEAR CREEK VALLEY TREATABILITY STUDY
METAL UPTAKE USING RHIZOFILTRATION**



BEAR CREEK VALLEY TECHNOLOGY DEMONSTRATION

Metal Uptake Using Rhizofiltration

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September, 1996

EXECUTIVE SUMMARY

Rhizofiltration is the use of plants to remove low concentrations of metals from water by sorption and uptake into roots, stems, and leaves. This approach has distinct advantages when compared to conventional sorbent technology because of its ability to be low cost, effective at very low concentrations, and with minimal residual wastes for disposal. This project tested one proprietary rhizofiltration system developed by Phytotech, Inc., Princeton, New Jersey. The primary objective of the study was to determine if rhizofiltration could be an effective tool for metal removal under field conditions with water from several sources that contained varying amounts of dissolved metals. Water for this demonstration came from shallow groundwater, creeks, and springs in Bear Creek Valley (BCV) near the U.S Department of Energy's Oak Ridge Y-12 facility in Oak Ridge, Tennessee. These water sources have unique chemical characteristics that may confound conventional sorbents or rhizofiltration.

A series of batch tests were completed using triplicate aliquots of water from a spring (SS-4), surface water from a tributary to Bear Creek (NT-1), and subsurface water from a piezometer placed near a seep that discharges into NT-1. Each aliquot was treated with a tray of six mature sunflower plants in a hydroponic growth system. Water samples collected before and after treatment were analyzed for target metals. Representative roots and stems were also analyzed to observe uptake. Due to the novelty of this approach, the operations and overall effort required to complete these tests were weighed equally with the treatment effectiveness to determine overall feasibility for this application.

Results showed that the hydroponic rhizofiltration system was effective in removing uranium, aluminum, cadmium, nickel, sodium, and manganese. Removal rates for a given metal were highly variable between batches, ranging from a low of 13% to a high of 96%. Since each batch was different and the screening period was brief, it was not possible to develop the results into a database that can be used to predict performance for a given target.

Several operational complications caused the tests to be run under adverse conditions. Less than optimal light and other minor factors during propagation resulted in lower root yield per plant compared to other studies. The extreme heat of the days during testing in August caused the plants to wilt during mid-day; although they recovered during evening hours, the stress may have impacted treatment. Waste management issues required that test plants be transported from the propagation site to the test site. Shock induced by transportation resulted in additional stress to test plants. Finally, all but the last batch test was completed without adequate aeration of test water. This caused two negative impacts: the plants did not get enough oxygen in the root environment which hindered adequate root growth, and the lack of circulation in the water limited contact between roots and dissolved metals.

The screening program provided the information necessary to understand the types of applications that may be appropriate for rhizofiltration. Rhizofiltration shows some promise as a tool to remove target metals from surface and groundwater. However, the stringent requirements for maintaining optimal conditions for plant growth may limit the applications of this remediation technology in BCV. As a result, phytoremediation may exceed acceptable requirements for low operation and maintenance for application in BCV.



1. INTRODUCTION

Phytoremediation has received significant consideration as a low cost alternative for the removal of metals from soil and water. Generally, this technology applies plants that are known to hyperaccumulate metals into their roots or upper plant mass. Target media can be soil or water; a multitude of site conditions have already been tested. In this study, rhizofiltration, using sunflower plants propagated in hydroponic growth systems, was employed to remove dissolved metals by either sorption to root mass, or transfer into the stems and leaves. Rhizofiltration is most competitive when applied to a waste stream with low metals concentrations, very low target metal concentrations, and flow rates between 100 and 1000 gpm. In addition to effective metal removal, rhizofiltration offers a unique advantage during disposal. The biomass used to sorb metals is minimal when air-dried. If allowable, the biomass can be treated by incineration or digestion to further reduce the waste volume and mass for disposal. This is a feature conventional sorbents cannot offer.

2. OBJECTIVE

The objectives of this project were to determine:

- plant tolerance of the harsh characteristics of water from Bear Creek Valley (BCV) tributaries,
- the effectiveness of the plants for metal removal from water, and
- operations and maintenance requirements for a field application.

3. METHODS

3.1 PLANT PROPAGATION

Sunflowers were grown in a hydroponic system according to proprietary methods developed by Phytotech, Inc. (Princeton, New Jersey). After 6 to 8 weeks of growth, trays of six sunflower plants were ready for testing. Plants were propagated in temperature and light-controlled greenhouses. Test plants were transported via covered vehicles several miles to the test site where they were placed in a polyethylene greenhouse without enhanced light or temperature control. Trays were placed such that roots were immersed in water at all times.

3.2 BATCH TESTS

Each test was completed in triplicate. For each water sample, approximately 40 gal of water were collected and evenly distributed into each of three 15-gal tubs. Aliquots of water from each test bucket were collected for analysis to determine pretreatment water quality conditions. The plants were placed in each test bucket within 2 hours after pretreatment sample collection.

Four batches were completed [(Table 1) All tables are at end of appendix]. With one exception, all tests were conducted for 48 hours. Batch 4 was allowed 72 hours. At the termination of the test, plant trays were removed from the water and their roots harvested and composited into a single sample per bucket. The shoots or upper plant mass used during Batch 4 were also harvested for analysis. Water samples were collected after the test period and submitted for analysis. Photographs of each batch test are provided in Fig. 1, parts a through d (figure is at end of appendix).

3.3 ANALYSES

Samples were collected and filtered at the test site. Prior to analysis, all samples were stored at 4°C. All metals analyses were conducted by Y-12 Analytical Services using ion coupled plasma spectroscopy according to EPA methods 6010 and 200.8.

Solids were prepared for analysis by initially air drying each sample in a paper bag. This was followed by heated drying at 100°C for at least 24 hours. Dried mass was then ground through a Wiley mill and passed through a 20 mesh screen. Sieved mass was acid digested and analyzed as described above for metal content.

4. RESULTS

4.1 PLANT VIABILITY

The photographs provided in Fig. 1, parts a through d, show the viability of plants during batch testing. All plants wilted in response to transport to the test site, but most plants recovered during the batch test. Plants in Batch 3 did not recover. In fact, within the test period, the plants wilted to the point where they would not stand. The stems were not brittle, so it was assumed there was some viability and some potential for treatment to occur.

4.2 WATER CHARACTERISTICS

The metal concentrations for test water samples prior to treatment are provided in Tables 2 and 3. Some species in NT-1 batches varied by more than two orders of magnitude. For example, aluminum values ranged from 0.035 mg/l in Batch 2 to 17.3 mg/l in Batch 4. This wide range is the difference between collecting surface water and seep water, all in close proximity. The range of metals concentrations provided an excellent set of test water to screen phytoremediation. In addition to aluminum, the primary constituents in NT-1 samples included barium, beryllium, boron, calcium, magnesium, manganese, potassium, sodium, thallium, uranium, and zinc.

The two SS-4 batches also varied with respect to metals concentration, but values for most species stayed within 50% variation. The primary constituents in SS-4 samples included calcium, magnesium, potassium, sodium, aluminum, barium, boron, and uranium.

4.3 METAL REMOVAL

Metal removal was determined primarily based on the change in aqueous water concentrations before and after treatment. The results of uranium removal are shown in Table 4. Four of the six tests showed a decline in uranium concentration after treatment, with a maximum removal of 50%. Uranium in SS-4 was slightly lower in post-treatment water, suggesting removals between 8 and 16% (Table 4).

Other metals that were removed from test water are listed in Table 5. The best and most consistent removal activity observed was aluminum. It was removed significantly in four of the six batch tests, with as much as 90% removed. The best aluminum removal was observed in Batch 4, which maintained the most ideal conditions relative to water aeration and air temperature as well as the highest initial aluminum concentration. Other metals were noted to decline after treatment, but the results were sporadic between batches. Even with the extreme stress endured during Batch 3, metals were removed.

Results from analysis of the roots and shoots samples were considered to account for the mass lost from the water during treatment. Data are provided in Table 6. Metal contents in the roots were highly variable, and it was not possible to account for mass balance comparing metals removed from water to those absorbed in the roots and shoots. Table 7 lists those metals that were detectable in plant shoots. Manganese, sodium, cadmium, and nickel were all found to be higher in shoots after treatment compared to shoots that were not exposed to test water. Strontium was actually lower after treatment. Further investigation discovered that strontium is a key component of the nutrients used to propagate plants; therefore, the presence of strontium due to treatment of test water could not be determined.

5. SUMMARY

The screening test was intended to demonstrate this new potential remediation application under realistic field conditions. The heat of the summer, harsh test water quality, and lack of aeration for roots in test water certainly provided severe but realistic conditions. Results of six different batch tests on NT-1 and SS-4 water samples showed that, even under adverse conditions, the sunflower-based rhizofiltration system developed by Phytotech, Inc. was effective in removing uranium, aluminum, sodium, potassium, nickel, and cadmium from test water. Removal rates were as high as 96% based on the difference in concentrations in water before and after treatment. However, data could not be compared to confirm that the mass removed from the water was the same as that which was absorbed by the roots system. In fact, the adverse conditions caused variability that prohibited using the results as a predictive database for future applications.

An important evaluation criterion for the BCV application is the degree to which the technology is passive. Phytotech, Inc. has demonstrated systems that are suspended in standing water (i.e., a pond) so that pumping is not required. This approach would be difficult to manage in the BCV tributaries due to their variable flow. If it was implemented in the tributaries, considerable effort still would be required to propagate and transfer plants on a daily basis. This requirement is a disadvantage for this specific application. Advantages of rhizofiltration and phytoremediation are the demonstrated ability to remove dissolved metals from water and residual wastes that are easily managed for disposal.

6. RECOMMENDATIONS

The ideal system for a BCV application would be passive and low operations and maintenance requirements. After testing this technology, it is clear that rhizofiltration would work best with a fully operational greenhouse and support facilities to propagate and care for plants. However, under field conditions at Y-12 Plant, rhizofiltration was found to be effective in removing metals from surface water and groundwater, even under the adverse conditions encountered. Therefore, it is recommended that this technology be considered for other potential applications, including the BCV application, if the requirement for passive treatment changes.

FIGURES

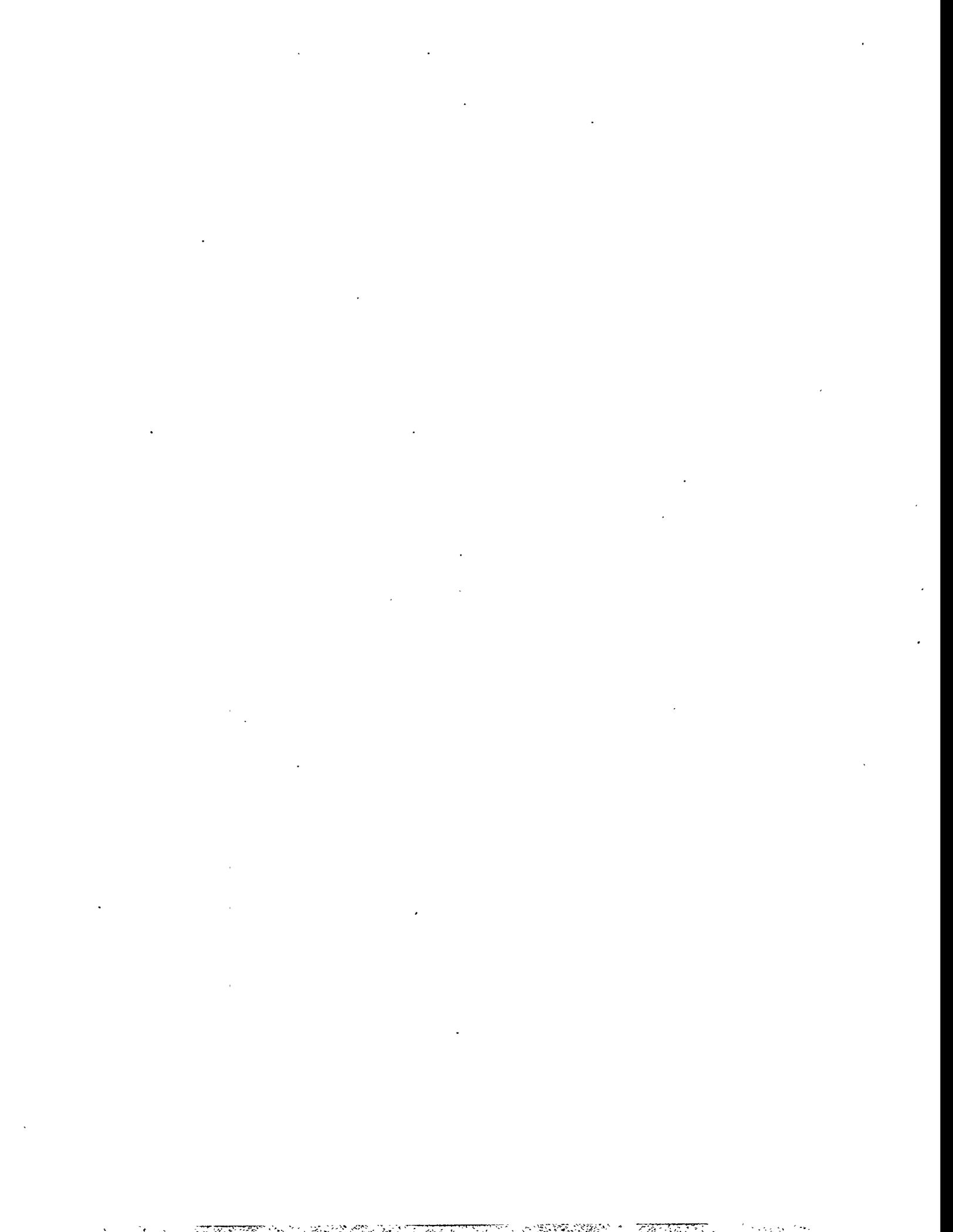




Fig. (a)



Fig. (b)

**Fig. 1. Phytoremediation batch tests: Batch 1 (a), Batch 2 (b).
Batches 1 and 2 used NT-1 surface water and SS-4 water.**

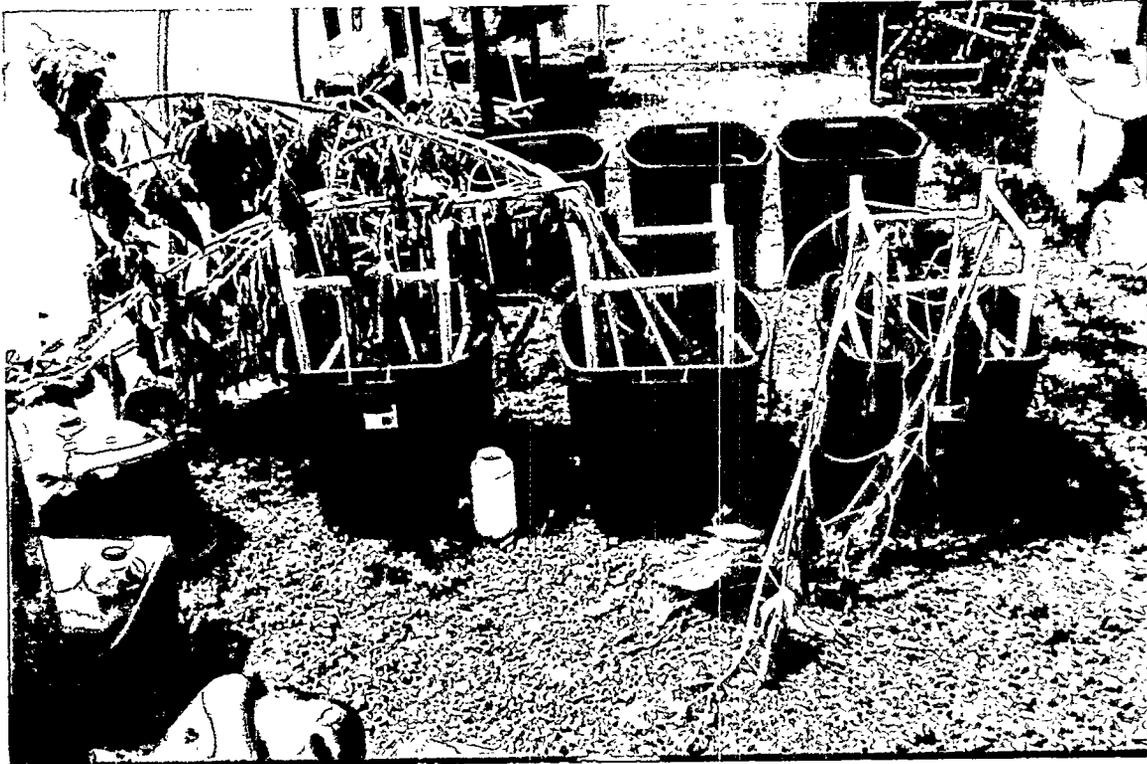


Fig. (c)



Fig. (d)

Fig. 1 (continued). Phytoremediation batch tests: Batch 3 (c), Batch 4 (d). Batch 3 used NT-1 piezometer water with no aeration provided during testing. Batch 4 used NT-1 piezometer water with intermittent aeration during testing.

File VII

TABLES



Table 1. Phytoremediation batch tests

Batch number	NT-1	SS-4	Note
1	X	X	Water was collected from surface water sources within days of heavy rainfall.
2	X	X	Water was collected from surface water close to baseline flow.
3	X		Water was collected from a piezometer (subsurface); no aeration was provided during testing.
4	X		Water was collected from a piezometer (subsurface); intermittent aeration was provided to each bucket during testing.

Table 2. Pretreatment values in test water from NT-1

Analyte	Values (mg/L) represent the average of three replicate samples prior to treatment			
	Batch 1	Batch 2	Batch 3	Batch 4
Aluminum	0.19	0.035	16.3	17.3
Barium	0.073	0.38	11.3	14
Beryllium			0.0123	0.0117
Boron	0.027	0.028	0.0663	
Cadmium		0.022	0.78	0.88
Calcium	40.7	140	2333	2533
Cobalt			0.51	0.58
Copper	0.0044	0.0058		
Iron	0.083	0.0056	0.19	0.21
Magnesium	0.083	21.3		380
Manganese	0.049	3.37	143	160
Nickel	0.0113	0.097	3.63	4
Phosphorous	0.22	0.22		
Potassium	3.9	4.4	40	51.7
Sodium	6.13	21	403	440
Strontium	0.15	0.43	6	6.53
Titanium	0.0038	0.0038	0.049	0.052
Thallium			6	0.0014
Uranium	0.00763	0.0176	0.006	0.006
Zinc	0.003	0.037	0.07	

Table 3. Pretreatment values in test water from SS-4

All values are mg/l

Analyte	Batch 1	Batch 2
Aluminum	0.053	0.0397
Barium	0.087	0.137
Boron	0.044	0.045
Calcium	57.7	73
Lithium	0.015	0.0187
Magnesium	13	18
Manganese	0.0032	0.00157
Potassium	2.97	2.4
Sodium	11	11.7
Strontium	0.15	0.2
Uranium	0.0757	0.16

Table 4. Uranium removal by rhizofiltration

Test water	Uranium concentration ($\mu\text{g/L}$)		
	Before	After	Percent removed
NT-1 Batch 1	7.6	3.8	50.2
NT-1 Batch 2	17.6	22.0	--
NT-1 Batch 3	6.1	5.1	16.4
NT-1 Batch 4	5.9	8.5	--
SS-4 Batch 1	75.7	69.3	8.4
SS-4 Batch 2	160	133	16.7

Table 5. Metals removed during rhizofiltration treatment

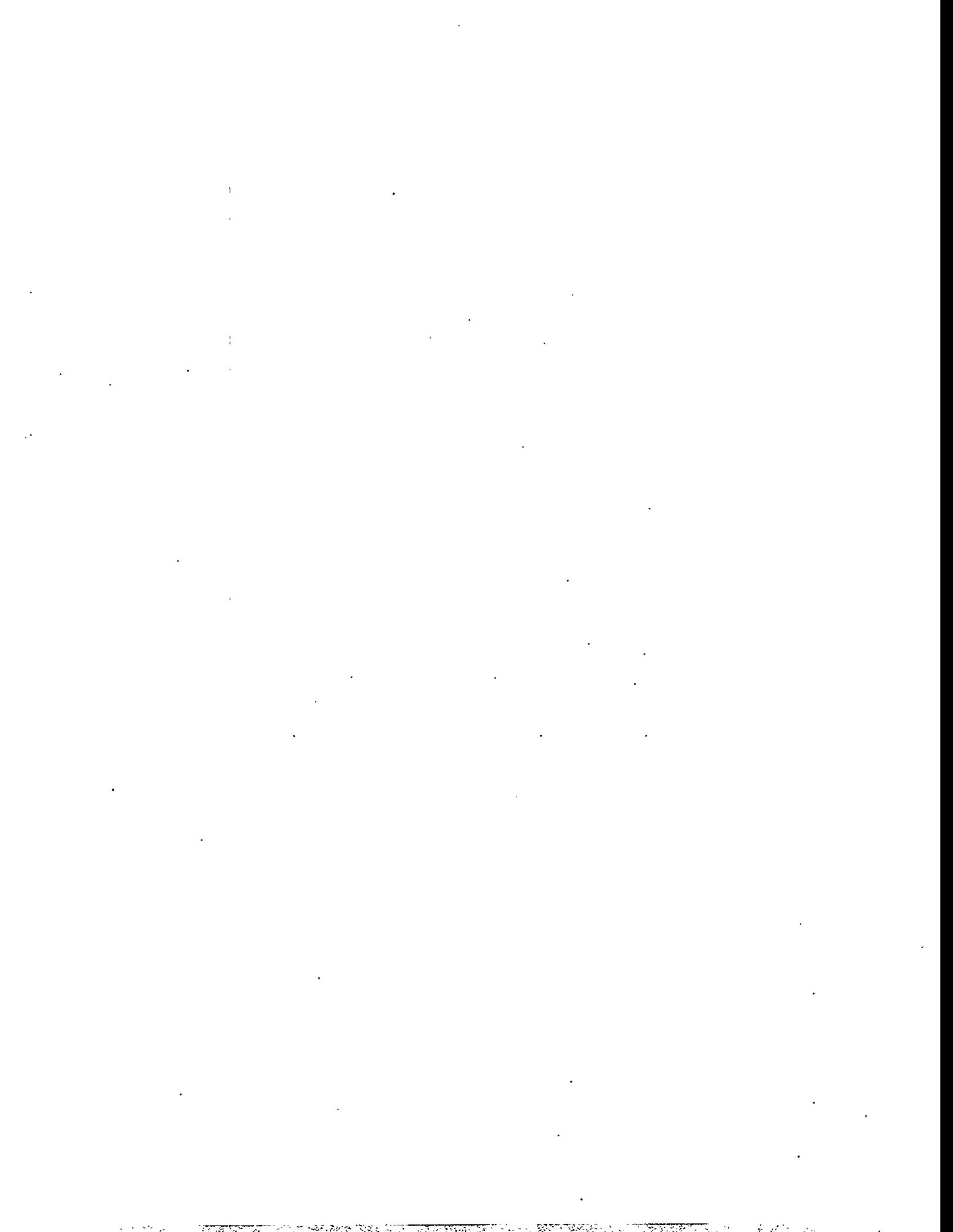
Analyte	Source	Concentration (mg/L)		Percent removed
		Before	After	
Aluminum	NT-1, Batch 1	0.19	0.39	80
	NT-1, Batch 3	16	12	24
	NT-1, Batch 4	17.3	1.77	90
	SS-4, Batch 1	0.053	0.046	13
Cadmium	NT-1, Batch 2	0.22	0.12	46
Iron	NT-1, Batch 1	0.083	0.0056	93
	NT-1, Batch 3	0.19	0.056	71
	NT-1, Batch 4	0.21	0.056	73
Manganese	NT-1, Batch 1	0.049	0.0018	96
Nickel	NT-1, Batch 2	0.106	0.086	19
Potassium	NT-1, Batch 1	3.9	2.06	47
Silver	NT-1, Batch 1	0.019	0.008	60

Table 6. Comparison of metals removed in water to metals absorbed by roots

Analyte	Source	Mass removed from water (μg)	Mass taken up in roots (μg)	Percent mass in roots compared to mass removed from water
Aluminum	NT-1, Batch 1	7768	10125	130
	NT-1, Batch 3	338162	91455	27
	NT-1, Batch 4	782116	243055	31
Iron	NT-1, Batch 1	3851	14864	386
	NT-1, Batch 3	7258	156	2
	NT-1, Batch 4	8048	5152	64
Manganese	NT-1, Batch 1	2345	4647	198
Sodium	NT-1, Batch 1	18745	-440	-2
Uranium	NT-1, Batch 1	218	51	24
	NT-1, Batch 3	108	-2.5	-2
	SS-4, Batch 1	840	387	46
	SS-4, Batch 2	2331	309	13

Table 7. Metal uptake in plant shoots from NT-1 Batch 4

Analyte	Treatment shoots ($\mu\text{g/g}$)	Control shoots ($\mu\text{g/g}$)
Manganese	280	68
Sodium	293	130
Cadmium	1.5	0.2
Strontium	273	430
Nickel	3.6	1.5



APPENDIX H

**SUMMARY OF GROUNDWATER AGGREGATE DATA
AND FURTHER REMEDIAL GOAL OPTIONS
FOR SURFACE WATER AND GROUNDWATER**

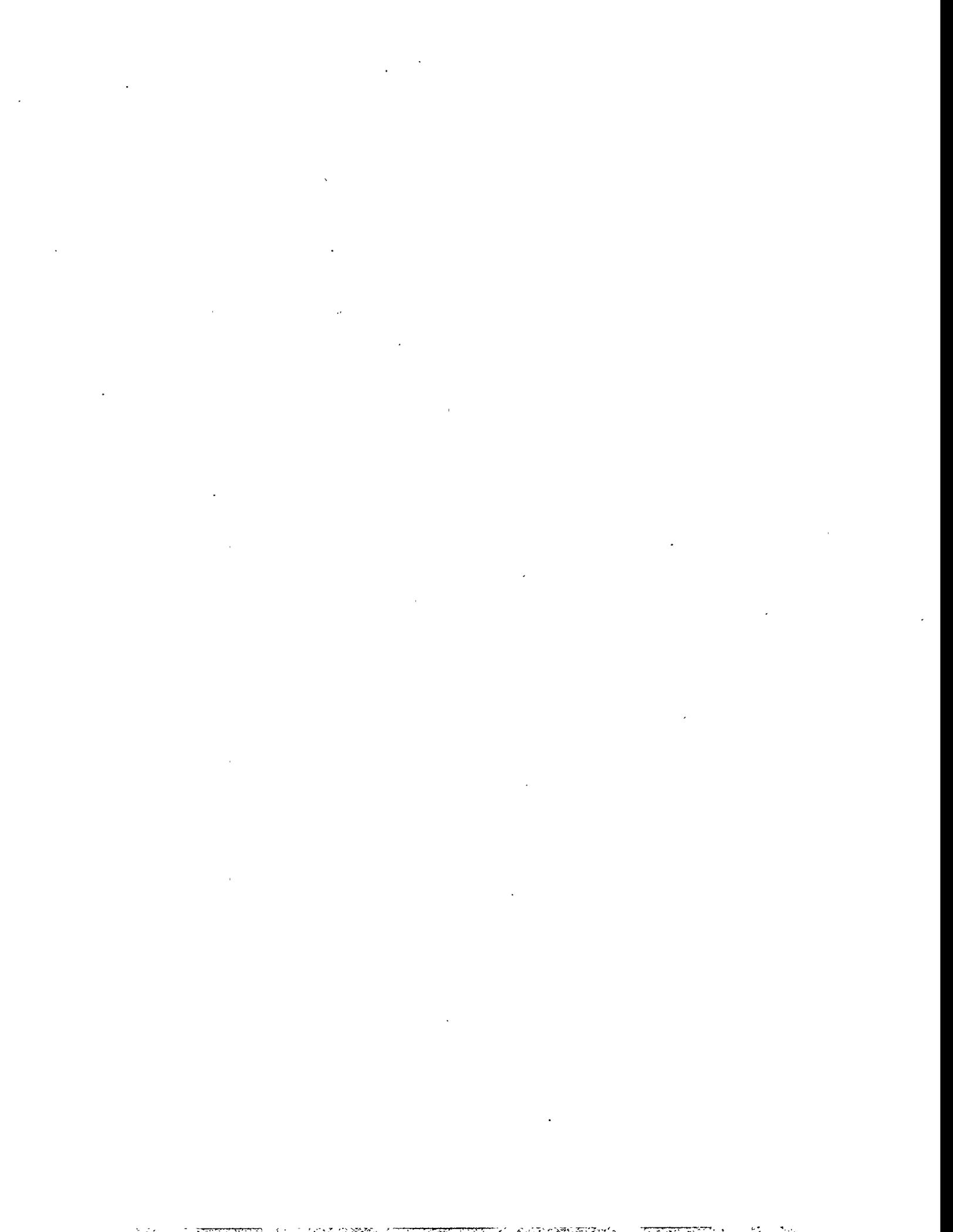


Table H.1. Summary of selection of site-related chemicals and radionuclides, S-3 Site groundwater aggregate

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
<i>Inorganics</i>							
Aluminum (mg/L)	130/160	23/23	6	0.0230	800	81.046	> 5% of wells with median > UTL
Antimony (mg/L)	0/149	0/20	0	0	0	0.0250	≤ 5% of wells with median > UTL
Arsenic (mg/L)	1/26	1/9	0	0.0090	0.0090	0.0032	≤ 5% of wells with median > UTL
Barium (mg/L)	192/192	24/24	10	0.0012	380	19.137	> 5% of wells with median > UTL
Beryllium (mg/L)	26/152	11/22	7	0.0003	0.1100	0.0119	> 5% of wells with median > UTL
Boron (mg/L)	161/175	24/24	10	0.0041	4.4000	0.2937	> 5% of wells with median > UTL
Cadmium (mg/L)	64/231	10/25	9	0.0020	4	0.1737	> 5% of wells with median > UTL
Calcium (mg/L)	235/235	26/26	15	0.6200	10,000	1,665.6	Mean concentration > 1,000 mg/L ^c
Chromium (mg/L)	34/235	13/25	2	0.0100	0.3100	0.0174	> 5% of wells with median > UTL
Cobalt (mg/L)	32/160	11/23	6	0.0051	2.3000	0.2678	> 5% of wells with median > UTL
Copper (mg/L)	96/161	20/21	8	0.0041	3.1000	0.2778	> 5% of wells with median > UTL
Iron (mg/L)	164/167	23/23	4	0.0051	28	3.5856	Essential element
Lead (mg/L)	80/244	21/26	4	0.0040	0.6000	0.0106	> 5% of wells with median > UTL
Lithium (mg/L)	13/13	7/7	NA ^d	0.0130	3.5000	0.8819	6/7 wells with median > WOE UTL ^e
Magnesium (mg/L)	235/235	26/26	14	0.0610	2,500	263.317	Essential element
Manganese (mg/L)	173/176	24/24	10	0.0011	220	24.162	> 5% of wells with median > UTL
Mercury (mg/L)	48/243	15/26	6	0.0002	0.1100	0.0042	> 5% of wells with median > UTL
Molybdenum (mg/L)	171/149	3/19	0	0.0110	0.0230	0.0062	≤ 5% of wells with median > UTL
Nickel (mg/L)	43/160	22/24	10	0.0110	20	2.0736	> 5% of wells with median > UTL

Table H.1 (continued)

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
Niobium (mg/L)	6/10	4/5	NA ^e	0.0075	0.1000	0.0271	4/7 wells with detects ^f
Potassium (mg/L)	208/228	26/26	13	0.6400	200	30.9542	Essential element
Selenium (mg/L)	3/50	3/10	0	0.0100	0.0140	0.0025	≤5% of wells with median > UTL
Silicon (mg/L)	88/88	24/24	2	0.1800	39	9.9865	> UTL in 2 wells; component of minerals
Silver (mg/L)	0/17	0/6	0	0	0	0.0050	≤5% of wells with median > UTL
Sodium (mg/L)	235/235	26/26	14	1.2000	3,200	357.61	Essential element
Strontium (mg/L)	150/150	22/22	11	0.0085	340	17.932	>5% of wells with median > UTL
Thallium (mg/L)	1/14	1/8	NA ^e	0.0100	0.0100	0.0050	1 detect at the detection limit ^f
Thorium (mg/L)	1/149	1/20	1	0.2800	0.2800	0.1090	≤5% of wells with median > UTL
Tin (mg/L)	3/6	3/6	0	0.0110	0.0180	0.0095	≤5% of wells with median > UTL
Titanium (mg/L)	10/13	7/7	NA ^e	0.0097	0.8500	0.2365	3/7 wells with median > WQE UTL ^f
Total uranium (fluorometric) (mg/L)	124/243	22/26	11	0.0010	44	2.8959	>5% of wells with median > UTL
Vanadium (mg/L)	9/149	5/20	2	0.0052	0.0360	0.0040	>5% of wells with median > UTL
Zinc (mg/L)	159/172	24/24	12	0.0012	26	0.4970	>5% of wells with median > UTL
Zirconium (mg/L)	4/9	3/4	0	0.0170	0.0510	0.0182	≤5% of wells with median > UTL
<i>Common Anions</i>							
Ammonia nitrogen (mg/L)	5/10	2/4	NA ^e	1.5000	4.7600	1.19	No background UTL; nitrate = SRC
Chloride (mg/L)	205/216	26/26	13	0.8600	1.341	106.2	>5% of wells with median > UTL

Table H.1 (continued)

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
Fluoride (mg/L)	118/253	23/25	7	0.1600	110	1.32	> 5% of wells with median > UTL
Kjeldahl nitrogen (mg/L)	6/10	4/4	NA ^e	0.2000	1.8000	0.73	No background UTL; nitrate = SRC
Nitrate (mg/L)	151/235	19/26	17	0.6400	13.400	1.659	> 5% of wells with median > UTL
Nitrite (mg/L)	1/8	1/4	NA ^e	6.7000	6.7000	20.2	No background UTL
Sulfate (mg/L)	171/174	23/23	5	2	2.204	204.7	> 5% of wells with median > UTL
<i>Organics</i>							
1,1,1-Trichloroethane (µg/L)	36/290	9/27	0.4900	28	3.8	> 5% of wells with detects	
1,1,2-Trichloroethane (µg/L)	1/288	1/26	1	1	2.5	< = 5% of wells with detects	
1,1-Dichloroethene (µg/L)	11/288	3/26	1	1	2.5	< = 5% of detects	
1,2-Dichloroethane (µg/L)	1/288	1/26	4	4	2.5	< = 5% of wells with detects	
1,2-Dichloroethene (µg/L)	10/240	3/25	1	100	5.0	> 5% of wells with detects	
2,4-Dinitrophenol (µg/L)	2/11	1/3	14	77	26.8	> 5% of wells with detects	
2-Butanone (µg/L)	19/288	9/26	2	32	5.0	> 5% of wells with detects	
2-Chloroethylvinyl ether (µg/L)	1/53	1/10	4	4	5	< = 5% detects	
2-Hexanone (µg/L)	4/288	3/26	1	4	5	< = 5% detects	
2-Nitrophenol (µg/L)	5/11	1/3	18	71	20.3	> 5% of wells with detects	
4-Methyl-2-pentanone (µg/L)	1/289	1/27	97	97	8.4	≤ 5% of wells with detects	
4-Nitrophenol (µg/L)	5/11	1/3	22	120	30.3	> 5% of wells with detects	
Acetone (µg/L)	62/294	19/27	2	6,000	51.8	> 5% of wells with detects	

Table H.1 (continued)

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
Benzene ($\mu\text{g/L}$)	17/288	4/26		0.0000	3	2.5	> 5% of wells with detects
Benzenemethanol ($\mu\text{g/L}$)	2/11	1/3		2	2	4.2	All detects < detection limit
Benzoic acid ($\mu\text{g/L}$)	2/11	2/3		6	58	25.0	> 5% of wells with detects
Bis(2-ethylhexyl)phthalate ($\mu\text{g/L}$)	6/11	2/3		1	32	6.3	> 5% of wells with detects
Bromodichloromethane ($\mu\text{g/L}$)	3/288	2/26		2	3	2.5	< = 5% detects
Bromoform ($\mu\text{g/L}$)	1/288	1/26		2	2	2.5	< = 5% of wells with detects
Butylbenzylphthalate ($\mu\text{g/L}$)	2/11	2/3		1	1	3.3	All detects < detection limit
Carbon disulfide ($\mu\text{g/L}$)	7/288	5/26		0.7	2	2.5	< = 5% detects
Carbon tetrachloride ($\mu\text{g/L}$)	1/288	1/26		0.7	0.7	2.5	< = 5% of wells with detects
Chlorobenzene ($\mu\text{g/L}$)	2/288	2/26		0.6	3	2.5	< = 5% detects
Chloroform ($\mu\text{g/L}$)	90/292	14/27		0.0000	69	7.0	> 5% of wells with detects
Chloromethane ($\mu\text{g/L}$)	1/288	1/26		10	10	5	< = 5% of wells with detects
Dibromochloromethane ($\mu\text{g/L}$)	1/288	1/26		1	1	2.5	< = 5% of wells with detects
Di-n-butylphthalate ($\mu\text{g/L}$)	1/11	1/3		2	2	4.2	All detects < detection limit
Di-n-octylphthalate ($\mu\text{g/L}$)	2/11	2/3		2	3	3.5	All detects < detection limit
Dimethylbenzene ($\mu\text{g/L}$)	15/288	5/26		1	16	2.5	> 5% of wells with detects
Ethylbenzene ($\mu\text{g/L}$)	7/288	3/26		0.6	4	2.5	< = 5% detects
Methylene chloride ($\mu\text{g/L}$)	88/296	19/27		1	560	17.3	> 5% of wells with detects
Naphthalene ($\mu\text{g/L}$)	4/11	1/3		1	1	3.7	All detects < detection limit
Phenols (mg/L)	2/15	2/7		0.0010	0.0020	0.0026	> 5% of wells with detects

Table H.1 (continued)

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
Tetrachloroethene (µg/L)	79/296	12/27		0.5000	9.000	269.9	> 5% of wells with detects
Toluene (µg/L)	44/298	11/27		0.4000	35	3.2	> 5% of wells with detects
trans-1,2-Dichloroethene (µg/L)	2/61	2/13		2	2	2.8	< = 5% detects
Trichloroethene (µg/L)	24/289	6/27		0.8000	16	2.9	> 5% of wells with detects
Vinyl acetate (µg/L)	1/288	1/26		1	1	5	< = 5% of wells with detects
<i>Radioactivity</i>							
Alpha activity (pCi/L)	50/156	14/18		5.1	24400	615.7	> 5% detects
Americium-241 (pCi/L)	5/9	1/4		27	36	7.5	> 5% detects
Beta activity (pCi/L)	75/156	17/18		11.09	75000	2620.8	> 5% detects
Cesium-137 (pCi/L)	2/4	2/4		6	9.7	5.25	> 5% detects
Iodine-125/129 (pCi/L)	/2	/1		.	.	2.7	No detects
Iodine-129 (pCi/L)	/1	/1		.	.	2.7	No detects
Iodine-131 (pCi/L)	/1	/1		.	.	0	No detects
Neptunium-237 (pCi/L)	7/11	1/4		40	1090	106.3	> 5% detects
Plutonium-238 (pCi/L)	/6	/3		.	.	0.14	No detects
Plutonium-239/240 (pCi/L)	/7	/4		.	.	0	No detects
Radium (pCi/L)	1/1	1/1		35.139	35.139	35.14	> 5% detects
Radium-228 (pCi/L)	/1	/1		.	.	0.34	No detects
Strontium-90 (pCi/L)	7/9	3/4		147	254	194	> 5% detects
Technetium-99 (pCi/L)	10/11	3/4		50	80400	17537.5	> 5% detects

Table H.1 (continued)

Analyte ^a	Freq of detect	Freq of wells w. detects	Wells w. median > bkgd ^b	Min detect	Max detect	Mean of the medians ^c	Comment
Thorium-228 (pCi/L)	1/4	1/4		3.2	3.2	0.95	> 5% detects
Thorium-230 (pCi/L)	2/4	2/4		0.41	0.59	0.56	> 5% detects
Thorium-232 (pCi/L)	/3	/3		.	.	0.03	No detects
Tritium (pCi/L)	9/12	2/4		620	5406	1245.4	> 5% detects
Uranium-234 (pCi/L)	10/11	3/4		1.5	4650	660.4	> 5% detects
Uranium-235 (pCi/L)	8/11	2/4		3.6	547	68.8	> 5% detects
Uranium-238 (pCi/L)	10/11	3/4		0.52	13600	1601.4	> 5% detects

^a Analytes detected at least once are summarized. Results reflect data validation and data usability screens.

^b Background criteria have been established by *Determination of Reference Concentrations for Inorganic Analytes in Groundwater at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee* (Energy Systems 1996). The background value for an analyte varies depending upon the groundwater cluster that a well has been assigned to so no single background value applies to each analyte. Refer to Sect. C.2 and the above referenced document for a discussion of the approach to evaluating groundwater background, the groundwater background values, and the well cluster assignments.

^c The mean of the medians is the arithmetic mean of the median concentration of an analyte for each well. In calculating the mean of the medians it was assumed that nondetects are equal to one-half the detection limit for chemicals. Radionuclide data qualified as nondetect based on comparison to minimal detectable activities or counting errors are set equal to the reported value.

^d High concentrations of calcium in solution may be harmful to the environment (see Appendix G for details).

^e No background value was available from the above referenced source. Values for lithium and titanium UTLs were calculated using data from 13 groundwater wells that were previously considered as reasonable background wells in the GWQRs (HSW 1995). The values are 0.071 mg/L for lithium and 0.12 mg/L for titanium. See text for further details. Niobium and thallium were not detected in 13 groundwater wells that were previously considered as reasonable background wells and the background UTL values was, therefore, assumed to be less than the detection limit and detected values are considered as above background.

Table H.2. Remedial goal options for chemicals of concern identified for BCV surface water

Chemicals	Risk-based			ARARs-based	
	Human health ^a			ARARs AWQC	
	Residential	Ecological ^b		Human health	Ecological
		Benthic invertebrates	Piscivores		
Example of Entire Risk Range (ILCR of 10^{-6} to 10^{-4} , or HQ of 0.1 to 10):					
	10^{-6}	10^{-5}	10^{-4}		
Chloromethane (entire range)	0.0019	0.019	0.19		
Chloromethane (table value)	0.019	(values for an ILCR of 10^{-5} or an HQ of 1 will be presented)			

Inorganics (mg/L)

Antimony	0.013				
Arsenic	0.00056			0.0014	0.19
Barium	2.5				
Beryllium	0.00016				
Boron	3.3				
Cadmium	0.015	0.002			0.0011
Calcium		116			
Chromium					0.1 ^c
Copper					0.0118
Cyanide				220	0.0052
Fluoride	2.2				
Lead					0.0032
Manganese	4.8	6.6			
Mercury			0.126	0.00015	0.000012
Nickel	0.72	0.015		4.6	0.158
Nitrate (as N)	58				
Selenium	0.18				0.005
Silver					0.0041 ^d
Thallium				0.0063	
Uranium (total)	0.11	0.142			
Zinc					0.106

Table H.2 (continued)

Chemicals	Risk-based		ARARs-based		
	Human health ^a	Ecological ^b		ARARs AWQC	
	Residential	Benthic invertebrates	Piscivores	Human health	Ecological
<i>Organics (mg/L)</i>					
1,1,2-Trichloroethane	0.0025			0.42	
1,1-Dichloroethene	0.00013			0.032	
1,2-Dichloroethane	0.0016			0.99	
1,2-Dichloroethene	0.33				
Benzene	0.0049			0.71	
Chloroform	0.0021			4.7	
Chloromethane	0.019				
Methylene Chloride				16	
Tetrachloroethene	0.0078			0.0885	
Toluene				200	
Trichloroethene	0.019			0.81	
Vinyl Chloride	0.00025			5.25	
<i>Radionuclides (pCi/L)</i>					
Neptunium-237	1.6				
Plutonium-238	1.6				
Potassium-40	38				
Radium (total Alpha)	1.6				
Strontium-90	8.5				
Technetium-99	340				
Thorium-228	2.1				
Uranium-233/234	11				
Uranium-235	10				
Uranium-238	7.7				

^a There are no chemicals of concern and therefore no Risk-based Human Health RGOs for the Recreational Scenario.

^b There are no Risk-based Ecological RGOs for Fish, Small Mammals, and Wide Ranging Species.

^c Value for Chromium total.

^d Maximum value.

Table H.3. Remedial goal options for chemicals of concern identified for BCV groundwater

Chemicals	Risk-based			ARAR-based		
	Human health		Ecological	ARARs AWQC		
	Residential	Plants		Federal primary MCLs	Human health	Ecological
Example of Entire Risk Range (ILCR of 10^{-5} to 10^{-4} , or HQ of 0.1 to 10):						
		10^{-5}	10^{-4}			
Chloromethane (entire range)		0.0019	0.019	(values for an ILCR of 10^{-5} or an HQ of 1 will be presented)		
Chloromethane (table value)		0.019				

Inorganics (mg/L)

Antimony	0.013	0.2 ^a	0.006		
Arsenic	5.6×10^{-4}			0.0014	0.19
Barium	2.5		2		
Beryllium	1.6×10^{-4}		0.004		
Boron	3.3				
Cadmium	0.015		0.005		0.0011
Chromium	0.16	0.05 ^a	0.1		0.1 ^b
Cobalt		0.06 ^a			
Copper		0.05 ^a	TT		0.0118
Cyanide			0.2	220	0.0052
Fluoride	2.2		4		
Iron		10 ^a			
Lead		0.02 ^a	TT		0.0032
Manganese	4.8	4 ^a			
Mercury	0.011		0.002	0.00015	1.2×10^{-5}
Molybdenum	0.18				
Nickel	0.72		-- 60FR33926	4.6	0.158
Nitrate (as N)	58		10		
Nitrite (as N)	3.6		1		
Nitrate + Nitrite (as N)			10		

Table H.3 (continued)

Chemicals	Risk-based		ARAR-based		
	Human health	Ecological	ARARs AWQC		
	Residential	Plants	Federal primary MCLs	Human health	Ecological
Selenium					0.005
Silver					0.0041 ^c
Strontium	22				
Sulfate			500		
Thallium			0.002	0.0063	
Vanadium	0.21				
Uranium (total)	0.11				
Zinc	11				0.106
<i>Organics (mg/L)</i>					
1,1,1-Trichloroethane	1.3		0.2		
1,1,2,2-Tetrachloroethane	7.1×10^4			0.11	
1,1,2-Trichloroethane	0.0025		0.005	0.42	
1,1-Dichloroethane	0.81				
1,1-Dichloroethene	1.3×10^4		0.007	0.032	
1,2-Dichloroethane	0.0016		0.005	0.99	
1,2-Dichloroethene	0.33				
1,2-Dichloropropane	0.0083				
1,4-Dichlorobenzene	0.03				
1,4-Dioxane	0.077				
2,4-Dimethylphenol	0.48				
2,4-Dinitrophenol	0.072			14	
2,4-Dinitrotoluene	0.0012				
2,6-Dinitrotoluene	0.0012				
2-Butanone	1.9				
4-Methyl-2-pentanone	0.16				

Table H.3 (continued)

Chemicals	Risk-based		ARAR-based		
	Human health	Ecological	ARARs AWQC		
	Residential	Plants	Federal primary MCLs	Human health	Ecological
Acetone	3.6				
Benzene	0.0049		0.005	0.71	
Benzidine	3.7×10^{-6}				
bis(2-Ethylhexyl)phthalate	0.047			0.059	
Bromodichloromethane	0.014				
Bromoform	0.11				
Carbon Tetrachloride	0.0021		0.005	0.044	
Chlorobenzene	0.039				
Chloroform	0.0021			4.7	
Chloromethane	0.019				
cis-1,2-Dichloroethene	0.36				
di-n-Octylphthalate	0.0099				
Dibromochloromethane	0.01				
Ethylbenzene			0.7	29	
Methylene Chloride	0.054		0.005	16	
PCB-1254	3.8×10^{-4}				
Pentachlorophenol	0.0028				
Phenol				4600	
Polychlorinated Biphenyls	5.7×10^{-5}			4.5×10^{-7d}	1.4×10^{-5d}
Tetrachloroethene	0.0078		0.005	0.0885	
Toluene	0.74		1	200	
trans-1,2-Dichloroethene	0.73		0.1	140	
Trichloroethene	0.019		0.005	0.81	
Trichlorofluoromethane	1.3				
Trihalomethanes (total)			0.1		
Vinyl Chloride	2.5×10^{-4}		0.002	5.25	

