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DEMONSTRATION RESULTS OF PHYTOREMEDIATION OF EXPLOSIVES-CONTAMINATED GROUNDWATER USING CONSTRUCTED WETLANDS AT THE MILAN ARMY AMMUNITION PLANT, MILAN, TENNESSEE

Volume I of IV
(Phase II Demonstration Results)

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
Aberdeen Proving Ground, Maryland 21010-5401

Funded Through

Prepared by
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Volume I of IV
(Phase II Demonstration Results)

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U.S. Army Environmental Center
Pollution Prevention and Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401
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14. ABSTRACT
This report describes a demonstration of phytoremediation methods to remediate explosives-contaminated groundwater. The demonstration was conducted at the Milan Army Ammunition Plant near Milan, Tennessee, using a gravel-based subsurface flow wetland and a lagoon-based surface flow wetland. The report provides demonstration results as they are related to the effectiveness of the wetlands; and provides cost and other information necessary for the transfer of the technology to the user community. The report concludes that gravel-based wetlands could be used to remediate groundwater contaminated with a variety of explosives including TNT and RDX and that, based on the demonstration results, the use of lagoon-based wetlands could not be recommended.

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Phytoremediation of Explosives-Contaminated Groundwater in Constructed Wetlands

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ABBREVIATIONS

A1	The Anaerobic Gravel-Based Demonstration Cell
A2	The Aerobic Gravel-Based Demonstration Cell
AAP	Army Ammunition Plant
2A-DNT	2-Amino-4,6-dinitrotoluene
4A-DNT	4-Amino-2,6-dinitrotoluene
AFUDC	Allowance for Funds Used During Construction
AL	Analytical Laboratory
B1	The First Lagoon-Based Demonstration Cell
B2	The Second Lagoon-Based Demonstration Cell
BOD-5	5-Day Biochemical Oxygen Demand
Br	Bromine
C	Carbon
°C	Degrees Celsius
Ca	Calcium
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
cm	Centimeter
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
CRREL	Cold Regions Research and Engineering Laboratory
CSTR	Continuous Stirred Tank Reactor
Cu	Copper
2,6-DANT	2,6-Diamino-4-nitrotoluene
2,4-DANT	2,4-Diamino-6-nitrotoluene
DAP	Diammonium Phosphate
1,3-DNB	1,3-Dinitrobenzene
DN-4,4-AZT	Dinitro-4,4'-azoxytoluene
3,5-DNA	3,5-Dinitroaniline
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
DO	Dissolved Oxygen
DoD	Department of Defense
EC	Electrical Conductivity
ECWTP	Explosives-Contaminated Wastewater Treatment Plants
EPA	Environmental Protection Agency
EPDM	Ethylene Propylene Diene Monomer
ESTCP	Environmental Security Technology Certification Program
Fe	Iron
FIA	Flow Injection Analyzer
FW	Fresh Weight
GAC	Granular Activated Carbon
g/m^2-day	grams per-square-meter per day
GMF	Granular Media Filter

ABBREVIATIONS (Continued)

GOCO	Government-Owned Contractor-Operated
gpm	Gallons per Minute
ha/day	Hectares/day
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High Performance Liquid Chromatography
hr	Hour
H_2SO_4	Sulfuric Acid
IC	Ion Chromatograph
IC_{25}	25% Inhibitory Concentration
ICP	Inductively Coupled Plasma
k	First-Order Rate Constant
Kg	Kilogram
Kg ha/day	Kg Hectares/day
Kg/hr	Kilograms/hour
k_{int}	Intrinsic First-Order Rate Constant
L	Liters
LAP	Load, Assemble, Pack
LIMS	Laboratory Information Management System
L/min	Liters per Minute
MAAP	Milan Army Ammunition Plant
MDL	Method Detection Limit
Mg	Magnesium
mg	Milligrams
mg/L	Milligrams per Liter
min	Minute
ml	Milliliter
Mn	Manganese
MOD	Milan Ordnance Depot
m-RDX	Mononitroso RDX
MRS	Milk Replacement Starter
mS/cm	milli-siemens per centimeter
NaBr	Sodium Bromide
NH_4-N	Ammonium Nitrogen
Ni	Nickel
NO_3	Nitrate
(NO_3+NO_2)-N	Nitrate + Nitrite Nitrogen
NPDES	National Pollutant Discharge Elimination System
NPOC	Non-Purgeable Organic Carbon
P	Phosphorus
Pb	Lead
PDA	Photodiode Array
PFR	Plug Flow Reactor
PO_4	Orthophosphate
PO_4-P	Orthophosphate - Phosphorus
ppb	Parts Per Billion
PVC	Polyvinyl Chloride
q	Hydraulic Loading Rate
QA	Quality Assurance

ABBREVIATIONS (Continued)

QC	Quality Control
R&D	Research and Development
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
STP	Sewage Treatment Plant
TAT	Triaminotoluene
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
TN-2,2-AZT	Tetranitro-2,2'-azoxytoluene
TN-2,4-AZT	Tetranitro-2',4-azoxytoluene
TN-4,4-AZT	Tetranitro-4,4'-azoxytoluene
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
t-RDX	Trinitroso RDX
TSS	Total Suspended Solids
TVA	Tennessee Valley Authority
TVA RM	Tennessee Valley Authority Resource Management
USACE	U.S. Army Corps of Engineers
USAEC	U.S. Army Environmental Center
USEPA	United States Environmental Protection Agency
WCOP	Wolf Creek Ordnance Plant
WES	Waterways Experiment Station
YSI	Yellow Spring Incorporated
Zn	Zinc

EXECUTIVE SUMMARY

Many Army ammunition plants across the country have problems with groundwater contaminated with explosives such as TNT, RDX, and HMX. To help address this problem, a field demonstration was initiated at the Milan Army Ammunition Plant (MAAP) near Milan, Tennessee, to demonstrate the feasibility of treating explosives-contaminated groundwater with constructed wetlands. The demonstration was funded by the Department of Defense Environmental Security Technology Certification Program (ESTCP).

This project was executed in three phases. During Phase I, the technology was prepared for use at MAAP. These preparations included conducting plant screening studies, conducting treatability studies, designing the demonstration facility, and constructing the demonstration facility. During Phase I, standard methods were developed to evaluate the ability of aquatic macrophytes (large aquatic plants) to lower the contaminant levels of TNT, RDX, and related compounds in explosives-contaminated water. Then, a variety of submergent and emergent aquatic macrophytes were screened for their ability to remediate the contaminated water. Next, treatability studies were undertaken to test the performance of surface and subsurface wetland configurations. Finally, the demonstration facility was designed and constructed. Two wetlands were constructed: a lagoon-based system and a gravel-based system. These systems will be described later.

During Phase II, the demonstration systems were operated for 16 months, monitored, and evaluated from both a technical and economic perspective. This document describes the results of the Phase II demonstration. Other aspects of the demonstration project (e.g., design, construction, technology transfer, and economic analysis) are also addressed.

During the course of Phase II, it became apparent that the gravel-based wetland's performance was better than the lagoon's and that acquiring additional data would be helpful to improve the design, operation, and economic success of commercial-scale gravel-based systems. Areas of interest included:

- Continuing to establish the effect of long-term plant growth on explosive remediation
- Continuing to examine nitrobody remediation at cold temperature

- Examining the use of alternate carbon sources in the anaerobic cell (cell A1)
- Establishing the anaerobic cell's performance at a lower flow rate
- Operate and maintain the system similar to that required for a full-scale remediation system to assist in obtaining accurate O&M cost data.

These issues were addressed by extending the operating period of the existing demonstration program. This extension is referred to as Phase III. The Phase III program ran from September 1997 to July 1998. To collect additional data, TVA funded portions of the Phase III demonstration. System operations and routine data collection activities were funded by ESTCP. The lagoon-based wetland was not operated during Phase III due to its poor performance in degrading RDX and difficulties in maintaining an adequate plant population within the lagoons.

The primary objective of the Phase II demonstration was to evaluate the technical feasibility of using wetlands for remediating explosives-contaminated water. The goal was to reduce TNT concentrations to levels less than 2 ppb and total nitrobody (including TNT, RDX, HMX, TNB, 2A-DNT, 4A-DNT) concentrations to levels less than 50 ppb.

Groundwater from two wells was used over the course of the Phase II demonstration. The first well, MI-146, was used from the start of the demonstration on June 17, 1996, until November 21, 1996. The groundwater from this well had an average total nitrobody concentration of 3,250 ppb. The second well, MI-051, was used from November 21, 1996, until the end of the Phase II demonstration on September 16, 1997. Well MI-051 continued to be used during Phase III. During Phase II, the groundwater from this well had an average nitrobody concentration of 9,200 ppb. Conversion to the second well was necessary due to falling explosive concentrations in the first well. Average influent concentrations of explosives in the water from each well were as follows:

Explosive	Well MI-146 (Before 11/21/96)	Well MI-051 (After 11/ 21/96)
TNT	1,250 ppb	4,440 ppb
RDX	1,770 ppb	4,240 ppb
TNB	110 ppb	330 ppb
HMX	110 ppb	91 ppb

To conduct the demonstration, two types of wetlands were designed and constructed. The first wetland was a lagoon-based surface-flow wetland and the second was a gravel-based subsurface-flow wetland. Both the gravel- and lagoon-based systems were designed for a total hydraulic retention time of approximately 10 days at an influent flow rate of 5 gpm per system. The lagoon-based system consisted of two lagoons (or cells) connected in series. Each cell had dimensions of 24 x 9.4 x 0.6 meters (length x width x height). The gravel-based system consisted of two gravel-filled beds (or cells) connected in series. The first cell was maintained in an anaerobic condition by adding milk replacement starter (MRS) to the water every two weeks. The second cell was maintained in an aerobic condition via a TVA patented process (patent 5,863,433). The anaerobic cell had dimensions of 32 x 11 x 1.4 meters (length x width x height). The aerobic cell had dimensions of 11 x 11 x 1.4 meters (length x width x height).

Both wetlands contained plants specifically selected to ensure explosives degradation. The lagoon-based system was planted with sago pond weed, water stargrass, elodea, and parrotfeather. The gravel-based system was planted with canary grass, wool grass, sweetflag, and parrotfeather.

Construction of the facility began on March 4, 1996, and was completed on June 15, 1996. The system operations began on June 17, 1996, with the introduction of explosives-contaminated water. The systems were operated until September 16, 1997, at which time the lagoon-based system was retired and the gravel-based system's operations were continued for Phase III.

During the course of the Phase II demonstration, influent and effluent water samples were regularly collected from the lagoon- and gravel-based systems on a biweekly basis (i.e., every two weeks). These samples were obtained to document the general performance of each wetland system. In addition, the wetland's water, gravel, sediment, and plants were subjected to an intensive sampling program every two months as a means of characterizing the state of each wetland and determining the general fate of explosives entering the wetlands.

While the Phase II demonstration results indicated that both the gravel- and lagoon-based systems could degrade explosives, the gravel-based system was clearly superior. The lagoon-based system met the goal of reducing TNT concentrations below 2 ppb only during the

first 50 days of the demonstration (to August 6, 1996) and was unable to satisfactorily degrade RDX or meet the total nitrobody-removal goals during the demonstration. In addition, it was difficult to maintain an adequate plant population within the lagoon-based system. Problems encountered included:

- A severe tadpole infestation which severely defoliated the plants within two months of the initial 1996 planting.

- Difficulty in reestablishing plant growth due to photodegradation of explosives in the contaminated groundwater which inhibited photosynthesis by coloring the water a dark red.

- A June 1997 hailstorm which decimated parrotfeather, one of the few plants able to reestablish itself during the spring of 1997.

In contrast, the gravel-based system was able to degrade TNT and RDX, was able to meet the demonstration goals during all but the coldest months; and was able to establish a sustainable ecosystem. During winter operations, the gravel-based system had difficulty meeting the total nitrobody reduction goal due to reduced microbial activity. Design and cost analysis indicate that a gravel-based system can be economically resized to overcome the winter performance issues.

Toxicity analyses were conducted on the water from both wetland systems during Phase II. Analysis of the influent water, using fathead minnows and daphnids, indicated that this water was toxic to the test organisms. In contrast, the toxicity of the effluent from both the lagoon- and gravel-based systems had been significantly reduced below EPA action levels for NPDES discharge. However, these conclusions should be considered preliminary in nature due to the limited scope of the toxicity tests conducted.

The gravel and sediment samples were also examined for toxicity to sediment invertebrates during Phase II. Test organisms used in the sediment toxicity tests were amphipods and midge larvae. Amphipods were used to test gravel toxicity. Amphipod toxicity was observed in the anaerobic gravel cell closest to the influent header on one sampling date and in the aerobic

gravel cell closest to the effluent header on another sampling date. The toxicity in the anaerobic cell was probably due to explosives sorbed onto the gravel closest to the influent where explosive concentrations in the water were greater. Possible causative agents for toxicity in the aerobic cell could not be identified. Death by starvation has been hypothesized since the amphipods were competing with the high aerobic metabolism of the local bacteria for nutrient resources.

Amphipod and midge larvae toxicity were observed in all sediment samples collected from the lagoon wetlands. Sorption of explosives and explosive by-products onto sediments in lagoon wetlands are thought to have contributed to toxicity. Conclusions regarding gravel and sediment toxicity should be considered preliminary in nature due to limited scope of the tests conducted.

Very little explosives were observed to accumulate in the gravel, sediment, and plants. The quantity of total nitrobodies (RDX, TNT, TNB, HMX, 2,4-DNT, and 2,6-DNT) and total explosives (nitrobodies plus measured by-products) on the gravel and sediments were always less than 1% to 1.4% of the mass of nitrobodies entering the lagoon- and gravel-based wetland, respectively. The percent accumulation was greatest in the winter of 1996/1997 and declined during the summer of 1997. The low accumulation of explosives in the wetland cells and the observation of explosive by-products indicated that explosives were being removed from the water via biological degradation.

Based on the data gathered during Phase II, the plants appeared to be metabolizing the explosives over time, thus, keeping the level of explosives or metabolites to a low level in the plant tissues. As a result, the explosive concentrations in the plants should not pose any adverse environmental effects and plant harvesting to prevent explosive release to the environment will not be required. Any low level explosive accumulation in any dead plants is expected to be re-released into the gravel-based system as the plants decay and the plant's hydrocarbons are consumed by the gravel-based system's microbial population.

The primary objective of the Phase III demonstration was to collect additional data to improve the design, operation, and economic success of scaled-up gravel-based systems. Specific objectives were to:

- Evaluate the use of a less expensive carbon source (molasses syrup)
- Evaluate the ability of the wetland plants to supply carbon to the gravel substrate by decreasing the amount of added carbon by one half
- Evaluate the gravel-based wetland's ability to degrade RDX and RDX by-products by increasing the retention time
- Gather additional winter performance data
- Operate and maintain the system similar to that required for a full-scale remediation system to assist in obtaining accurate O&M cost data

To conduct Phase III, the gravel-based system's operating parameters were modified to:

- Use a less expensive carbon source (molasses syrup as opposed to MRS)
- Allow frequent addition of the carbon source (twice daily versus biweekly)
- Decrease the rate of carbon addition (carbon rate cut in half)
- Lower the influent flow rate from 5 to 3 gpm.

The Phase III demonstration was conducted from September 17, 1997, to July 21, 1998. During this period, the total nitrobody concentration in the incoming groundwater from well MI-051 steadily decreased over Phase III. The average total nitrobody concentration during Phase III was 7,990 ppb.

The gravel-based system's performance during Phase III was about equal to its Phase II performance. As in Phase II, the gravel-based system was generally able to meet the demonstration goals. However, during Phase III, the gravel-based system was unable to meet the 50 ppb total nitrobody limit from December 7, 1997, to June 20, 1998, due to the combined effects of decreased microbial activity due to low water temperatures, an increase in influent nitrate concentrations which compete with the reactions leading to explosive degradation, and an increase in the anaerobic cell's (cell A2) redox potential. The system's higher redox potential was attributed to the absence of sufficient carbon to support the optimum level of microbial activity. Additional carbon was not added to the system during Phase III because one of the Phase III goals was to determine if the gravel-based system was mature enough to

provide a substantial portion of its own carbon needs (dead plant matter) during any portion of the demonstration phase.

Due to the reduced microbial activity, TVA concluded that the Phase III degradation rate data should be interpreted cautiously since prior research indicated that there is a strong correlation between low redox potential and high TNT and RDX removal rates[Ref. 9] and research with molasses syrup indicates the redox potential in the gravel-based system's anaerobic cell should be below -6 mV to ensure efficient explosives removal.[Ref. 12] As a consequence, the commercial-scale system described in this report was designed using the Phase II RDX rate constant from April 1997. This rate constant was the lowest reliable number available.

Operationally, the gravel-based system performed better in Phase III than it did in Phase II. During Phase II winter operations, the gravel-based system experienced blockages of the A1 and A2 outlet headers due to the buildup of excess MRS and microorganisms. These problems led to ponding, flow restrictions, and a periodic discontinuance of MRS addition. As a consequence of the switch to molasses syrup, flow rates through the gravel-based system were more stable during Phase III. During this period, the system did not experience ponding and the carbon source was added regularly via an automated pumping system.

SECTION 1.0
INTRODUCTION

1.1 Background

The fate of explosive residues in soil and groundwater is a concern to the Department of Defense (DoD). To date, numerous DoD sites have been identified as having explosives-contaminated groundwater and additional sites continue to be identified. Hence, the Army has prioritized "Explosives in Groundwater" as the fourth highest requirement in the area of environmental restoration research and development. The Army Requirements Statements being addressed includes explosives in groundwater, organics in groundwater, and solvents in groundwater.[Ref. 1] Explosive contaminants found at the DoD sites include TNT, RDX, HMX, and DNT. Because the explosives-contaminated groundwater is affecting drinking water supplies both on and off several Army installations, the DoD is currently providing potable water to some affected communities.

As part of the DoD's program to combat groundwater contamination, the DoDs' Environmental Security Technology Certification Program (ESTCP) funded this project to demonstrate phytoremediation (i.e., vegetation-induced remediation) of explosives-contaminated groundwater using constructed wetlands and planted lagoons. This project was executed under a partnering agreement among:

- U.S. Army Environmental Center (USAEC)
- Tennessee Valley Authority Resource Management (TVA RM)
- USACE's Waterways Experiment Station (WES)

The USAEC, as the lead agency, selected Milan Army Ammunition Plant (MAAP), located near Milan, Tennessee, as the demonstration site. The other groups provided technical expertise in phytoremediation and in the design, construction, and operation of constructed wetlands and plant lagoons.

The project was executed in three phases. Phase I involved a series of plant screening and treatability studies. During Phase I, standard methods were developed to evaluate the ability of

aquatic macrophytes (large aquatic plants) to lower the contaminant levels of TNT, RDX, and related compounds in explosives-contaminated water. Then, a variety of submergent and emergent aquatic macrophytes were screened for their ability to remediate the contaminated water. Finally, treatability studies were undertaken to test the performance of various wetland configurations.

In Phase II, the field demonstration system was designed, installed at MAAP, monitored for 16 months, and evaluated from both a technical and economic perspective. Volume I of this document describes the results of the Phase II demonstration. Other aspects of the project (e.g., design, construction, technology transfer, and economic analysis) are also addressed in Volume I.

During the course of Phase II, it became apparent that the gravel-based wetland's performance would be better than that of the lagoon and that acquiring additional data would be helpful to improve the design, operation, and economic success of commercial-scale gravel-based systems. Areas of interest included:

- Continuing to establish the effect of long-term plant growth on explosive remediation
- Continuing to examine nitrobody remediation at cold temperatures
- Examining the use of an alternate carbon source in the anaerobic cell (cell A1)
- Establishing the anaerobic cell's performance at a lower flow rate
- Operating and maintaining the system similar to that required for a full-scale remediation system

These issues were addressed by extending the operating period of the existing demonstration program. The extension is referred to as Phase III. The Phase III program ran from September 1997 to July 1998. To collect additional data, TVA funded portions of the Phase III demonstration. System operations and routine data collection activities were funded by ESTCP. The lagoon-based wetland was not operated during Phase III due to its poor performance in degrading RDX and difficulties in maintaining an adequate plant population within the lagoons. The Phase II results are provided as Volume II of this report.

1.2 Site Description

The demonstration was conducted at the Milan Army Ammunition Plant. MAAP is a government-owned contractor-operated (GOCO) military industrial installation under the jurisdiction of the Commanding General, Headquarters, United States Army Industrial Operations Command. The facility is now operated by General Dynamics Ordnance Systems, Inc., and employs approximately 1,100 people.

MAAP is located in western Tennessee straddling portions of Gibson and Carrol Counties (Figure 1-1). The city of Milan lies approximately one mile west; Humboldt lies 17 miles southwest; Trenton lies 18 miles northwest; and Jackson lies 28 miles south. The facility is bordered on the northeast and east by land owned by the Tennessee National Guard and on the northwest by lands owned by the city of Milan and the University of Tennessee.

The original facility, constructed during World War II, encompassed 28,521.4 acres. The installation currently encompasses 22,436 acres, as tracts of land have been sold, deeded, leased, or transferred. Approximately 548 acres of the installation enclose various production lines; storage areas total 7,930 acres; and approximately 1,395 acres are used for administrative, shop maintenance, housing, recreation, and other functions. Other acreage is necessary to allow safe distances between areas containing explosives.

Acreage not designated as load, assemble, and pack (LAP) lines are often used for agricultural purposes. Approximately 13,600 acres within the MAAP boundary are leased for agricultural use. Approximately 3,984 acres are used as cropland. Cotton, corn, and soybeans are the main crops, with smaller amounts of grain sorghum and wheat also grown. In 1990, there were 2,746 head of cattle grazing on the facility. The cattle graze between April and November on approximately 8,700 acres. In addition, MAAP has more than 6,000 acres of managed timberland.

MAAP facilities include: nine active ammunition LAP lines, one washout/rework line, one experimental line, one X-ray facility, one test area, two shop maintenance areas, storage areas, demolition and burning grounds area, an administrative area, a family housing area, and recreational facilities. In addition, there are medical facilities, fire/ambulance stations, ten

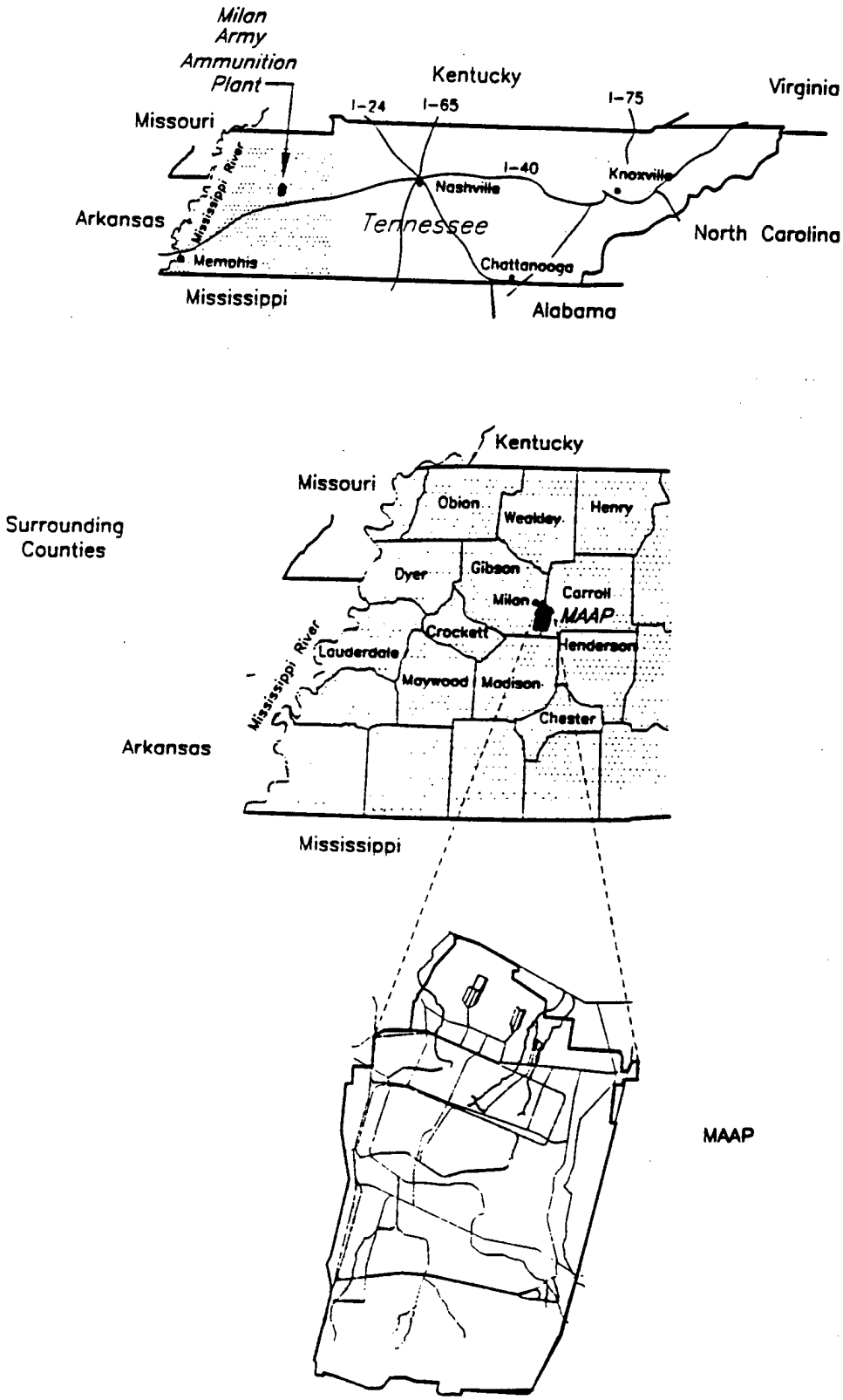


Figure 1-1

Location of MAAP in Western Tennessee

high-pressure heating/process steam plants, 16 low-pressure heating plants, one solar pond, and seven explosives-contaminated wastewater treatment plants (ECWTPs). The ECWTPs treat explosives-contaminated wastewater from the production facilities. In addition, there are two sewage treatment plants (STPs) located on the facility; the Wolf Creek Ordnance Plant (WCOP) STP in the northern portion of the site and the Milan Ordnance Depot (MOD) STP in the south.

1.3 Source of Groundwater Contamination

The available evidence suggests that the groundwater contamination at MAAP is related to discharges which occurred prior to the installation of explosives-contaminated wastewater treatment plants (ECWTP) in 1981. Before 1981, MAAP's production facilities discharged explosives-contaminated wastewater directly into open ditches that drained from sumps or surface impoundment into local streams (both intermittent and perennial streams). The direct discharges were stopped in 1981 and redirected to newly constructed ECWTP. However, over a period of many years, several of the drainage ditches were contaminated with explosive residuals which, in turn, leached into the groundwater. These contaminants then moved off-post along the natural course of groundwater flow (to the north-northwest).

Discharges from the existing ECWTPs are not thought to be a significant factor because the discharge levels are low--about 20 parts per billion (ppb) total nitrobodies. In addition, it has been shown that the nitrobodies are not accumulating in the ditch's sediment or soils.

Unfortunately, a number of off-post areas may be affected by the MAAP-derived groundwater contaminants including:

- Areas within the city of Milan
- An area between the installation and the city of Milan
- The area of Rutherford Fork, Obion River
- Residential wells
- University of Tennessee's Agricultural Station

The bulleted areas listed above are located near or adjacent to the off-post sites where contamination from explosive compounds has been detected.

Regular sampling of off-post residential wells since 1982 indicate that contamination has been detected in residential wells at the Bledsoe residence and New Hope Church. Ditch D, located on-post, is the suspected source of this contamination. In early 1994, during a monthly monitoring program, the Army detected RDX in two of the city of Milan's public water supply wells (wells 3 and 4), but at levels below the USEPA health advisory level of 2 ppb. RDX concentrations exceeding a 2 ppb health advisory level were detected in city well 5. Subsequently, the well was shut down. These wells are located northwest of the post within the city limits. Suspected source areas are Z line, which has discharged to ditch D, and X line, which has discharged to ditch E, prior to 1981.

1.4 Project Objectives

The objectives of this demonstration were to design, construct, and operate a facility demonstrating the use of gravel- and lagoon-based wetlands in remediating explosives-contaminated groundwater and to evaluate the technical feasibility of using these treatment systems for remediating explosives-contaminated groundwater.

Evaluation of treatment efficacy was based on removal efficiencies for:

- Specific explosives
- Their known by-products
- Biochemical and chemical oxygen demand
- Suspended solids
- Selected nutrients

The analysis of feasibility is based on technical and cost considerations.

1.5 Approach

To demonstrate the effectiveness of wetlands-based phytoremediation, two demonstration-scale systems were constructed on a parcel of land at MAAP. These systems consisted of gravel- and lagoon-based wetlands.

The primary objective of the Phase II demonstration was to evaluate the technical feasibility of using wetlands for remediating explosives-contaminated water. The goal was to reduce TNT concentrations to levels less than 2 ppb and total nitrobody concentrations to levels less than 50 ppb. Total nitrobodies are defined to mean the sum of the concentrations of TNT, RDX, HMX, TNB, 2A-DNT, and 4A-DNT.

The demonstration began at 3 p.m. on June 17, 1996, when contaminated water was introduced into gravel- and lagoon-based systems. The lagoon-based system operated on contaminated water through August 19, 1997, when the feed was switched to clean potable water for transition to a non-operational state. Contaminated water continued to be fed to the gravel-based system as part of the Phase II and Phase III efforts. Phase II sampling activities in the gravel-based system were continued through September 16, 1997. Volume I of this report covers the operation and monitoring activities for Phase II (i.e., through September 16, 1997). Volume II covers the operation and monitoring activities for Phase III (i.e., from September 17, 1997, to July 21, 1998).

The demonstration system was constructed in MAAP Area K adjacent to Building K-100 (see the plot of land designated as Area A just east of Building K-100 in Figure 1-2). Contaminated groundwater used in the demonstration system was obtained initially from well MI-146. Analysis of well MI-146 water, obtained on October 4, 1995, indicated that the groundwater initially contained the following explosives:

- TNT - 1,990 ppb
- RDX - 2,980 ppb
- HMX - 178 ppb
- TNB - 150 ppb
- 2,4-DNT - 26 ppb

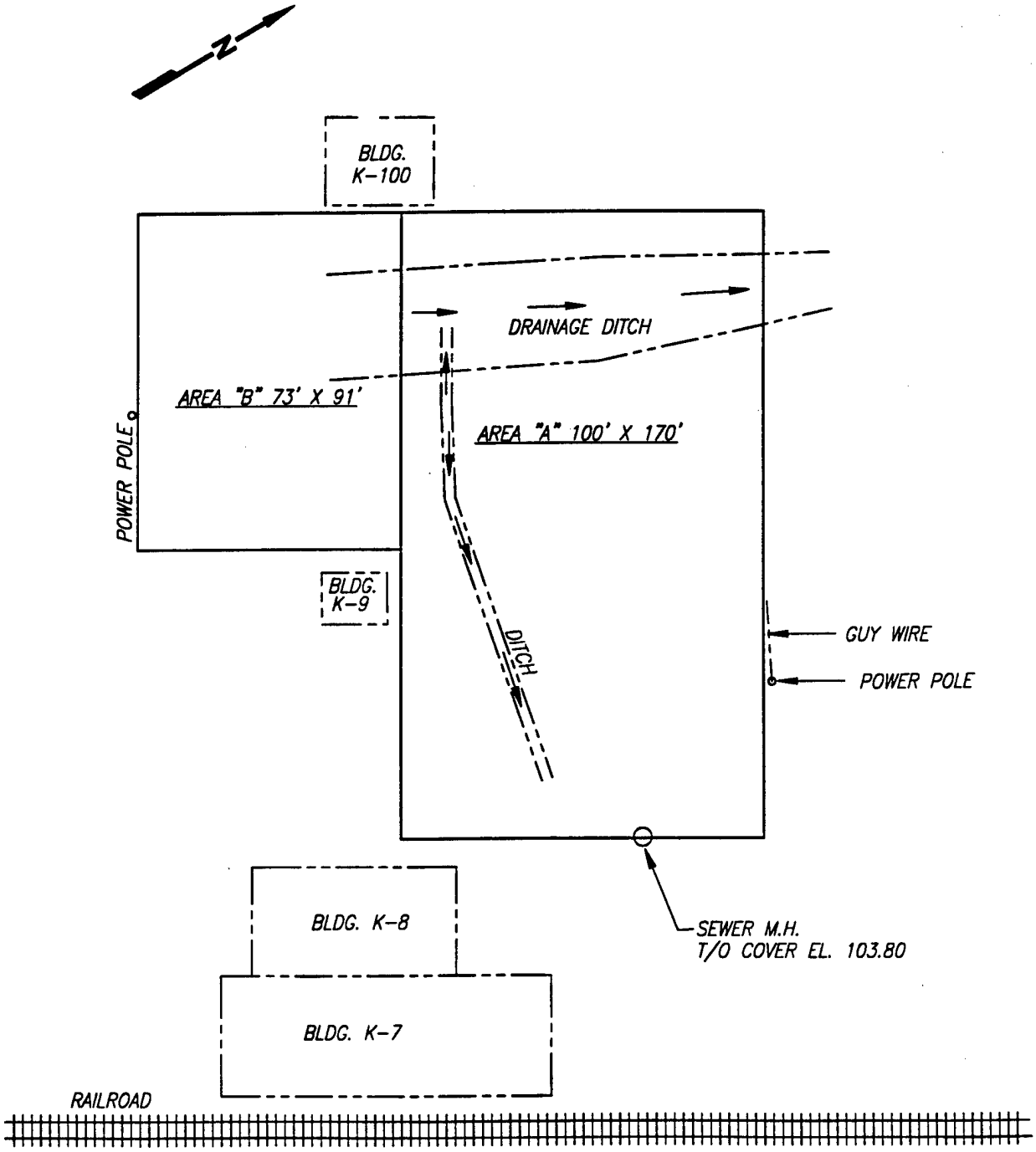


Figure 1-2

Milan Army Ammunition Plant Sites for Constructed Wetlands Demonstration for Remediating Explosives in Groundwater.

Nitrate concentrations were also reported at 10.0 mg NO_3-N/liter. During the fall of 1996, explosive concentrations in well water from MI-146 began to decrease. Water from well MI-051 was utilized instead. The wells were switched on November 21, 1996.

Analysis of well MI-051 water, obtained on December 3, 1996, indicated that the groundwater initially contained the following explosives:

- TNT - 4,332 ppb
- RDX - 3,920 ppb
- HMX - 101 ppb
- TNB - 359 ppb
- 2,4-DNT - 65 ppb

During the course of the Phase II demonstration, water, plant, gravel, and sediment samples were collected on a biweekly and bimonthly basis. Water samples were analyzed for the following:

- Explosives
- Explosive by-products
- Nutrients
- Dissolved oxygen
- pH
- Temperature
- Suspended solids
- Metals
- Chlorides
- Redox potential
- Electrical conductivity
- Chemical oxygen demand
- Biochemical oxygen demand

During Phase II, intensive sampling was conducted every two months to quantify removal kinetics. During these periods, plant, sediment, and gravel samples were collected in addition

to the water samples described above. Plant tissues were evaluated with respect to root-shoot weights, nutrient content, dry matter content, explosives content, and explosive by-products. Sediment (including gravel) samples were analyzed for explosives content and explosive by-products. The sediment and water samples were subjected to toxicity testing using *Hyalella azteca* (sediment), *Ceriodaphnia dubia* (water), *Pimephales promelas* (water), and *Chironomus tentans* (sediment). In addition, WES conducted bench-scale tests with radiolabled TNT and RDX to determine the fate of explosives in aquatic and wetland plants (Appendix F).

During Phase III, elements of the Phase II routine biweekly sampling program and bimonthly intensive sampling program were combined into a single sampling program which was conducted monthly. During this period, only water samples were collected. Plant and sediment samples were not collected during this period nor were any toxicity tests conducted. The routine portions of the Phase III sampling program (performed monthly) were collected from the beginning of Phase III until the end of Phase III. The intensive portion (performed monthly) of the Phase III sampling program were started in December 1997 and continued until the end of Phase III. The intensive sampling portion of the Phase III sampling program was funded by TVA and the routine portions were funded by ESTCP. During the routine sampling program, only the minimum number of samples necessary to document system performance and meet NPDES permit requirements were conducted.

1.6 Schedule

A Gantt chart of TVA RM-related activities is provided in Table 1-1. Phase II began on August 1, 1995, and was completed on December 31, 1997. As indicated on the GANTT chart, there was some overlap between Phase I and Phase II. Phase I was completed on June 28, 1996. Phase III activities began on September 17, 1997, and continued through July 21, 1998.

ID	Task Name
1	Receive Funding
2	Phase I
3	Treatability Study #1 Initiated
4	Treatability Study
5	Treatability Study #1 Draft Report Submitted
6	Treatability Study #2 Initiated
7	Treatability Study
8	Treatability Study #2 Draft Report Submitted
9	Plant Screening Study Initiated
10	Plant Screening Study
11	Plant Screening Study Draft Report Submitted
12	Regulatory Analysis - Field TS Test Initiated
13	Regulatory Analysis - Field TS Test
14	Phase I Completed
15	Phase II
16	Test Plan Development
17	Test Plan Draft Submitted
18	Test Plan (Final) Submitted
19	Detailed Design
20	Detailed Design Completed
21	Construction
22	Construction Completed
23	Phase II Field Demonstration
24	Biweekly and Bimonthly Sampling
25	Winter Bromide Testing
26	Winter toxicity Testing
27	Spring Bromide Testing
28	Summer Toxicity Testing

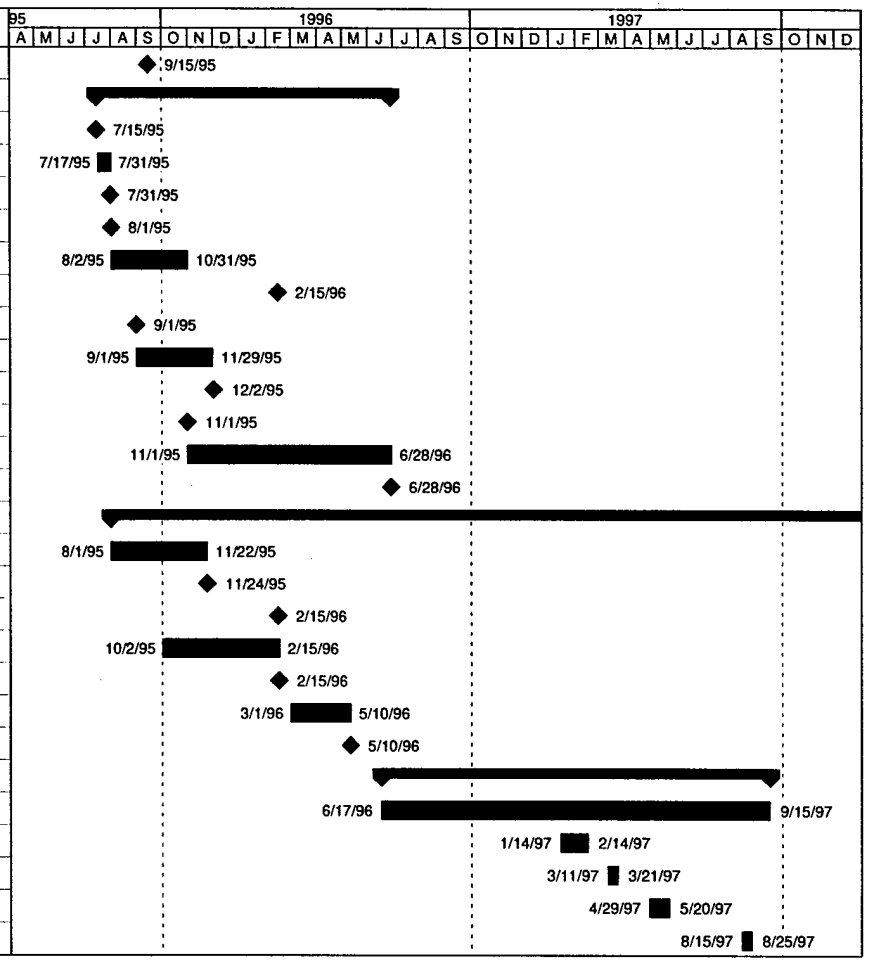


Table 1-1

Gantt Chart for Wetlands Project

ID	Task Name
29	Summer Bromide Testing
30	Economic Analysis Report
31	Economic Analysis Report Completed
32	Draft Demonstration Results Report Submitted
33	Final Demonstration Results Report Submitted
34	Phase III Field Demonstration
35	Operations with Monthly Sampling
36	Bromide Tracer Testing
37	Prepare Results Report
38	Draft Report Submitted
39	Final Report Submitted

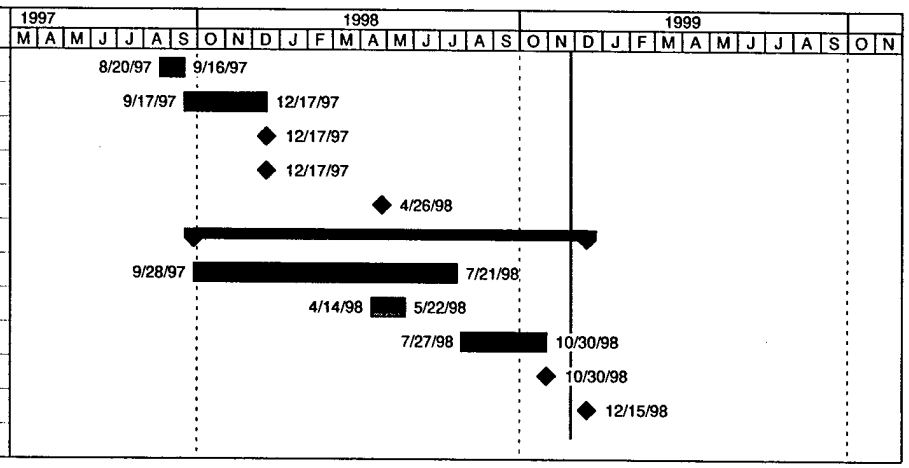


Table 1-1

Gantt Chart for Wetlands Project (Continued)

SECTION 2.0
TECHNOLOGY DESCRIPTION

2.1 Applications

Constructed wetlands and planted lagoon systems are used for removing a broad range of contaminants from surface and groundwater sources. Degradation pathways in these systems are complex, but are generally based on the combined action of higher aquatic plants (emergent or submergent) and microbial populations composed of algae, bacteria, and fungi. Important parameters known to influence degradation pathways and kinetic degradation rates include:

- Temperature
- pH
- Dissolved oxygen concentration
- Redox potential
- Nutrient mix

2.2 Performance Criteria

The primary goal of the project was to demonstrate the remediation of groundwater such that each system effluent had:

- TNT concentrations below 2 ppb
- Total nitrobody concentrations below 50 ppb

The 50 ppb nitrobody limit was chosen to ensure a discharge limit below the 70 ppb limit designated by MAAP's NPDES permit for the WCOP sewage water treatment plant. Total nitrobodies are defined to include the sum of the concentrations of TNT, RDX, HMX, 2,4-DNT, 2,6-DNT, and TNB. The average total nitrobody concentration in the contaminated groundwater was 3,250 ppb prior to November 21, 1996; 9,200 ppb during the remainder of Phase II; and 7,984 during Phase III. Therefore, the wetland's total nitrobody removal efficiency needed to be greater than 99% to successfully meet the demonstration goal.

Secondary goals were to produce effluent waters that would be acceptable for surface water discharge – beyond the mere removal of total nitrobodies. Since BOD-5, pH, and TSS analyses are commonly required in NPDES surface water discharge permits, these parameters were analyzed in effluent waters. In addition, by-products of explosive degradation, such as 2,6-DANT and 2,4-DANT, and the toxicity of effluent waters, were analyzed to evaluate whether or not effluent waters would be safe for surface water discharge.

2.3 Theory Behind Unit Operations

A major difference between the gravel- and lagoon-based wetlands lay in what type of organism supplied the enzymes for mediating the reduction process. In the gravel-based wetland, microorganisms were the primary source of various enzymes for reducing explosives.[Ref. 2] In the lagoon-based wetland, the submergent plants were the primary source of the nitroreductase enzyme for reducing explosives. Explosives reduction and breakdown in the gravel-based wetland occurred primarily in the anaerobic cell which was fed a carbon source (MRS). Theoretically, explosives reduction should have occurred in the lagoon cells.

For TNT, enzymes reduced the nitro groups to amino groups. By-products observed to form in the Milan AAP demonstration were 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), and 2,4-diamino-6-nitrotoluene (2,4-DANT). [Ref. 3] Further reduction may occur with formation of triaminotoluene (TAT), which has all of the nitro groups reduced to amino groups. The amino by-products can then polymerize to form harmless humic-like substances or the ring can be cleaved to produce aliphatic organic acids.[Ref. 4]

In removal of RDX, reduction of nitro groups to nitroso groups occurs via enzymatic activity, as well.[Refs. 3,5] RDX by-products observed in the Milan AAP demonstration were mononitroso RDX and trinitroso RDX. These by-products undergo further degradation with ring cleavage occurring to form aliphatic organic acids and CO_2. [Ref. 3] The removal of HMX is suspected to occur under a mechanism similar to RDX where nitro groups are reduced to nitroso groups with further degradation occurring via ring cleavage.[Ref. 3] The removal of TNT and RDX follows first-order removal kinetics. Once formed, the removal of TNT and RDX by-products also follow first-order kinetics.

Explosive by-products, nutrients, and residual BOD_5 entering the gravel-based aerobic cell were further treated via aerobic microbial treatment in aerobic cell.

2.4 Process Description

Two demonstration systems were constructed at MAAP (Figure 2-1). The first system, Demonstration A, consisted of a gravel-based *subsurface flow (SSF) constructed wetland.* The second system, Demonstration B, was a lagoon-based *surface flow (SF) constructed wetland.* Contaminated water entered both systems via 3-inch PVC inlet headers, as shown in Figure 2-2.

The gravel-based system consisted of one gravel-filled anaerobic cell (cell A1) and one gravel-filled aerobic cell (cell A2). The cells were connected in series with the anaerobic cell being the first cell (Figure 2-3). The gravel depth in both cells was four feet. Selected emergent plants were grown on the cell's gravel surface. These plants were: canary grass (*Phalaris arundinacea*), wool grass (*Scirpus cyperinus*), sweetflag (*Acorus calamus*), and parrotfeather (*Myriophyllum aquaticum*). In addition, the anaerobic cell was initially inoculated with commercially available forms of anaerobic bacteria (i.e., bacteria commonly used in household septic tanks). The microbial population were thought to have increased rapidly due to the available nutrient supply from fertilization with milk replacement starter (MRS).

Plant species used in both the gravel- and lagoon-based demonstration systems were selected based on biomass-normalized kinetic constants (k) for TNT and RDX removal. The choice of plants used in the gravel-based system were also influenced by the plant's ability to supply carbon to the incoming water. The selection process occurred in 1995 as part of the Phase I treatability studies. The process used for selecting these species can be found in Appendix D.

To operate the gravel-based system, 5 gpm of contaminated groundwater was continuously pumped into the anaerobic cell. The contaminated water entering the gravel-based system took eight days to pass through the anaerobic cell, while microbial and plant enzymes in the anaerobic cell broke down the explosive-related contaminants. The water leaving the

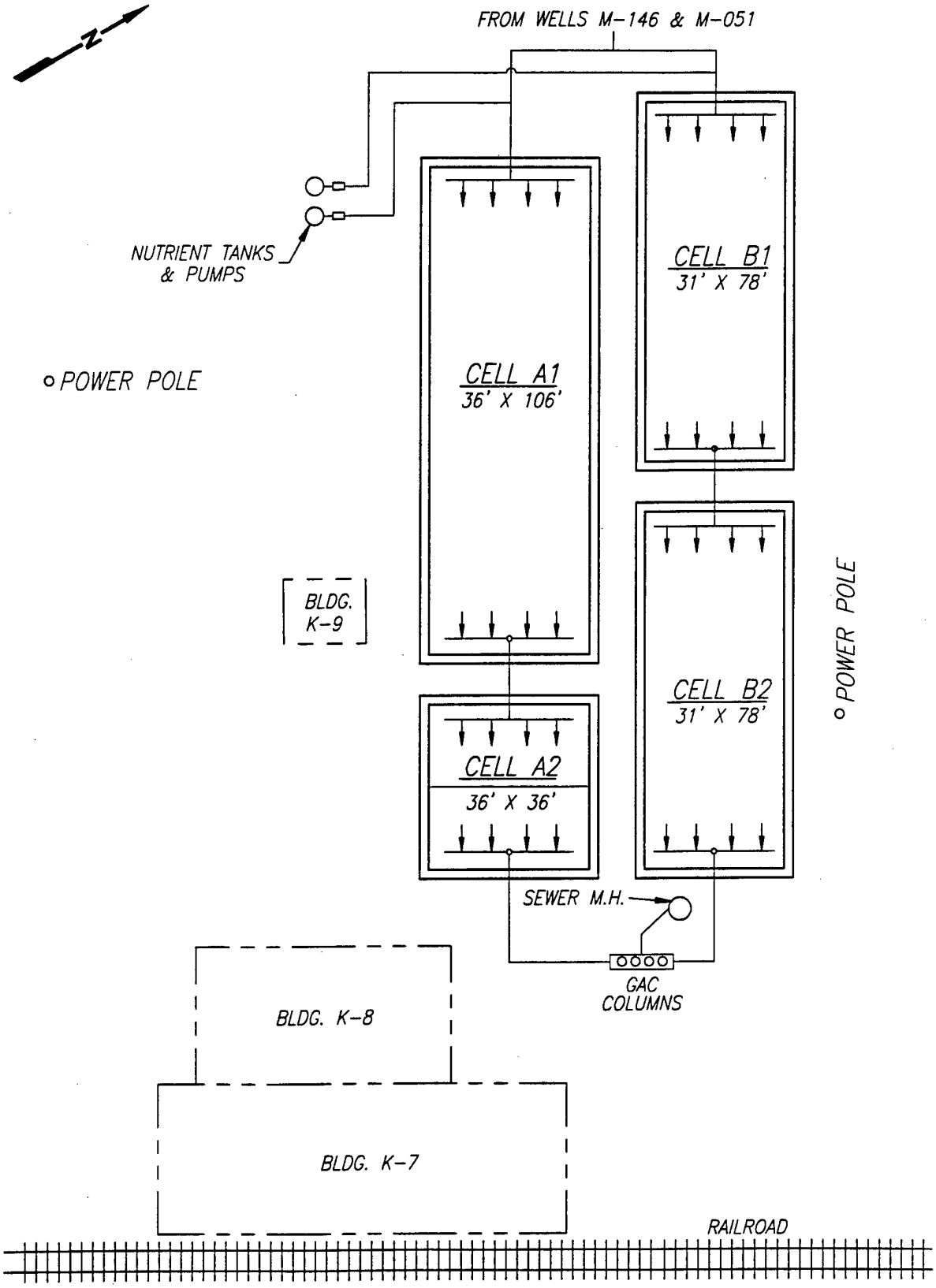


Figure 2-1

Site Plan for MAAP Demonstration Systems

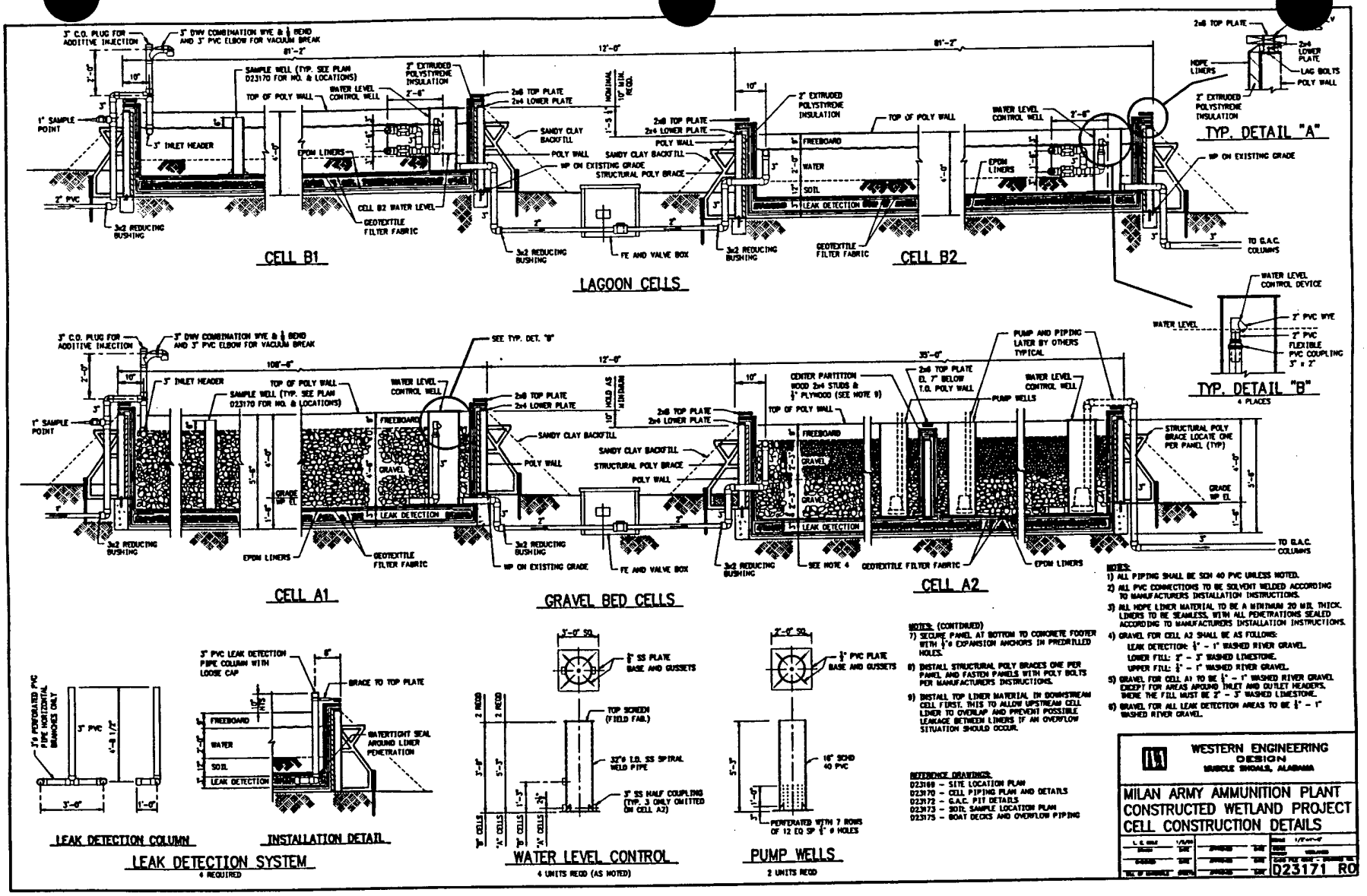


Figure 2-2

Cell Construction Details

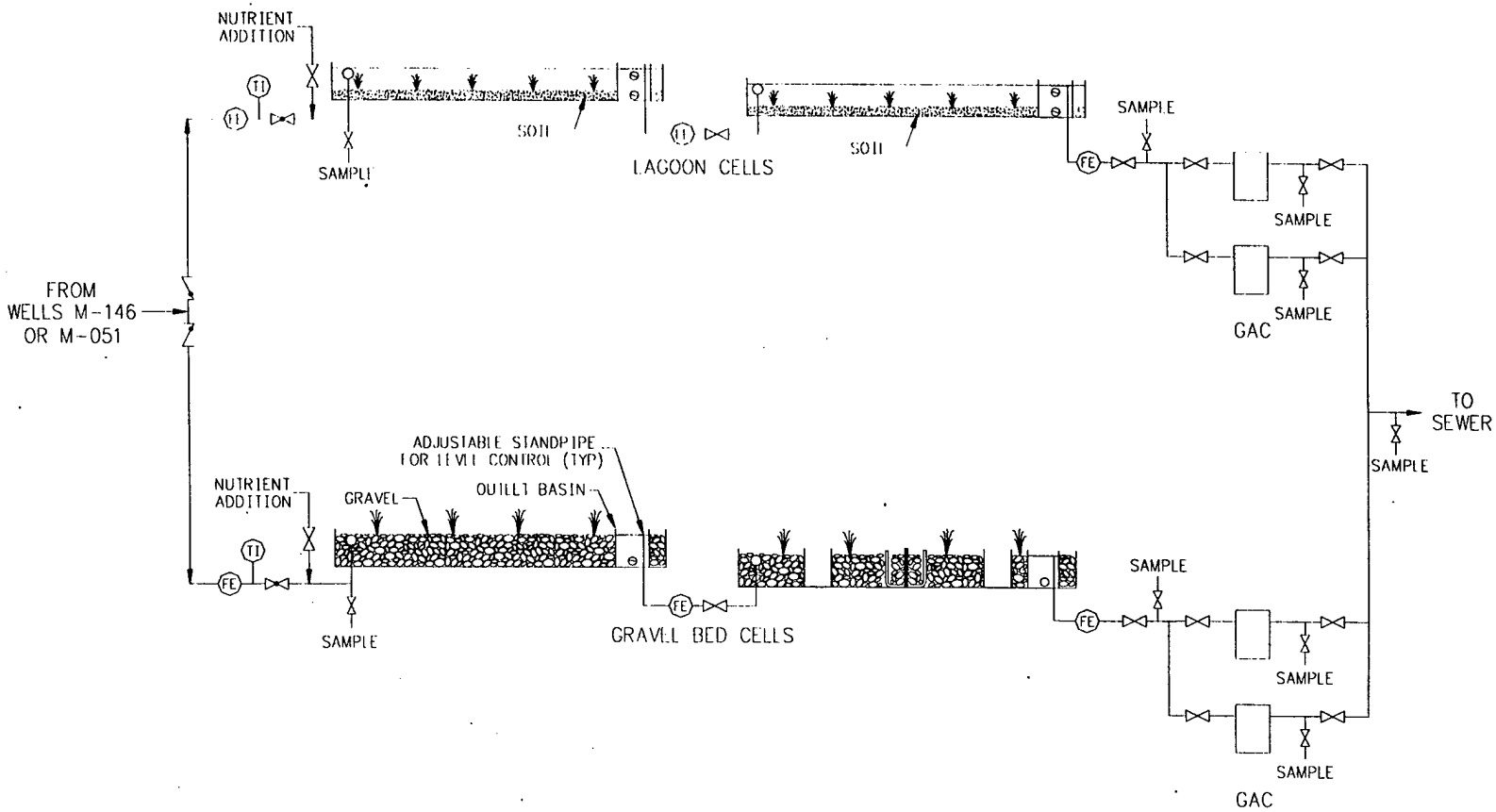


Figure 2-3

Wetlands Demonstration

anaerobic cell was continuously discharged to the aerobic cell through a header located at the discharge end of the anaerobic cell. The water was hydraulically retained in the aerobic cell for two days. Originally, the water moved from the anaerobic cell to the aerobic cell by gravity flow. However, due to difficulties encountered in accurately measuring flow rate, a demand-type pumping system was installed in April 1997.

The aerobic cell was designed to remove explosive degradation by-products, BOD-5, nutrients, and total suspended solids. The aerobic cell is a proprietary TVA design (patent number 5,863,433) which consists of two internal cells and a pumping system. Water leaving the aerobic cell was collected in a discharge header, pumped through drums containing granular activated carbon (GAC), and then flowed into the plant sewer system. A GAC unit will not be required in a commercial wetland. The GAC unit was added to ensure explosives removal prior to discharge to the sewer. The purpose of the GAC unit was to reduce total nitrobodies to below 50 ppb in the event the wetlands failed to perform as expected. The sewer led to the WCOP sewage treatment plant, having outfall 009. The sewage treatment plant's total nitrobody levels are limited to 70 ppb by MAAP's NPDES permit. Hence, the total nitrobodies in the water entering the sewage plant were below the NPDES permit requirement.

Demonstration B, the lagoon-based system, consisted of two lagoons in serial arrangement. Each lagoon-based wetland consisted of a two-foot-deep (water depth) lagoon with one foot of soil placed at the bottom of each lagoon. The soil provided a rooting substrate for submergent plants. Submerged aquatic plants selected for use in the lagoons included: sago pond weed (*Potamogeton pectinatus*), water stargrass (*Heteranthera dubia*), elodea (*Elodea canadensis*), and parrotfeather (*Myriophyllum aquaticum*). The process used for selecting these species can be found in Appendix E.

To operate the lagoon-based system, 5 gpm of contaminated water was continuously pumped into the first lagoon. The contaminated water entering the lagoon-based system took five days to pass through the first lagoon. During this time, microbial activity, photodegradation, and plant enzymes broke down explosive-related contaminants. The water was then discharged to the second lagoon for similar treatment (again retained for 5 days). Originally, the water from both lagoons was collected in headers and discharged by gravity flow. However, due to difficulties encountered in accurately measuring flow rate in a gravity flow system, a

demand-type pumping system was installed in April 1997. Again, water leaving the second lagoon was pumped through drums containing granular activated carbon (GAC) and then discharged into the sewer. A GAC unit will not be required in a commercial wetland.

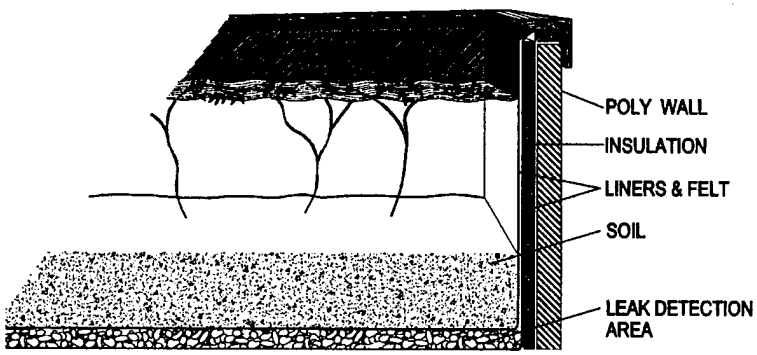
Construction of the demonstration systems followed protocols developed by TVA RM in the development of their Constructed Wetlands R&D Facility (see also Steiner and Watson, 1993[Ref. 6]). General design calculations for the systems were based on a total hydraulic retention time of 10 days and a minimum demonstration flow rate of 5 gpm (19 L/min to each system).

All cells were constructed aboveground, using insulated 4-foot prefabricated poly wall panels surrounded by earthen berms. Some excavation and earth moving was required to obtain the required depths and to provide backfill against the panels. All basins were lined with two layers of liner (20-mil 12-ply cross grain laminate polyethylene) to prevent seepage of contaminated water to the underlying soil. Eight-ounce geotextile mats were installed above and below each liner to prevent sharp rocks from penetrating each liner (Figure 2-4). The first liner held the basin contents. The second liner provided secondary containment and served as part of a leak detection system. Three inches of gravel separated the first and second liners; the void space within the gravel matrix provided storage capacity for the leak detection system. The leak detection system for each cell consisted of the gravel catch basin, the secondary liner, and a standpipe for accessing the gravel basin.

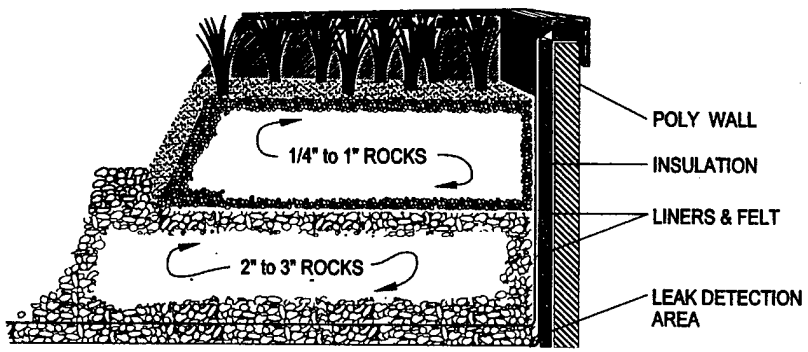
The bottom of the lagoon-based cells was located at ground level. The earthen berms surrounding the lagoon-based cells rose four feet above ground level. Nine inches of freeboard existed between the top of the berm and the lagoon surface. This freeboard space was used to retain rainwater entering the system.

The bottom of the gravel-based cells was located 18" below ground level. The earthen berms surrounding the gravel-based cells rose four feet above ground level. Nine inches of freeboard existed between the top of the berm and the gravel bed. Again, this freeboard space was used to retain rainwater entering the system.

CELL CONSTRUCTION



LAGOON



GRAVEL-BASED

Each of the cells is constructed above ground, with only a minimal amount of soil excavation required for proper elevation of the second cell in each system. Prefabricated poly wall panels were installed in sections to construct the sides of the cells. The walls were insulated, with soil being placed around the outside walls for additional insulation. Layers of felt and two geosynthetic liners were used to provide containment for the soil and gravel. Piping, sumps, and pumps were installed to move water into, through, and out of the cells. A leak detection monitoring area exists between the two liners.

Figure 2-4

Sectional of Liner Arrangement

Flow to the demonstration site was limited by the capacity of well MI-146. Based on pump tests, well MI-146 was expected to deliver 16 gpm. Consequently, the piping to each of the demonstration systems was designed to handle a maximum inflow of 8 gpm (30 L/min). This was done to allow for possible operation at shorter retention times. In the fall of 1996, the explosive concentrations in the water from well MI-146 began to decline. Consequently, this well was abandoned and water was used from well MI-051 (see the discussion in Section 5.2.1 for details).

Influent and effluent manifolds were installed on all of the wetland cells. Water entered cells A1, A2, B1, and B2 through a distribution header located near the top of the cells (Figures 2-2 and 2-3) just below the surface of the gravel bed or lagoon. Flow out of each cell was through a collection header located at the opposite end of the cell near the bottom. After reaching the collection header, the water flowed into a standpipe-based discharge system located in an outlet control sump near the end of the cell. Water in the A1 and B1 outlet control sumps flowed into the inlet manifold of cells A2 and B2, respectively. Water discharged from the A2 and B2 outlet control sumps flowed through pipes to granulated activated carbon (GAC) drums and was then discharged to the sewer. The use of activated carbon assured that any explosive residuals leaving the systems would be removed prior to discharge. The activated carbon units were used for demonstration purposes only and would not be utilized in a full-scale system.

Originally, the water flow between the first and second cells was controlled by a gravity flow system based on the use of standpipes (Figure 2-2). The water level in each cell was controlled by the height of a standpipe located in the outlet control sump. Flow from cell B2 to the GAC drums was also controlled by a gravity flow-based standpipe system. However, these gravity flow-based systems were later converted to demand-type pumping systems due to flow meter failures.

Originally, each inlet and discharge line contained an electronic flow meter/totalizer (six meters total). The meters were intended to record flow data, to quantify rates of evapotranspiration, and to facilitate mass balance calculations. However, the original meters were unable to maintain their accuracy over the range of flows encountered and suffered from water leakage into their electrical components (see discussion in Section 5.2.2). Consequently, the electronic meters were replaced with mechanical meters in April 1997. To ensure that the

mechanical meters would work properly, the gravity flow discharge systems at the end of the lagoon cells (B1 and B2) and anaerobic cell (A1) were converted to a demand-type pumping system. Conversion was accomplished by placing a 30-gallon plastic barrel at the bottom of the control sump and placing a submersible pump, with a float-type level controller, at the bottom of the barrel. Should the pump fail, the water simply overflowed the barrel and drained into the original gravity flow system. This modification ensured that sufficient velocity was maintained in the discharge systems to accurately record the discharge flow rates.

Flow and level control through the aerobic cell (A2) was similar to that of the anaerobic cell (A1), described above, except the water was always discharged by a demand-type pumping system. The demand-type pumping system consisted of a submersible pump and a float-type level controller located at the bottom of the control sump (see location of control sump in Figure 2-2). The water level within the gravel-based cells was set approximately 2 inches (5.0 cm) below the surface of the gravel beds.

Sampling wells were installed throughout the wetland systems to allow ease of sampling, to ensure samples were consistently taken at the same location, and to enable estimation of spatial variability in both horizontal and vertical planes (Figure 2-5). These slotted PVC wells were designed to enable use of in situ sampling instrumentation (sondes), as well as hand-held sampling devices. These wells are described in more detail in Sections 3.5.3 and 3.7.2.

The demonstration facility was also equipped with a nutrient delivery system. To promote anaerobic conditions within the gravel-based wetland during Phase II, a solution containing 250 pounds (113.4 Kg) of MRS was added to the anaerobic cell every 14 days. The solution was mixed in two vats located just to the west of the gravel-based wetland (Figure 2-1) and was equipped with a submerged pump to facilitate mixing. Approximately 125 pounds of MRS (56.7 Kg) were poured into each vat and mixed. The solution from each vat was then pumped, over a 5-hour period, to one of two dedicated headers at a flow rate of 0.7 gpm (2.6L/min). The first header was placed 4 feet downstream of the influent header. The second header was placed 24 feet downstream of the inlet header. Both headers were installed on the gravel surface. Each header contained six evenly spaced ¼-inch holes. To ensure complete

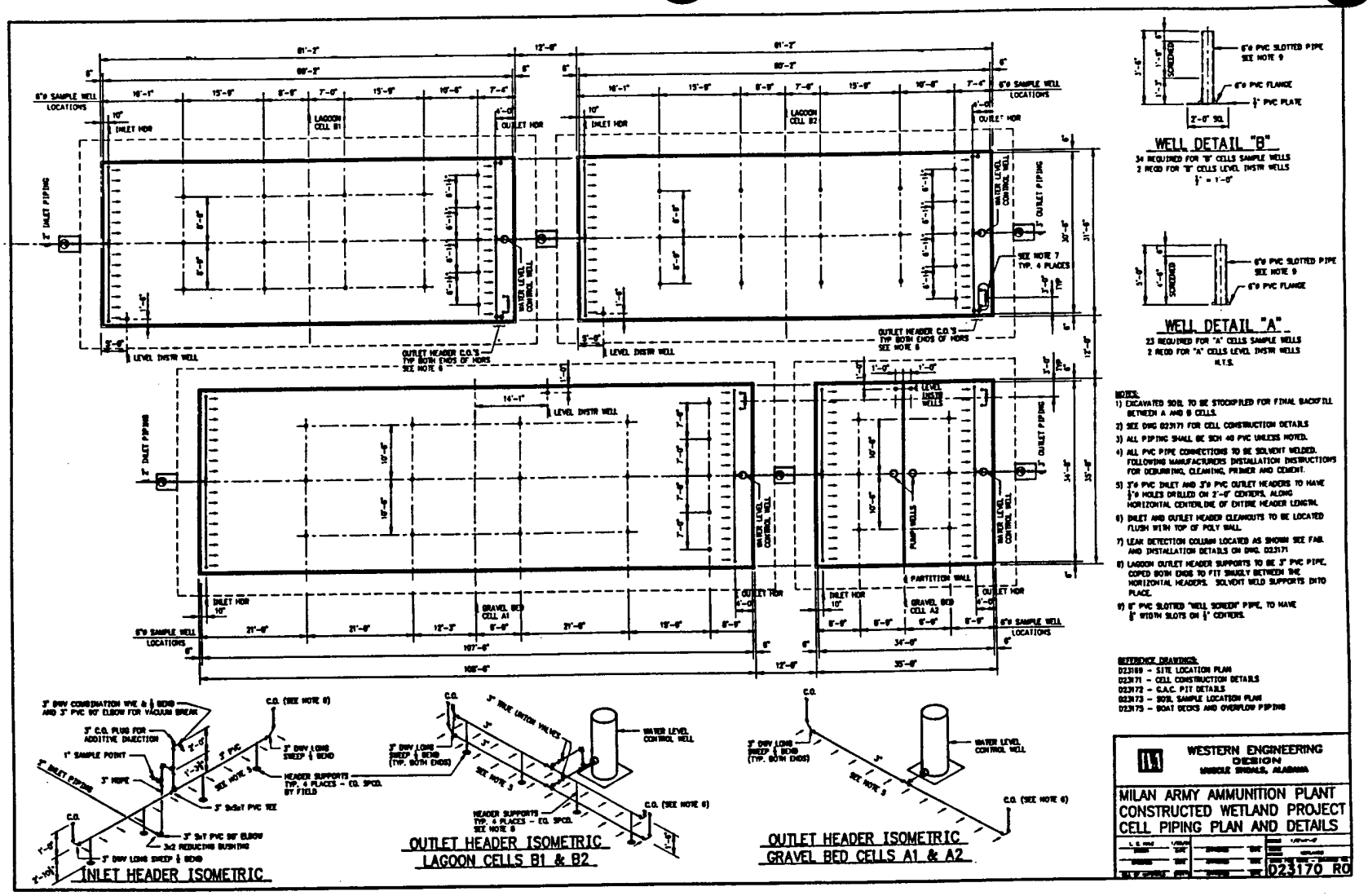


Figure 2-5

Cell Piping and Plan Details

mixing of MRS with the anaerobic cell's water, one bed volume of water was recirculated from the outlet of the anaerobic cell to the anaerobic cell's inlet while the MRS was being pumped into the anaerobic cell. The recirculated water was pumped from the outlet control well at a rate of 150 gpm (568 L/min) to the surface of the anaerobic cell's gravel bed just downstream of the inlet manifold. Recirculation at 150 gpm ensured that one bed volume of wetland water was recirculated over the 5-hour period. One bed volume was recirculated to ensure that the explosive concentration profile remained high near the inlet and low near the outlet.

As part of the Phase III program, the MRS system was replaced on September 10, 1997, with a new system designed to distribute a nutrient solution containing cane molasses syrup instead of MRS. Each gallon of nutrient solution (3.78 liters) consisted of 3.71 liters of cane molasses syrup and 40 grams of diammonium phosphate dissolved in 0.07 liters of water.

The new system was designed around two subsystems (units 1 and 2). The first subsystem (unit 1) was located near cell A1's inlet header and the second subsystem (unit 2) was located one third of the distance down the anaerobic gravel bed.

Unit 1 consisted of a tank containing the nutrient solution, a peristaltic pump, an on/off timer, and an injection header with five insertion wells. The nutrient solution and pump were housed in a 4-foot x 4-foot x 4-foot insulated container located in the center of the gravel bed about 10 feet from the north wall. The timer (used to control both units) was located in a similar container located at the unit 2 site. Half a gallon of molasses syrup was pumped into cell A1's inlet header each day (two injections per day at a rate of a quarter gallon per injection). After pumping molasses syrup into cell A1, the lines to the inlet header were flushed with water from cell A1.

Unit 2 consisted of a tank containing the nutrient solution, a peristaltic pump, an on/off timer, an injection header with five insertion wells, and a submerged sump pump. The nutrient solution, peristaltic pump, and timer were housed in an insulated container located near the north wall of the gravel bed. A sump pump was located close to the insulated container in a 5-gallon perforated container buried in the gravel bed. Like unit 1, unit 2 pumped half a gallon of solution into the injection header each day (two injections per day at a rate of a quarter gallon per injection). The injection header is of the same design as the header of unit 1. The

nutrient solution was flushed into the header by the simultaneous operation of both the sump pump and the peristaltic pump. The flow of water was about 3 gpm at each of the five injection wells.

SECTION 3.0
SAMPLING PLAN (PHASE II)

3.1 Overview of Sampling Operations

The goal of this demonstration was to evaluate the technical feasibility of using gravel- and lagoon-based wetlands to remediate explosives-contaminated groundwater. This goal was met by constructing two demonstration-scale wetlands, exposing them to contaminated water, and monitoring explosive removal dynamics. Monitoring was expected to provide insight into:

- The wetlands' comparative ability to remediate explosives-contaminated water
- The general condition of the wetlands
- The potential for producing toxic effluents
- Fate of explosives entering the wetlands systems

A generalized list of characteristics monitored is provided in Table 3-1.

The wetlands' ability to remove explosives were examined by: monitoring the wetlands' degradation kinetics, verifying hydraulic retention times, and measuring the system's efficiency at removing explosives. To obtain these figures, a number of constants were calculated. The necessary calculation methods are referenced in Table 3-2. This table also provides a general outline of the plan used to analyze the wetlands' comparative abilities to remove explosives and by-products. This plan called for:

- Characterizing degradation kinetics by determining the wetlands' ability to remove explosives as expressed by first-order rate constants,
- Verifying hydraulic retention time via bromide tracer tests,

Table 3-1

Sampling Goals for the MAAP Demonstration

Demonstration Goal	General Characteristic Measured	Specific Characteristic Measured or Calculated	Sampling Program	Sampling Frequency
Measure Wetlands' Ability to Remediate Explosives-Contaminated Water	Degradation Kinetics	First-Order Rate Constant	Routine	Biweekly
	Retention Time Verification	Preferential Flow to Specific Wells Across a Cell	Intensive	Twice
	System Efficiency	Explosive Removal Efficiency	Routine	Biweekly
Monitor the General Condition of the Wetland	Water Chemistry	Various Analytes (See Table 3-3)	Routine	Biweekly
	Physical Characteristics	Miscellaneous Characteristics (See Table 3-3)	Routine	Biweekly
Measure the Potential for Producing Toxicity	Water Toxicity	Survival, Growth, Reproduction, and IC_{25}	Intensive	Twice
	Sediment Toxicity	Survival, Growth, and IC_{25}	Intensive	Twice
Determine the Fate of Explosives Entering the Wetlands	Fate in Water	Explosive and By-Product Concentrations	Routine	Biweekly
		Additional Sample Points and Explosive By-Products	Intensive	Bimonthly
	Fate in Sediment	Explosive and By-Product Concentrations	Intensive	Bimonthly
	Fate in Plants	Explosive and By-Product Concentrations	Intensive	Bimonthly

Table 3-2

Wetland Performance - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/Frequency
Degradation Kinetics	First-Order Rate Constant	Plotted Explosive Concentration Versus Sample Position (See Description of Method in Section 3.6.1)	Intensive/Bimonthly
Retention Time Verification	Preferential Flow to Specific Wells Across a Cell	Hydraulic Tracer Test: Results of Overall Mixing and Short-Circuiting Test	Intensive/Every Six Months. (Twice Over the Duration of the Demonstration)
System Efficiency	Explosive Removal Efficiency	Calculated from Influent and Effluent Explosive Concentrations	Routine/Biweekly

- And characterizing system efficiency by calculating the removal efficiencies of explosives, explosive by-products, nutrients, and carbon (BOD-5, COD).

The general condition of each system was monitored throughout the demonstration by discreet sampling of various water quality characteristics. These parameters included chemical and physical variables which provided insight about the general health and condition of the wetlands (Table 3-3).

The potential for producing toxic effluents was investigated by conducting toxicity tests on the wetlands' water and sediments (Table 3-4). The water toxicity tests were conducted to evaluate the relative toxicity of the influent and effluent water. The water analysis consisted of screening tests to determine if the waters were toxic and follow-up tests were to be conducted if toxicity was found. The follow-up tests were designed to quantify the extent of the toxicity. Sediment toxicity tests were conducted to determine whether toxic substances were accumulating within the wetlands.

Finally, the fates of explosives entering the wetlands were determined by looking for explosives and explosive by-products in the wetlands' water, plants, and sediments. A general outline showing the specific analytes monitored is provided in Table 3-5.

To meet the objectives outlined in the tables above, two sampling programs were developed:

- A routine sampling program for monitoring the wetlands' general condition and determining treatment system efficiency (conducted biweekly)

- An intensive sampling program for assessing explosive fate, water toxicity, kinetics of explosive degradation, and verifying retention times (conducted bimonthly)

The intensive sampling program consisted of the routine program supplemented with additional analyses necessary to meet the objectives. These sampling programs are described in greater detail below. Also, supplemental descriptions are provided for the toxicity and hydraulic tracer tests needed to support the routine and intensive sampling programs.

Table 3-3

Wetland Water Conditions - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/Frequency
Water Chemistry	Metals (Ca, Mg, Fe, Mn, Cu, Ni, Zn, Pb, Cd)	Chemical Analysis	Routine/Biweekly
	Non-Purgeable Organic Carbon (NPOC)	Chemical Analysis	Routine/Biweekly
	Biochemical Oxygen Demand (BOD)	Chemical Analysis	Routine/Biweekly
	Chemical Oxygen Demand (COD)	Chemical Analysis	Routine/Biweekly
	Plant Nutrients (Nitrogen and Phosphorus)	Chemical Analysis	Routine/Biweekly
	Chlorides	Chemical Analysis	Routine/Biweekly
	Dissolved Oxygen (DO)	Chemical Analysis	Routine/Four times a day
	pH	Chemical Analysis	Routine/Four times a day
	Electrical Conductivity (EC)	Chemical Analysis	Routine/Four times a day
Physical Characteristics	Water Temperature	Instrumentation	Routine/Four times a day
	Water Flow Rate	Flowmeter	Routine/Biweekly
	Suspended Solids	Chemical Analysis	Routine/Biweekly

Table 3-4

Effluent Toxicity - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/ Frequency
Water Toxicity - Screening Test	Survival and Growth Using *Pimephales promelas* (Fathead Minnow Larvae)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97
	Survival and Reproduction Using *Ceriodaphnia dubia* (Daphnid)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97
Water Toxicity - Optional Follow-up Test	Survival, Growth, and IC_{25}[1] Using *Pimephales promelas* (Fathead Minnow Larvae)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97[1]
	Survival, Reproduction, and IC_{25} Using *Ceriodaphnia dubia* (Daphnid)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97[1]
Sediment Toxicity	Survival, Growth, and IC_{25} Using *Hyalella azteca* (Amphipods)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97
	Survival, Growth, and IC_{25} Using *Chironomus tentans* (Midge)	Toxicity Analysis	Intensive/Winter of '96/'97 and Summer of '97

1) Inhibitory concentration: The concentration of a toxic material that reduces the normal response of an organism by twenty-five percent.

Table 3-5

Fate of Explosives - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/Frequency
Explosives and By-Product Concentration in Water	**Explosives Concentration**		
	2,4,6-Trinitrotoluene (TNT)	Chemical Analysis	Routine/Biweekly
	Hexahydro-1,3,5-trinitro-1,3,5-trizaine (RDX)	Chemical Analysis	Routine/Biweekly
	Trinitrobenzene (TNB)	Chemical Analysis	Routine/Biweekly
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	Chemical Analysis	Routine/Biweekly
	2,4-Dinitrotoluene (2,4-DNT)	Chemical Analysis	Routine/Biweekly
	2,6-Dinitrotoluene (2,6-DNT)	Chemical Analysis	Routine/Biweekly
	TNT By-Product Concentration		
	2-Amino-4,6-dinitrotoluene (2A-DNT)	Chemical Analysis	Routine/Biweekly
	4-Amino-2,6-dinitrotoluene (4A-DNT)	Chemical Analysis	Routine/Biweekly
	2,6-Diamino-4-nitrotoluene (2,6-DANT)	Chemical Analysis	Routine/Biweekly
	2,4-Diamino-6-nitrotoluene (2,4-DANT)	Chemical Analysis	Routine/Biweekly
	3,5-Dinitroaniline (3,5-DNA)	Chemical Analysis	Routine/Biweekly
	1,3-Dinitrobenzene (1,3-DNB)	Chemical Analysis	Routine/Biweekly
	Azoxy Compounds		
	Tetranitro-2,2'-azoxytoluene (TN-2,2-AZT)	Chemical Analysis	Routine/Biweekly
	Tetranitro-2',4-azoxytoluene (TN-2,4-AZT)	Chemical Analysis	Routine/Biweekly
	Tetranitro-4,4'-azoxytoluene (TN-4,4-AZT)	Chemical Analysis	Routine/Biweekly
	Dinitro-4,4'-azoxytoluene (DN-4,4-AZT)	Chemical Analysis	Routine/Biweekly
	RDX By-Product Concentration		
	Mononitroso RDX	Chemical Analysis	Routine/Biweekly
	Trinitroso RDX	Chemical Analysis	Routine/Biweekly
Explosives and By-Product Concentration in Gravel & Sediment (Continued on next page)	**Explosives Concentration**		
	2,4,6-Trinitrotoluene (TNT)	Chemical Analysis	Intensive/Bimonthly
	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	Chemical Analysis	Intensive/Bimonthly
	Trinitrobenzene (TNB)	Chemical Analysis	Intensive/Bimonthly

Table 3-5 (Continued)

Fate of Explosives - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/Frequency
Explosives and By-Product Concentration in Gravel & Sediment (Continued)	**Explosives Concentration (Continued)**		
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	Chemical Analysis	Intensive/Bimonthly
	2,4-Dinitrotoluene (2,4-DNT)	Chemical Analysis	Intensive/Bimonthly
	2,6-Dinitrotoluene (2,6-DNT)	Chemical Analysis	Intensive/Bimonthly
	TNT By-Product Concentration		
	2-Amino-4,6-dinitrotoluene (2A-DNT)	Chemical Analysis	Intensive/Bimonthly
	4-Amino-2,6-dinitrotoluene (4A-DNT)	Chemical Analysis	Intensive/Bimonthly
	2,6-Diamino-4-nitrotoluene (2,6-DANT)	Chemical Analysis	Intensive/Bimonthly
	2,4-Diamino-6-nitrotoluene (2,4-DANT)	Chemical Analysis	Intensive/Bimonthly
	3,5-Dinitroaniline (3,5-DNA)	Chemical Analysis	Intensive/Bimonthly
	1,3-Dinitrobenzene (1,3-DNB)	Chemical Analysis	Intensive/Bimonthly
	Azoxy Compounds		
	Tetranitro-2,2'-azoxytoluene (TN-2,2-AZT)	Chemical Analysis	Intensive/Bimonthly
	Tetranitro-2',4-azoxytoluene (TN-2,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	Tetranitro-4,4'-azoxytoluene (TN-4,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	Dinitro-4,4'-azoxytoluene (DN-4,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	RDX By-Product Concentration		
	Mononitroso RDX	Chemical Analysis	Intensive/Bimonthly
	Trinitroso RDX	Chemical Analysis	Intensive/Bimonthly
Explosives and By-Product Concentration in Plants (Continued on next page)	**Explosive Concentration**		
	2,4,6-Trinitrotoluene (TNT)	Chemical Analysis	Intensive/Bimonthly
	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	Chemical Analysis	Intensive/Bimonthly
	Trinitrobenzene (TNB)	Chemical Analysis	Intensive/Bimonthly
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	Chemical Analysis	Intensive/Bimonthly
	2,4-Dinitrotoluene (2,4-DNT)	Chemical Analysis	Intensive/Bimonthly

Table 3-5 (Continued)

Fate of Explosives - Characteristics Measured During the MAAP Demonstration

General Characteristic	Specific Characteristic Measured or Calculated	General Method	Sampling Program/Frequency
Explosives and By-Product Concentration in Plants (Continued)	**Explosives Concentration (Continued)**		
	2,4-Dinitrotoluene (2,4-DNT)	Chemical Analysis	Intensive/Bimonthly
	2,6-Dinitrotoluene (2,6-DNT)	Chemical Analysis	Intensive/Bimonthly
	TNT By-Product Concentration		
	2-Amino-4,6-dinitrotoluene (2A-DNT)	Chemical Analysis	Intensive/Bimonthly
	4-Amino-2,6-dinitrotoluene (4A-DNT)	Chemical Analysis	Intensive/Bimonthly
	2,6-Diamino-4-nitrotoluene (2,6-DANT)	Chemical Analysis	Intensive/Bimonthly
	2,4-Diamino-6-nitrotoluene (2,4-DANT)	Chemical Analysis	Intensive/Bimonthly
	3,5-Dinitroaniline (3,5-DNA)	Chemical Analysis	Intensive/Bimonthly
	1,3-Dinitrobenzene (1,3-DNB)	Chemical Analysis	Intensive/Bimonthly
	Azoxy Compounds		
	Tetranitro-2,2'-azoxytoluene (TN-2,2-AZT)	Chemical Analysis	Intensive/Bimonthly
	Tetranitro-2',4-azoxytoluene (TN-2,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	Tetranitro-4,4'-azoxytoluene (TN-4,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	Dinitro-4,4'-azoxytoluene (DN-4,4-AZT)	Chemical Analysis	Intensive/Bimonthly
	RDX By-Product Concentration		
	Mononitroso RDX	Chemical Analysis	Intensive/Bimonthly
	Trinitroso RDX	Chemical Analysis	Intensive/Bimonthly

3.2 Description of the Routine Sampling Program

During the routine sampling program, a set of discrete water samples was obtained from selected points in the treatment systems and used to monitor water characteristics. These sampling points (Figure 3-1) are located at the:

- First cells' inlet (sample points 1 and 4)
- First cells' outlet (sample points 2 and 5)
- Second cells' outlet (sample points 3 and 6)
- GAC unit's outlet to sewer (sample point 7)
- Instrument (sonde) monitoring points within the cells (sample points 8-15)

The water samples collected at points 1-7 were analyzed at TVA RM's analytical laboratory in Muscle Shoals, Alabama, for: explosives, explosive by-products, selected metals, chemical oxygen demand, biochemical oxygen demand, non-purgeable organic carbon, plant nutrients (i.e., ammonium, nitrate, nitrite, and phosphate levels), suspended solids, and chlorides (Table 3-6).

The water samples were collected for a variety of reasons. The samples collected at points 1-6 were collected as a means of assessing treatment efficiency. Samples collected at points 3, 6, and 7 were used to determine the treatment efficiency of the granular activated carbon (GAC) in the GAC drums. The samples collected at point 7 also provided a means of determining when the GAC needed to be replaced. The GAC was replaced when the total nitrobody, or explosives, concentration at the GAC outlet (sampling point 7) became greater than 50 ppb.

Explosives monitored during the demonstration were:

- 2,4,6-Trinitrotoluene (TNT)
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
- Trinitrobenzene (TNB)
- Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

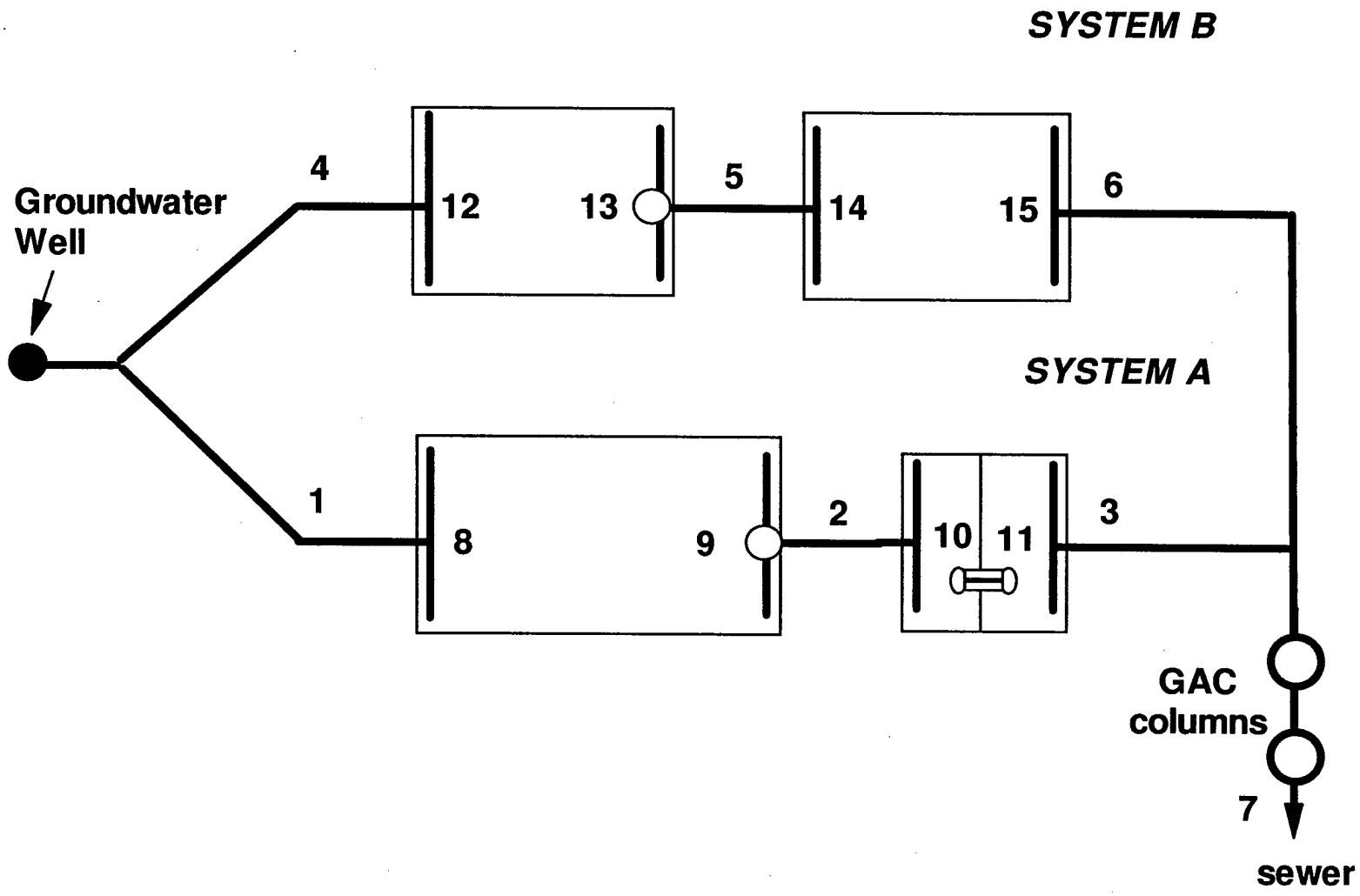


Figure 3-1

Location of Sampling Points 1-15.

Table 3-6

Outline of the Routine Biweekly Sampling Plan

Water Quality Parameters	Frequency	Method[1]	Position Number[2]
Regulatory Issues			
Explosives (Total Nitrobodies)			
TNT	Every 2 weeks	AP-0062	1-7
RDX	Every 2 weeks	AP-0062	1-7
TNB	Every 2 weeks	AP-0062	1-7
HMX	Every 2 weeks	AP-0062	1-7
2,4-DNT	Every 2 weeks	AP-0062	1-7
2,6-DNT	Every 2 weeks	AP-0062	1-7
Explosive By-Products			
2A-DNT (TNT by-product)	Every 2 weeks	AP-0062	1-7
4A-DNT (TNT by-product)	Every 2 weeks	AP-0062	1-7
2,6-DANT (TNT by-product)	Every 2 weeks	AP-0062	1-7
2,4-DANT (TNT by-product)	Every 2 weeks	AP-0062	1-7
3,5-DNA (TNT by-product)	Every 2 weeks	AP-0062	1-7
1,3-DNB (TNB by-product)	Every 2 weeks	AP-0062	1-7
Mononitroso RDX (RDX by-product)	Every 2 weeks	AP-0062	1-7
Trinitroso RDX (RDX by-product)	Every 2 weeks	AP-0062	1-7
Azoxy compounds	Every 2 months	AP-0062	1-7
Other			
Metals (Ca, Mg, Fe, Mn, Cu, Ni, Zn, Pb, Cd)	Every 2 weeks	200 Series	1-7
Biochemical Oxygen Demand (BOD-5)	Every 2 weeks	405.1 Series	1-7
Total Suspended Solids	Every 2 weeks	160.2 Series	1-7
Chlorides	Every 2 weeks	AP-0300	1-7
Environmental Monitoring			
Dissolved Oxygen, pH, Electrical Conductivity, and Temperature	Every 2 weeks	Meter[3] (YSI sonde)	1-7
Oxidation Reduction Potential	Every 2 weeks	Method 2580	1-7
Dissolved Oxygen, pH, Electrical Conductivity, and Temperature.	Four measurements a day, downloaded every 2 weeks	Meter[3] (YSI sonde)	8-15 at mid-depth
Total Flow Rate	Every 2 weeks	Meter	1-6
Non-purgeable organic carbon (NPOC)	Every 2 weeks	415 Series	1-7
Chemical Oxygen Demand (COD)	Every 2 weeks	410 Series	1-7
Plant Nutrients			
Ammonia Nitrogen (NH_4-N)	Every 2 weeks	350 Series	1-7
Total Kjeldahl Nitrogen (TKN)	Every 2 weeks	351 Series	1-7
Nitrate and Nitrite Nitrogen ((NO_3+NO_2-N)	Every 2 weeks	353 Series	1-7
Orthophosphate (PO_4-P)	Every 2 weeks	AP-0060	1-7

1) See Appendix A for details on methods and procedures.
2) See location of sampling positions in Figure 3-1.
3) Meter methods: pH method 150.1, dissolved oxygen method 360.1, temperature 170.1, and electrical conductivity method 120.1.

- 2,4-Dinitrotoluene (2,4-DNT)
- 2,6-Dinitrotoluene (2,6-DNT)

The total nitrobody concentration is defined as the sum of the explosives listed above (starting on page 3-10).

Both TNT and RDX by-products were monitored. The TNT-related by-products were:

- 2-Amino-4,6-dinitrotoluene (2A-DNT)
- 4-Amino-2,6-dinitrotoluene (4A-DNT)
- 2,6-Diamino-4-nitrotoluene (2,6-DANT)
- 2,4-Diamino-6-nitrotoluene (2,4-DANT)
- 3,5-Dinitroaniline (3,5-DNA)
- Azoxy compounds

Analysis for azoxy compounds were included because these compounds are toxic and their presence suggests different degradation pathways. The specific azoxy compounds sought were:

- Tetranitro-2,2'-azoxytoluene (TN 2,2-AZT)
- Tetranitro-2',4-azoxytoluene (TN 2,4-AZT)
- Tetranitro-4,4'-azoxytoluene (TN 4,4-AZT)
- Dinitro-4,4'-azoxytoluene (DN 4,4-AZT)

The RDX-related by-products were:

- Mononitroso RDX
- Trinitroso RDX

The dinitroso RDX by-product should be formed as a breakdown product, however, it was not quantified as part of this project because there are no standards currently available for this compound.

Data on the systems' water condition was also collected by monitoring the water quality parameters at sample points 1-15. This monitoring included analysis for:

- Dissolved oxygen content,
- pH,
- Oxidation-reduction potential,
- Water temperature,
- and Electrical conductivity.

Water conditions at sample points 1-7 were monitored with hand-held field instruments (YSI 600 Sondes) during each biweekly sampling event. To collect this data, a sonde's probe was lowered into each sampling well to mid-depth, the instrument was read, and the data recorded.

Water conditions at sampling points 8-15 were monitored by sensors (YSI 6000 Sondes) installed near permanent sampling wells. These sensors, eight sondes modified to collect data, provided a daily record of the wetlands' general condition. Each sonde was located in a sampling well with its probe positioned at mid-depth within the well. Four measurements were obtained each day and recorded in the memory of the sonde. Each sonde was capable of monitoring and recording the five parameters listed above and was equipped with an independent data logger. Every two weeks, the information was downloaded and the sonde was recalibrated. The sondes were positioned within each cell to quantify differences within the cell.

In addition to the chemical analyses described above, total flow volumes were obtained at the entrance and exit of each cell (positions 1-6). These figures were used to determine the average water flow entering and leaving each wetland cell.

Weather information (rainfall and air temperature) was also collected. This information was obtained from the University of Tennessee's Agricultural Experimental Station at Milan, Tennessee.

3.3 Description of the Intensive Sampling Program

The intensive sampling program was designed to determine the effects of season and wetland age on explosive fate, explosive removal kinetics, retention time, and water toxicity. The intensive sampling program was conducted every two months and consisted of the routine sampling program supplemented with additional analyses, as outlined in Table 3-7. Supplemental analyses added during the intensive program included:

- Additional sampling for explosives, explosive by-products, and metal analytes in the wetland waters
- Additional environmental monitoring of the wetland waters
- Analysis of the explosive and explosive by-product content in the treatment systems' sediment, gravel, and plants
- Toxicity testing of the treatment systems' waters and sediments
- Hydraulic tracer analysis of the cells

A composite water sample was obtained from sample positions 16 to 29 (Figure 3-2) when collecting samples for the additional explosives, explosive by-products, and metal analyses. Sample positions 16-19 and 22-29 represent the area in each quadrant of the gravel-based anaerobic cell and two lagoon-based cells. Sample positions 20 and 21 each represent the area in each half of the gravel-based aerobic cell. Each composite sample consisted of three whole water column samples obtained from three sampling wells located across the width of the cell in that sampling position. To obtain the whole water column samples, a coliwasa tube was submerged in each well. The coliwasa tube captured a small portion of the whole column of water in the well--hence, the term whole water column sample.

The data above was used to calculate first-order kinetic constants for explosives removal. Obtaining these constants was an important part of the demonstration since they can be used to design larger systems. This data was also used to ensure that first-order equations adequately described explosive removal. Methods for determining the kinetic constants are described in Section 3.6.

Table 3-7

Outline of the Intensive Bimonthly Sampling Plan

Parameters	Frequency	Method[1]	Position[2]
Water Quality Parameters			
TNT	Every 2 months	AP-0062	1-7,16-29
RDX	Every 2 months	AP-0062	1-7,16-29
TNB	Every 2 months	AP-0062	1-7,16-29
HMX	Every 2 months	AP-0062	1-7,16-29
2,4-DNT	Every 2 months	AP-0062	1-7,16-29
2,6-DNT	Every 2 months	AP-0062	1-7,16-29
2A-DNT (TNT by-product)	Every 2 months	AP-0062	1-7,16-29
4A-DNT (TNT by-product)	Every 2 months	AP-0062	1-7,16-29
2,6-DANT (TNT by-product)	Every 2 months	AP-0062	1-7,16-29
2,4-DANT (TNT by-product)	Every 2 months	AP-0062	1-7,16-29
3,5-DNA (TNT by-product)	Every 2 months	AP-0062	1-7,16-29
1,3-DNB (TNB by-product)	Every 2 months	AP-0062	1-7,16-29
Mononitroso RDX (RDX by-product)	Every 2 months	AP-0062	1-7,16-29
Trinitroso RDX (RDX by-product)	Every 2 months	AP-0062	1-7,16-29
Azoxy Compounds	Every 2 months	AP-0062	1-7,16-29
Chemical Oxygen Demand (COD)	Every 2 months	410 Series	1-7,16-29
Environmental Monitoring			
Non-Purgeable Organic Carbon (NPOC)	Every 2 months	415 Series	1-7,16-29
Ammonia Nitrogen (NH_4-N)	Every 2 months	350 Series	1-7,16-29
Total Kjeldahl Nitrogen (TKN)	Every 2 months	351 Series	1-7,16-29
Nitrate & Nitrite Nitrogen (NO_3+NO_2-N)	Every 2 months	353 Series	1-7,16-29
Orthophosphate (PO_4-P)	Every 2 months	SP-0060	1-7,16-29
pH (Lab Samples)	Every 2 months	150 Series	1-7, 16-29
Dissolved Oxygen, pH, Temperature, Electrical Conductivity	Every 2 months	Meter [3] (YSI sonde)	1-7, 16-29
Oxidation Reduction Potential	Every 2 months	Method 2580	1-7, 16-29
Total Suspended Solids	Every 2 months	160.2 Series	1-7, 16-29
Chlorides	Every 2 months	AP-0300	1-7, 16-29
Metals (Ca, Mg, Fe, Mn, Cu, Ni, Zn, Pb, Cd)	Every 2 months	200 Series	1-7, 16, 19, 21, 22, 25, 26, 29
Toxicity Test With *Pimephales promelas* (Fathead Minnow)	Winter of '96/'97 and Summer of '97	EPA Method 1000.0 (Survival and Growth)	3,6, and Composite of 1 and 4
Toxicity Test With *Ceriodaphnia dubia* (Daphnid)	Winter of '96/'97 and Summer of '97	EPA Method 1002.0 (Survival and Reproduction)	3,6, and Composite of 1 and 4
Sediment Quality Parameters			
TNT	Every 2 months	AP-0062	30-37
RDX	Every 2 months	AP-0062	30-37
TNB	Every 2 months	AP-0062	30-37
HMX	Every 2 months	AP-0062	30-37
2,4-DNT	Every 2 months	AP-0062	30-37
(Table continued on next page)			

Table 3-7 (Continued)

Outline of the Intensive Bimonthly Sampling Plan

Parameters	Frequency	Method[1]	Position[2]
Sediment Quality Parameters (Cont.)			
2,6-DNT	Every 2 months	AP-0062	30-37
2A-DNT (TNT by-product)	Every 2 months	AP-0062	30-37
4A-DNT (TNT by-product)	Every 2 months	AP-0062	30-37
2,6-DANT (TNT by-product)	Every 2 months	AP-0062	30-37
2,4-DANT (TNT by-product)	Every 2 months	AP-0062	30-37
3,5-DNA (TNT by-product)	Every 2 months	AP-0062	30-37
1,3-DNB (TNB by-product)	Every 2 months	AP-0062	30-37
Mononitroso RDX (RDX by-product)	Every 2 months	AP-0062	30-37
Trinitroso RDX (RDX by-product)	Every 2 months	AP-0062	30-37
Azoxy Compounds	Every 2 months	AP-0062	30-37
Toxicity Test With *Hyalella azteca* (Amphipods)	Winter of '96/'97 and Summer of '97	EPA Method 100.1 (Survival Test)	16-21, 24, and 28
Toxicity Test With *Chironomus tentans* (Midge)	Winter of '96/'97 and Summer of '97	EPA Method 100.2 (Survival Test)	24 and 28
Explosives & Related By-Products in Plants			
TNT	Every 2 months	AP-0062	30-37
RDX	Every 2 months	AP-0062	30-37
TNB	Every 2 months	AP-0062	30-37
HMX	Every 2 months	AP-0062	30-37
2,4-DNT	Every 2 months	AP-0062	30-37
2,6-DNT	Every 2 months	AP-0062	30-37
2A-DNT (TNT by-product)	Every 2 months	AP-0062	30-37
4A-DNT (TNT by-product)	Every 2 months	AP-0062	30-37
2,6-DANT (TNT by-product)	Every 2 months	AP-0062	30-37
2,4-DANT (TNT by-product)	Every 2 months	AP-0062	30-37
3,5-DNA (TNT by-product)	Every 2 months	AP-0062	30-37
1,3-DNB (TNB by-product)	Every 2 months	AP-0062	30-37
Mononitroso RDX (RDX by-product)	Every 2 months	AP-0062	30-37
Trinitroso RDX (RDX by-product)	Every 2 months	AP-0062	30-37
Azoxy compounds	Every 2 months	AP-0062	30-37
Hydraulic Tracer Analysis			
Bromide (Overall Mixing)	Every 4 months	AP-0300	2,3,5,6
Bromide (Short-Circuiting)	Every 6 months	AP-0300	38-52

1) See Appendix A for details on methods and procedures.
2) See location of sampling positions in Figures 3-1 and 3-2.
3) Meter methods: pH method 150.1, dissolved oxygen method 360.1, temperature 170.1, and electrical conductivity method 120.1.

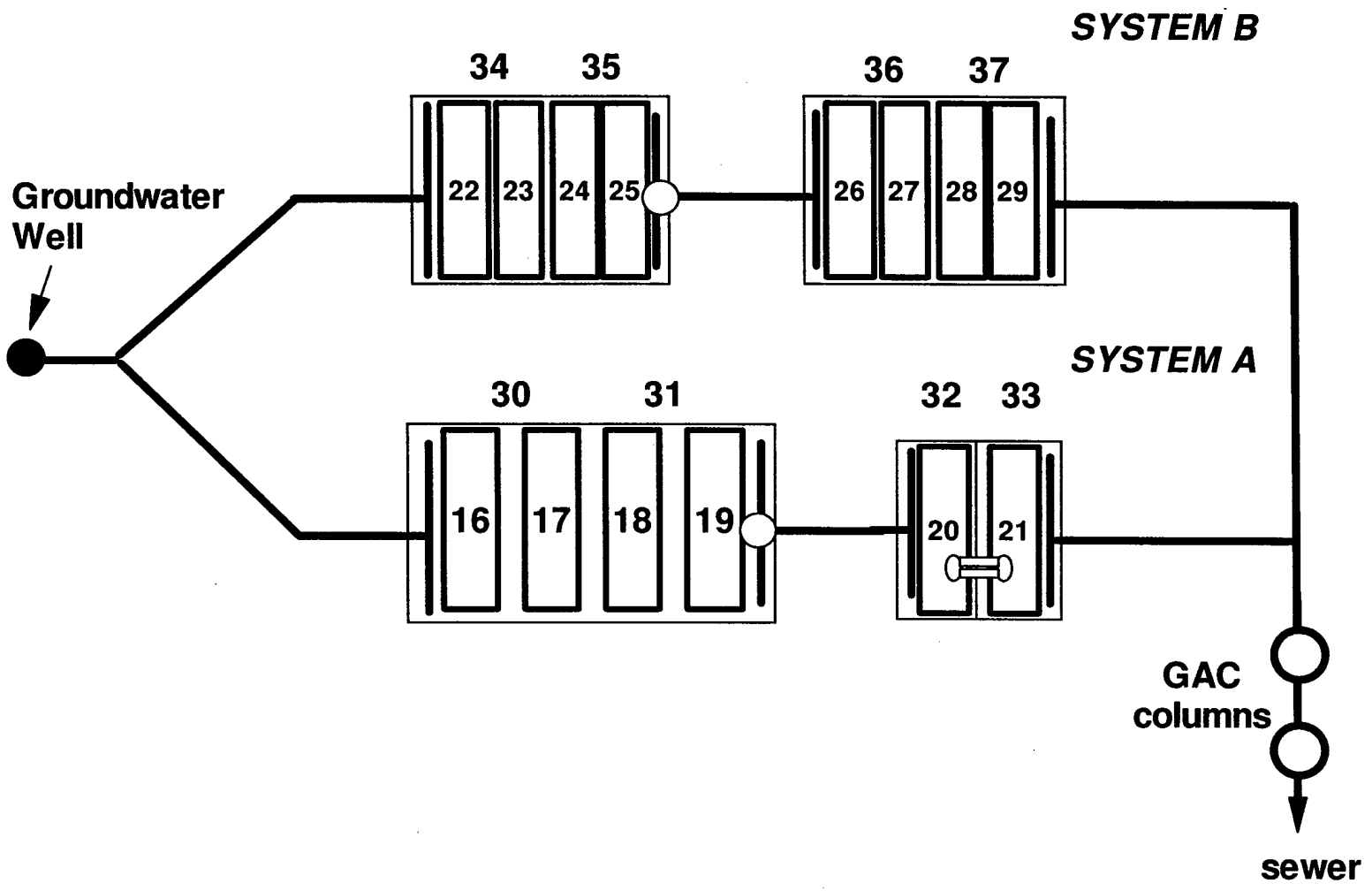


Figure 3-2

Location of Sampling Points 16-37

The fate of explosives entering the demonstration wetlands was assessed by collecting composite sediment, gravel, and plant samples from the area within sampling positions 30-37. These sampling positions were created by dividing each wetland cell into front and back halves (Figure 3-2). Each composite sample consisted of six randomly collected subsamples.

After collection, the composite samples were analyzed for bound or assimilated by-product and explosive content. The analyses were used to determine if toxic by-products were forming in the wetland systems due to incomplete degradation.

The environmental monitoring program was expanded to include monitoring of wells in the interior of each wetland at sample points 16-29 (Table 3-7). To measure dissolved oxygen, water temperature, electrical conductivity, and pH, sonde probes were placed at mid-depth to collect data. To measure oxidation-reduction potential, a platinum electrode was kept in each well at mid-depth. Its potential was measured against a reference electrode with a portable millivolt meter. Water samples were also collected and analyzed for various nutrients, non-purgeable organic carbon, total suspended solids, and chlorides.

3.4 Description of the Toxicity Tests

3.4.1 General Introduction

As part of the intensive sampling program, TVA RM conducted a series of ecological toxicity tests during the winter of 1996-1997 and summer of 1997 (Tables 3-4 and 3-7). These tests consisted of two types:

- Toxicity testing of the water entering and leaving the wetlands
- Toxicity testing of the gravel and sediments within the wetlands

3.4.2 Description of the Water Toxicity Tests

The water toxicity tests consisted of three subtests: a preliminary screening test and two follow-up tests. The preliminary screening test (Table 3-8) was conducted during the winter of 1996-1997 and consisted of:

Table 3-8

Outline of the Preliminary Screening Test for Water Toxicity

Indicator Species	Sample Point	Parameter Measured	Variables	Replicates
Pimephales promelas (Fathead Minnow Larvae)	Control	Survival and Growth	0% source water	4
	Adjusted Control	Survival and Growth	0% source water with pH adjusted[1]	4
	Points 1 & 4 (Well MI-051)	Survival, Growth, and IC_{25}[2]	12.5% source water	4
			25% source water	4
			50% source water	4
			75% source water	4
			100% source water	4
			100% source water with pH adjusted[1]	4
	Point 3	Survival and Growth	100% source water	4
	Point 3 (Replicate)	Survival and Growth	100% source water	4
	Point 6	Survival and Growth	100% source water	4
	Point 6 (Replicate)	Survival and Growth	100% source water	4
Ceriodaphnia dubia (Daphnid)	Control	Survival and Reproduction	0% source water	10
	Adjusted Control	Survival and Reproduction	0% source water with pH adjusted[1]	10
	Points 1 & 4 (Well MI-051)	Survival, Reproduction, and IC_{25}[2]	12.5% source water	10
			25% source water	10
			50% source water	10
			75% source water	10
			100% source water	10
			100% source water with pH adjusted[1]	10
	Point 3	Survival and Reproduction	100% source water	10
	Point 3 (Replicate)	Survival and Reproduction	100% source water	10
	Point 6	Survival and Reproduction	100% source water	10
	Point 6 (Replicate)	Survival and Reproduction	100% source water	10

1) pH adjusted to the EPA-required limits between 6.0 and 9.0.
2) IC_{25} is the inhibitory concentration that reduces the normal response of an organism by 25 percent estimated by graphical or computational means.

- Toxic screening tests for each effluent stream (sample points 3 and 6)
- A serial dilution test on the incoming stream (a composite of sample points 1 and 4)

The toxic screening tests were conducted to determine if the effluent waters were toxic. To conduct the screening tests, two indicator species were placed in aquaria containing undiluted sample while the organisms' rates of survival, growth, and reproduction were measured. The methods used to determine toxicity for each species are shown in Table 3-7. If an effluent stream was found to be toxic by the screening test, then the EPA methods used required follow-up serial dilution tests conducted for that effluent stream.

Serial dilution tests were conducted to quantify the toxicity of MI-051's well water. To conduct these tests, composite water samples from sample points 1 and 4 were placed in replicate aquaria at various concentrations (Table 3-8). Indicator species were then placed in the aquaria and their survival, growth, and reproduction responses were measured at each concentration. Using this data, the degree of toxicity was found and expressed as a 25% inhibitory concentration number or IC_{25}. This number is the concentration of a toxic material that reduces the normal response of an organism by 25%.

Both the screening and serial dilution tests were conducted using *Ceriodaphnia dubia* (daphnid) and *Pimephales promelas* (fathead minnow larvae) as the indicator species. The fathead minnow larvae were used to measure growth and survival utilizing EPA Method 1000.0. The daphnids were used to measure survival and reproduction utilizing EPA Method 1002.0.

Follow-up serial dilution tests were conducted in the winter of 1996/1997 and summer of 1997. Each follow-up test consisted of two serial dilution tests–one for each indicator species (Table 3-9). The follow-up tests were designed to determine the IC_{25} for these waters. Samples used to conduct the follow-up tests were collected at sample points 3 and 6. In addition, chemical analyses of the samples were forwarded to TVA's toxicologist as a means of identifying a probable cause of any toxic response. A list of the analyses sent to the toxicologist is provided in Table 3-10.

Table 3-9

Outline of the Water Toxicity Follow-up Serial Dilution Test

Indicator Species	Sample Point	Parameter Measured	Variables	Replicates
Pimephales promelas (Fathead Minnow Larvae)	Control	Survival and Growth	0% source water	4
	Point 3 (gravel system)	Survival, Growth, and IC_{25}[1]	12.5% source water	4
			25% source water	4
			50% source water	4
			75% source water	4
			100% source water	4
	Point 6 (lagoon system)	Survival, Growth, and IC_{25}[1]	12.5% source water	4
			25% source water	4
			50% source water	4
			75% source water	4
			100% source water	4
Ceriodaphnia dubia (Daphnid)	Control	Survival and Reproduction	0% source water	10
	Point 3 (gravel system)	Survival, Reproduction, and IC_{25}[1]	12.5% source water	10
			25% source water	10
			50% source water	10
			75% source water	10
			100% source water	10
	Point 6 (lagoon system)	Survival, Reproduction, and IC_{25}[1]	12.5% source water	10
			25% source water	10
			50% source water	10
			75% source water	10
			100% source water	10

1) IC_{25} is the inhibitory concentration that reduces the normal response of an organism by 25% estimated by graphical or computational means.

Table 3-10

Water Toxicity Testing - Water Analyses Sent to Toxicologist

Parameters	Frequency	Method[1]	Position[2]
Explosives and Explosive By-Products			
TNT	One to three times[3]	AP-0062	1, 3, 4, & 6
RDX	One to three times[3]	AP-0062	1, 3, 4, & 6
TNB	One to three times[3]	AP-0062	1, 3, 4, & 6
HMX	One to three times[3]	AP-0062	1, 3, 4, & 6
2,4-DNT	One to three times[3]	AP-0062	1, 3, 4, & 6
2,6-DNT	One to three times[3]	AP-0062	1, 3, 4, & 6
2A-DNT (TNT by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
4A-DNT (TNT by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
2,6-DANT (TNT by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
2,4-DANT (TNT by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
Mononitroso RDX (RDX by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
Trinitroso RDX (RDX by-product)	One to three times[3]	AP-0062	1, 3, 4, & 6
Azoxy Compounds			
Tetranitro-2,2'-azoxy-azoxytoluene	One to three times[3]	AP-0062	1, 3, 4, & 6
Tetranitro-2',4-azoxytoluene	One to three times[3]	AP-0062	1, 3, 4, & 6
Tetranitro-4,4'-azoxytoluene	One to three times[3]	AP-0062	1, 3, 4, & 6
Dinitro-4,4'-azoxytoluene	One to three times[3]	AP-0062	1, 3, 4, & 6
Metals			
Cadmium (Cd)	One to three times[3]	200 Series	1, 3, 4, & 6
Calcium (Ca)	One to three times[3]	200 Series	1, 3, 4, & 6
Copper (Cu)	One to three times[3]	200 Series	1, 3, 4, & 6
Iron (Fe)	One to three times[3]	200 Series	1, 3, 4, & 6
Lead (Pb)	One to three times[3]	200 Series	1, 3, 4, & 6
Manganese (Mn)	One to three times[3]	200 Series	1, 3, 4, & 6
Nickel (Ni)	One to three times[3]	200 Series	1, 3, 4, & 6
Zinc (Zn)	One to three times[3]	200 Series	1, 3, 4, & 6
Other			
Non-Purgeable Organic Carbon (NPOC)	One to three times[3]	415 Series	1, 3, 4, & 6
Total Kjeldahl Nitrogen (TKN)	One to three times[3]	351 Series	1, 3, 4, & 6
Nitrate Nitrogen (NO_3-N)	One to three times[3]	353 Series	1, 3, 4, & 6
Orthophosphate (PO_4-P)	One to three times[3]	AP-0060	1, 3, 4, & 6
Chloride	One to three times[3]	AP-0300	1, 3, 4, & 6
Suspended Solids	One to three times[3]	160.2 Series	1, 3, 4, & 6

1) See Appendix A for details on methods and procedures.
2) See location of sampling positions in Figures 3-1 and 3-2.
3) Sampling points 1 and 4 were tested once. Sampling points 3 and 6 were sampled three times--during the screening test and during two definitive tests.

3.4.3 Description of the Sediment Toxicity Tests

The toxicity of the wetlands' sediments were also measured. The sediment toxicity tests were conducted in the winter of 1996/1997 and summer of 1997. Each test consisted of two serial dilution tests (Tables 3-4 and 3-11). The first serial dilution test was conducted using *Hyalella azteca*, or amphipods, as the indicator species. These tests were conducted using sediment from both the gravel- and lagoon-based wetlands. Gravel was considered sediment in the gravel-based wetlands. Amphipods were tested because these organisms live and feed on the surface of the substrate. The second serial dilution test was conducted using *Chironomus tentans* (midge). Tests with midge were limited to lagoon-based sediments because midge burrow into sediment and could not do so in gravel. Both organisms were used to measure growth and survival responses. The amphipods were tested utilizing EPA Method 100.1; the midge were tested utilizing EPA Method 100.2 (Table 3-7).

The gravel-based wetland's sediment (gravel) underwent extensive scrutiny during the sediment toxicity tests, since the gravel is in intimate contact with contaminated water throughout the entire water column. During the toxicity tests, gravel samples were taken from each quadrant of the anaerobic cell and each half of the aerobic cell at a depth of approximately 1 foot. These sample points correspond to sampling points 16-21 in Figure 3-2.

In contrast, the sediment from the lagoon-based system underwent testing at sampling points 24 and 28 only at a depth of approximately 4 inches. These points are located in each lagoon's third sampling quadrant. The lagoons required less extensive sampling because the sediments are more uniform and only the surface of the sediments are in intimate contact with contaminated water. In addition to the toxicity tests, the sediment at sample points 16-21, 24, and 28 underwent chemical analysis for explosives and explosive by-products (Table 3-12). These analyses were forwarded to TVA's toxicologist as a means of identifying a probable cause of any toxic response.

Table 3-11

Outline of the Sediment Serial Dilution Test

Indicator Species	Sample Point	Parameter Measured	Replicates	Sample Required (ml)
Hyalella azteca (Amphipods)	Sediment Control	Survival and Growth	8	2,000
	Gravel Control		8	2,000
	Point 16		8	2,000
	Point 17		8	2,000
	Point 18		8	2,000
	Point 19		8	2,000
	Point 20		8	2,000
	Point 21		8	2,000
	Point 24		8	2,000
	Point 28		8	2,000
Chironomus tentans (Midge)	Sediment Control	Survival and Growth	8	2,000
	Point 24		8	2,000
	Point 28		8	2,000

Table 3-12

Sediment Toxicity Testing - Sediment Analysis

Parameters	Frequency	Method[1]	Position[2]
TNT	Twice	AP-0062	16-21, 24, & 28
RDX	Twice	AP-0062	16-21, 24, & 28
TNB	Twice	AP-0062	16-21, 24, & 28
HMX	Twice	AP-0062	16-21, 24, & 28
2,4-DNT	Twice	AP-0062	16-21, 24, & 28
2,6-DNT	Twice	AP-0062	16-21, 24, & 28
2A-DNT (TNT by-product)	Twice	AP-0062	16-21, 24, & 28
4A-DNT (TNT by-product)	Twice	AP-0062	16-21, 24, & 28
2,6-DANT (TNT by-product)	Twice	AP-0062	16-21, 24, & 28
2,4-DANT (TNT by-product)	Twice	AP-0062	16-21, 24, & 28
Mononitroso RDX (RDX by-product)	Twice	AP-0062	16-21, 24, & 28
Trinitroso RDX (RDX by-product)	Twice	AP-0062	16-21, 24, & 28
Azoxy Compounds			
Tetranitro-2,2'-azoxytoluene	Twice	AP-0062	16-21, 24, & 28
Tetranitro-2',4-azoxytoluene	Twice	AP-0062	16-21, 24, & 28
Tetranitro-4,4'-azoxytoluene	Twice	AP-0062	16-21, 24, & 28
Dinitro-4,4'-azoxytoluene	Twice	AP-0062	16-21, 24, & 28

1) See Appendix A for details on methods and procedures.
2) See location of sampling positions in Figure 3-2.

3.5 Description of the Hydraulic Mixing Tests

3.5.1 General Background

Hydraulic mixing in the wetlands was assessed as part of the intensive sampling program. Two hydraulic tracer tests were used. In the first test, the overall mixing characteristics of each cell were investigated. In the second test, the possible existence of short circuiting was examined. The overall mixing test was conducted three times (once every 4 months) and the short-circuiting test was conducted twice (once every six months) [Table 3-7].

3.5.2 Description of the Overall Mixing Test

During an overall mixing test, a slug of sodium bromide (NaBr) was added to the influent of each wetland cell while the effluent's bromide (Br^-) concentration was monitored at the effluent sump. Water samples collected during the monitoring process were transported to TVA RM's analytical laboratory in Muscle Shoals, Alabama, for analysis by ion chromatography. To ensure that sufficient data was collected, each cell was monitored longer than the cell's estimated retention time. Cells A1, B1, and B2 were monitored over a 16-day period. Cell A2 was monitored over a 7-day period. In addition, the volume of effluent leaving the cells was recorded using a flow meter. The total flow and flow rate were recorded every day.

The actual weight of NaBr added to each cell was varied with the size of the cell. Cells B1 and B2 were fed 702 grams of NaBr, while cell A1 was fed 948 grams and cell A2 was fed 280 grams. Each NaBr slug was dissolved in a plastic bucket containing five gallons of water.

The NaBr slugs were added to the cells at different times. The slugs to cells A1, A2, and B2 were introduced at approximately the same time. Cell B1's slug was added eight days later to avoid interference from the slug added to cell B2. Each NaBr slug was introduced to a cell over a 20-minute period. The slugs added to cells A1 and B1 were introduced through 3-inch sampling ports located above the inlet headers. One gallon of the 5-gallon slugs was poured into each sampling port every five minutes. Sufficient suction existed at the sampling ports to ensure that the fluid was sucked into the inlet header. The slugs added to cells A2 and B2 were

introduced through the effluent sumps in cells A1 and B1, respectively. The slugs were added to the sump by pouring a single gallon into the sump at five-minute intervals.

The effluent's bromide concentration was monitored by collecting water samples at the effluent sumps of cells A1, A2, B1, and B2. These sumps correspond with sampling points 2, 3, 5, and 6, respectively (Figure 3-1). The effluent samples were collected using four autosamplers--one for each effluent sump. The autosamplers were fed by plastic tubing. The inlet to each tube was placed in the standpipe of the respective effluent header. The autosamplers were positioned just outside the sumps. The autosamplers collected a 50-ml sample at 1-hour increments and stored the samples in 200-ml plastic containers. Each container held a 4-hour composite sample. The containers were collected for transportation to a TVA RM laboratory at 4-day intervals.

3.5.3 Description of the Short-Circuiting Test

During the short-circuiting test, a NaBr slug was added to the influent of cells A1, B1, and B2, while the bromide concentration was monitored in each of the five wells parallel to each cell's effluent header. The sampling wells were located at sampling points 38-52 (Figure 3-3). Each sampling well consisted of a 6-inch-diameter slotted PVC pipe placed vertically to a depth of 4 feet. Each well was spaced equally across the width of the cell. Short-circuit testing was not conducted on well A2 since this cell's design precludes short-circuiting (i.e., the cell is a complete-mix reactor).

Short-circuiting tests were conducted concurrent with the overall mixing tests. So, the bromide used to conduct the overall mixing test was also used to conduct the short-circuiting test. Bromide was prepared and added to the influent of each wetland, as described for the overall mixing tracer test above.

Sampling for the short-circuiting test began approximately five days after the bromide slug was added to each wetland. After the sampling process began, the sampling wells were manually sampled at 4-hour increments for an additional five days. Each sample was taken as a whole-water column sample.

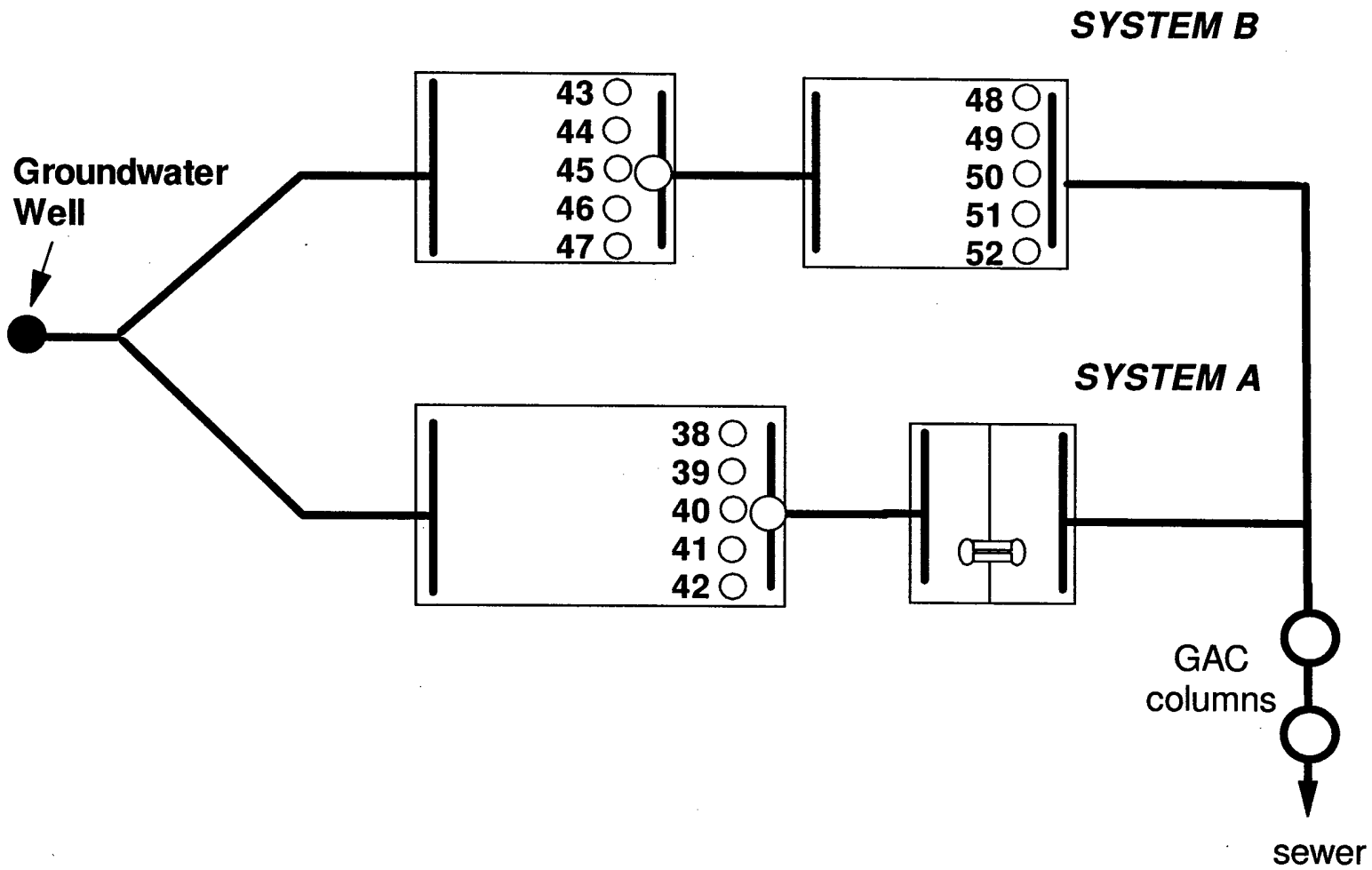


Figure 3-3

Location of Sampling Points 38-52

In August 1997, the usual short-circuiting test was supplemented by monitoring the bromide concentration at sampling points 53-64 (Figure 3-4). This monitoring was conducted to get a better picture of the gravel bed's mixing characteristics. Water samples were collected at three depths within each well. These depths were 8, 24, and 40 inches from the surface of the water.

3.6 Theoretical Background and Methods for Supporting Calculations

3.6.1 Calculation of the First-Order Kinetic Rate Constants

Analyses of water samples taken every other month were used to calculate first-order rate constants for TNT and RDX assuming plug-flow hydraulics.[Ref. 9] The first-order rate equation is:

$$\ln (C/ Ci) = -y (k/q) \qquad \text{[Equation 1]}$$

Where:

y is the fractional distance between the cell's inlet to outlet (ranging from 0 to 1)

C is the pollutant concentration at y

Ci is the influent concentration of the pollutant

k is the first-order rate constant (with units in meter/year)

q is the hydraulic loading rate (in meters/year)

The TNT and RDX removal rate constants for the anaerobic gravel-based wetland (A1) were determined via linear regression of the equation $\ln(C/Ci) = b_0 + k(-y/q)$ where the intercept (b_0) is assumed to equal zero. The regression analyses included six data points: the influent (y=0), the effluent (y=1), and four water samples taken at interior locations. The slope of the resulting regression line was the rate constant (k). Rate constants were not determined for the aerobic cell (cell A2) due to the cell's complete-mix characteristics.

The TNT and RDX removal rate constants for the lagoon-based system were also determined via linear regression of equation 1. However, only three data points were used to determine the rate constant--those corresponding to information collected at sampling points 4, 5, and 6

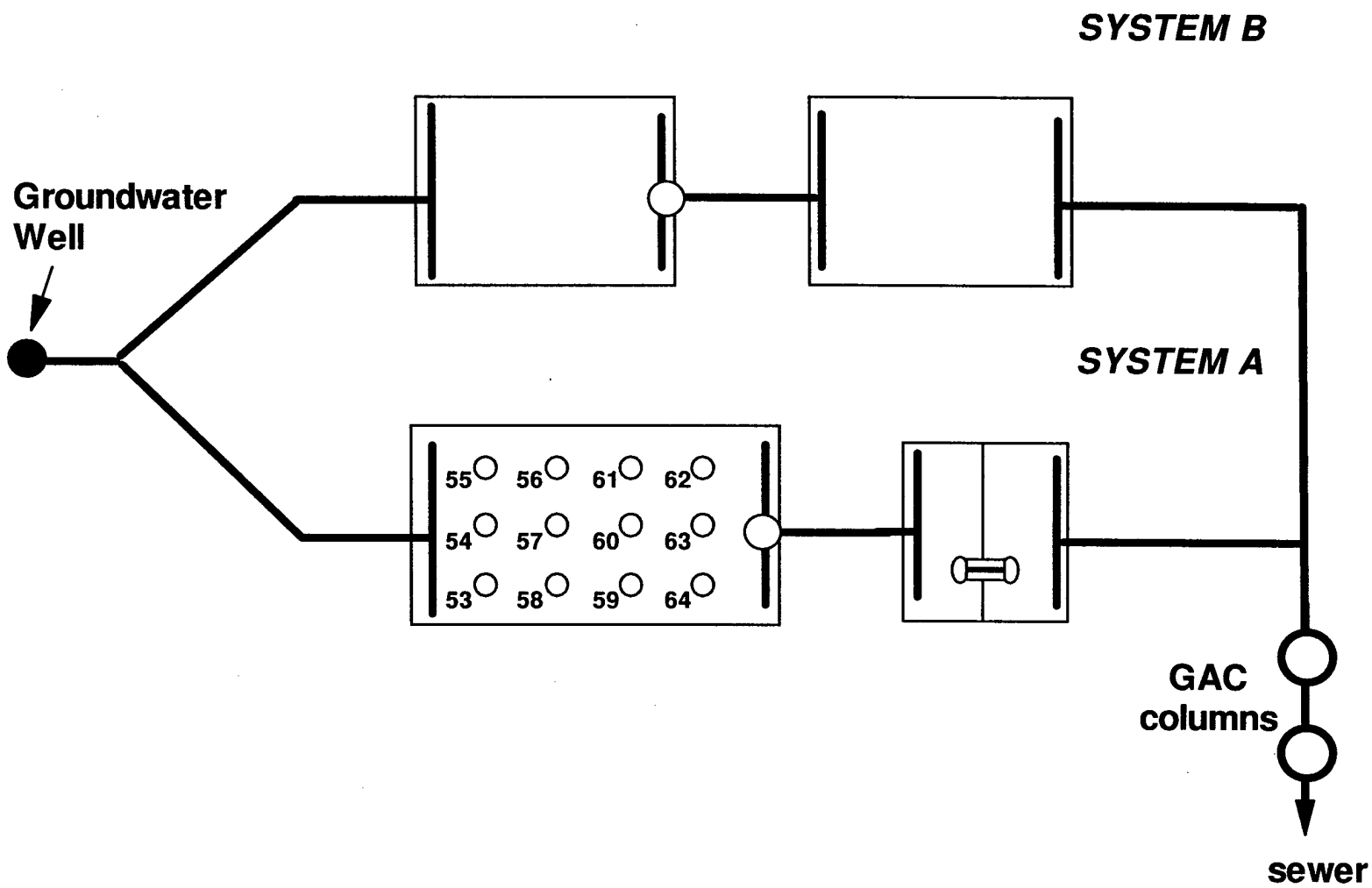


Figure 3-4

Location of Sampling Points 53-64

(Figure 3-1). In this case, C was the concentration of TNT or RDX in the influent to B1, effluent to B1, and effluent to B2 with y = 0, 0.5, and 1, respectively. Data collected in the interior of the lagoon-based cells could not be used to determine the rate constants because the water in each lagoon was well-mixed and the lagoons behaved like well-mixed reactors. Obtaining data from the interior of a well mixed reactor would not have produced meaningful results.

3.7 Sample Collection and Laboratory Procedures

3.7.1 Water-Sampling Procedures for the Routine Biweekly Sampling Program

During the routine biweekly sampling program, water samples were collected from sample points 1-7 (Figure 3-1). At sample points 1, 4, and 7, the samples were collected by opening sampling valves placed in process lines. At sample points 2, 4, and 6, the samples were collected from sumps located at the end of each wetland. The sump samples were collected by placing a 4-L stainless steel beaker beneath the sump pump outlet. At sample point 3, the water was collected in the sump with a whole-water column sampler (coliwasa tube) and poured into a 4-L stainless steel beaker.

Part of the solution in the 4-L beaker was transferred into two 1-L wide-mouth plastic bottles. The contents of the first 1-L container were analyzed for biochemical and chemical oxygen demand. The contents of the second 1-L container were analyzed for suspended solids. Next, two 50-ml subsamples were transferred from the 4-L beaker to two 60-ml amber glass bottles, sealed with a Teflon-lined lid, and wrapped in aluminum foil and plastic bubble wrap. The contents of the amber glass containers were analyzed for explosives and explosive by-products. Next, approximately 120 ml of water from the 4-L beaker were filtered through a Whatman Number 42 filter paper and transferred to a 120-ml plastic bottle. The contents of this bottle were analyzed for metals and chlorides. Finally, approximately 120 ml of water from the 4-L beaker were poured into a 120-ml plastic bottle to be analyzed for total Kjeldahl nitrogen, total organic nitrogen, ammonia nitrogen, nitrate and nitrite nitrogen, and orthophosphate. The contents of each of the two 120-ml containers described above were preserved with 1.12 ml of 1N H_2SO_4. All sample containers were labeled to identify date collected, location, and project identification. Field collection sheets were used to document the date, location, sample

identification codes, and identity of the sampler. All of the containers were placed in an ice chest containing ice or a commercial ice substitute and were transported to the laboratory in the custody of a TVA RM employee. All samples were refrigerated upon arrival at the lab. All samples received from the test site were handled in accordance with TVA's chain of custody procedure (Appendix A-21).

In addition to the water samples described above, a number of measurements were taken directly from the wetlands. These measurements included dissolved oxygen, pH, temperature, and electrical conductivity using hand-held instruments (YSI sonde). At sampling positions 1, 4, and 7, where the wetland water was accessed from a valve, the water was first transferred to a 4-L stainless steel beaker. To obtain the required measurements, the probes of a YSI sonde were submerged in the beaker. Where a sump provided access to the wetland's water, a YSI sonde was placed into the water at mid-depth. Sumps are located at sampling positions 2, 3, 5, and 6. The pH, dissolved oxygen, temperature, and electrical conductivity readings were recorded on a data collection sheet.

3.7.2 Water-Sampling Procedures for the Intensive Bimonthly Sampling Program

During the bimonthly program, the biweekly program was augmented by measurements of various parameters at sampling points 16-29 (Figure 3-2). Water samples normally collected at positions 1-7 in the biweekly program were also collected in the bimonthly program. These samples were collected in the same fashion as described above for the biweekly program.

Sampling points 16-29 were created by dividing each wetland cell into quadrants. Each of the quadrants contained three sampling wells–these wells collectively constituted a sampling point. Each sampling well consisted of a 6-inch-diameter slotted PVC pipe placed vertically to a depth of 4 feet. Each well was spaced equally across the width of each quadrant. During the sampling process, a whole-water column sample was taken from each of the three wells with a coliwasa tube and the samples were composited. The composite sample was intended to represent the average condition of wetland waters at a specific distance between the influent and effluent headers.

When sampling the wells at sampling points 16-29, the whole-water column samples were placed in a single 4-L stainless steel beaker for distribution to other containers. Part of the solution in the 4-L beaker was transferred into two 1-L wide-mouth plastic bottles. The contents of the first 1-L container were analyzed for biochemical oxygen demand and chemical oxygen demand. The contents of the second 1-L container were analyzed for suspended solids. Next, two 50-ml subsamples were transferred from the 4-L beaker to two 60-ml amber glass bottles, sealed with a Teflon-lined lid, and wrapped in aluminum foil and plastic bubble wrap. The contents of the amber glass containers were analyzed for explosives and explosive by-products. Next, approximately 120 ml of water from the 4-L beaker were filtered through a Whatman Number 42 filter paper and transferred to a 120-ml plastic bottle. The contents of this bottle were analyzed for metals and chlorides. Finally, approximately 120 ml of water from the 4-L beaker were poured into a 120-ml plastic bottle to be analyzed for total Kjeldahl nitrogen, total organic nitrogen, ammonia nitrogen, nitrate and nitrite nitrogen, and orthophosphate. The contents of each of the two 120-ml containers described above were preserved with 1.12 ml of 1N H_2SO_4. All sample containers were labeled to identify date collected, location, and project identification. All of the containers were placed in an ice chest containing ice or a commercial ice substitute and were transported to the laboratory in the custody of a TVA RM employee. All samples were refrigerated upon arrival to the lab. All samples received from the test site were handled in accordance with TVA's chain of custody procedure (Appendix A-21).

Using the same procedures described for the biweekly program, a YSI sonde probe was used to determine pH, dissolved oxygen, temperature, and electrical conductivity at sampling positions 16-29, that is by placing the probe at mid-depth within each PVC well. The measured parameters were recorded on a data collection sheet.

3.7.3 Sediment-Sampling Procedures for the Intensive Bimonthly Sampling Program

As part of the goal to determine the explosives' fate, composite sediment samples were collected on a bimonthly basis (Table 3-7). The sediment samples were taken from each wetland at sampling points 30-37 (Figure 3-2).

In the gravel-based wetland, the sediment consisted of the existing gravel beds. The gravel was collected from six random locations within each cell half. During the collection process, the gravel was dug by shovel from the surface to a depth of about 12 inches (approximately quarter-depth). The gravel collected from the six locations was mixed in a large bucket. A subsample was placed in a 2-gallon plastic container–a plastic container was used to avoid breakage. The 2-gallon container was wrapped with aluminum foil and placed in an ice chest containing ice or a commercial ice substitute. All sample containers were labeled to identify date collected, location, and project identification. All of the containers were transported to the laboratory in the custody of a TVA RM employee. All samples received from the test site were handled in accordance with TVA's chain of custody procedure. Upon receipt at the laboratory, the gravel samples were refrigerated until analyzed for explosive and explosive by-products, as outlined in Table 3-7. The sediment's explosive content was normalized to dry matter weight of sediment by correcting for moisture content.

In the lagoon-based wetland, the sediment consisted of the soil lying at the bottom of each lagoon. Sampling was conducted from a flat-bottomed boat. Sediment samples were collected to a depth of 4 inches using a soil probe. Sediment was collected from six locations within each half section of each cell. Sediments from each cell's half section were manually mixed and subsamples were stored in two 60-ml wide-mouth brown glass containers. The containers were wrapped in aluminum foil and stored in an ice chest containing ice or a commercial ice substitute. The containers were labeled to identify date of collection, location, and project identification. All of the containers were transported to the laboratory in the custody of a TVA RM employee. All samples received from the test site were handled in accordance with TVA's chain of custody procedure. Upon receipt at the laboratory, the sediment samples were refrigerated until analyzed for explosives and explosive by-products, as outlined in Table 3-7. The sediment's explosive content was normalized to dry matter weight of sediment by correcting for moisture content.

3.7.4 Plant-Sampling Procedures for the Intensive Bimonthly Sampling Program

As part of the goal to determine the explosives' fate, composite plant samples were collected on a bimonthly basis (Table 3-7). The plant samples were taken from each wetland at sampling points 30-37.

The fate of the explosives in the plants was assessed by analyzing the plant tissue for bound and assimilated explosives and explosive by-products. If, during any bimonthly sampling period, TVA RM personnel felt that at least 100 grams of a particular plant species could be harvested without affecting crop health, then samples of that species were taken. Otherwise, that plant species was not sampled. The plant samples were taken from the front and back half of each wetland cell at sampling locations 30 to 37 (Figure 3-2). A representative composite sample was collected for each species from six random sites within each sampling location. A flat bottomed boat was used to collect submergent plants in the lagoon system. Prior to sampling the lagoons, the influent and effluent pumps were shut down and any sediment disturbed during the sampling process was allowed to settle prior to restarting the pumps. Emergent plant species were collected by cutting down each plant near the base of the plant using cutting shears. Submergent plant species were collected by shearing the plant stems near the base using a submerged rake and then capturing the plants with the rake.

The species samples were composited by placing each species in a separate large plastic bag and homogenized by mixing. A subsample (2-gram minimum) was removed from the large plastic bag and placed in a Ziploc plastic bag. The remaining plant material in the large plastic bag was placed back into the wetland cell from which it was obtained. Each bag was labeled to identify the sample according to plant species, date collected, location collected, and project description. All samples were stored in ice or commercial ice substitute and transported to a TVA RM laboratory in the custody of a TVA RM employee. Upon arriving at the lab, the subsamples in the Ziploc bags were rinsed, frozen, and saved for explosive and explosive by-product analysis, as outlined in Table 3-7.

3.7.5 Water-Sampling Procedures for Water Toxicity Tests

During selected sampling times, water samples were collected from sample points 1, 3, 4, and 6 (Figure 3-1) for use in toxicity testing. At sample points 1 and 4, the samples were collected by opening sampling valves placed in process lines. At sample points 3 and 6, the samples were collected from sumps located at the end of each wetland. The sump samples were collected by placing a stainless steel beaker beneath the sump pump outlet.

Water samples collected from all of these locations were initially placed in a 4-L stainless steel beaker and transferred to 5-gallon plastic containers. Five gallons per sample point were obtained from sample points 1 and 4. These samples were considered replicates of well MI-051's water. Two 5-gallon samples per sampling point were obtained from sample points 3 and 6. All sample containers were labeled to identify date collected, location, and project identification. All of the containers were placed in ice chests containing ice or a commercial ice substitute and were transported, in the custody of a TVA RM employee, to TVA's toxicity laboratory at the Browns Ferry Nuclear Plant. All samples were refrigerated upon arrival at the lab. At TVA's toxicity laboratory, the samples underwent toxicity analysis using *Ceriodaphnia dubia* and *Pimephales promelas* as the indicator species. The procedures used to conduct the toxicity test are described in the reports listed in Appendix B. All samples received from the test site were handled in accordance with TVA's chain of custody procedure. The water-sampling procedure above was repeated every two days over the course of the seven-day toxicity test. Repeated sampling was required to ensure that fresh water was available during the course of the test.

3.7.6 Sediment-Sampling Procedures for Sediment Toxicity Tests

In addition to the water samples described above, the toxicity in the wetlands' sediments was assessed (Table 3-7). The sediment samples were taken from each wetland at sampling points 16-21, 24, and 28. Sampling points 16-19 were created by dividing the gravel-based anaerobic cell into quadrants (Figure 3-2). Sampling points 20 and 21 were created by dividing the gravel-based aerobic cell into front and back halves. Sampling points 24 and 28 represented the third quadrant of each lagoon. The sediment samples were collected randomly throughout the area represented by each sampling point.

In the gravel-based wetland, the sediment consisted of the gravel and deposited carbonaceous material. Aliquots of gravel were collected from six randomly selected locations within each sampling point. During the collection process, the gravel was dug by shovel from the surface to a depth of about 12 inches (approximately quarter-depth). The gravel samples collected from the six locations were mixed in a large bucket. The gravel was then divided into two subsamples. The first subsample was placed in a 2-gallon plastic container–a plastic container was used to avoid breakage. The 2-gallon container was wrapped with aluminum foil and

placed in an ice chest containing ice or a commercial ice substitute. Upon receipt at TVA's toxicity laboratory at the Browns Ferry Nuclear Plant, the samples underwent toxicity analysis using *Hyalella azteca* (Table 3-11). The procedures used to conduct the toxicity test are described in the reports provided in Appendix B.

The second subsample was placed in four 500-ml wide-mouth amber glass bottles. The amber bottles were sealed with Teflon lids, wrapped with aluminum foil, and placed in an ice chest containing ice or a commercial ice substitute. Upon receipt at TVA RM's analytical laboratory in Muscle Shoals, Alabama, the samples were analyzed for explosives and explosive by-products (Table 3-12). The gravel's explosive content was normalized to dry matter weight by correcting for moisture content. These analyses were forwarded to TVA's toxicologist as means of identifying a probable cause of any toxic response.

In the lagoon-based wetland, the sediment consisted of the soil lying at the bottom of each lagoon. The sediment was collected from a flat bottomed boat. Sediment was collected to a depth of 4 inches using a soil probe. The sediments were collected from six locations within each sampling quadrant and mixed. Two subsamples were created. The first subsample was stored in four 500-ml wide-mouth amber glass bottles. The amber bottles were labeled, sealed with Teflon lids, wrapped with aluminum foil, placed in an ice chest containing ice or a commercial ice substitute, and submitted to the laboratory for toxicity testing. Upon receipt at TVA's toxicity laboratory, the samples underwent toxicity analysis using *Hyalella azteca* and *Chironomus tentans*. The procedures used to conduct the toxicity test are described in the reports provided in Appendix B.

The second subsample was stored in two 60-ml wide-mouth brown glass containers. These containers were wrapped in aluminum foil, stored in an ice chest containing ice or a commercial ice substitute, and submitted to the TVA RM analytical laboratory for analysis of explosives and explosive by-products (Table 3-12). Analysis of the sediment's explosive content was normalized to dry matter weight of gravel by correcting for moisture content.

All of the sample containers above were labeled to identify date collected, location, and project identification. All of the containers were transported to the laboratories in the custody of a TVA RM employee. All samples received from the test site were handled in accordance with

TVA's chain of custody procedure. Upon receipt at the laboratories, all samples were kept refrigerated until analyzed.

3.7.7 Water-Sampling Procedure for the Overall Mixing Tests

The effluent's bromide concentration was monitored by collecting water samples from the effluent pipes delivering water to the sumps of cells A1, A2, B1, and B2. These locations correspond with sampling points 2, 3, 5, and 6, respectively (Figure 3-1). The effluent samples were collected using four autosamplers--one for each effluent sump. The autosamplers were fed by plastic tubing. The inlet to each tube was placed in the standpipe of the respective effluent header. The autosamplers were positioned just outside the sumps. Each autosampler collected approximately 50 ml of sample each hour. Four samples were collected in each of the sampler's plastic 200-ml storage containers; hence, each container held a 4-hour composite sample. The containers were collected for transportation to TVA RM laboratory at 4-day intervals. Each autosampler contained 24 bottles during each sampling interval.

During sample collection, the sampling process was similar to that described for other sampling programs. All of the sample containers above were labeled to identify date collected, location, and project identification. The samples were then stored in ice or commercial ice substitute and transported to the laboratory in the custody of a TVA RM employee. All samples received from the test site were handled in accordance with TVA's chain of custody procedure. Upon receipt at the laboratory, the samples were kept refrigerated until analyzed for bromide by ion chromography.

3.7.8 Water-Sampling Procedure for the Short-Circuiting Tests

Short-circuit sampling began five days after the bromide slug was added to each wetland. After the sampling process began, the sampling wells were sampled at 4-hour increments for approximately five days. Each sample was taken as a whole-water column sample using a coliwasa tube. Each whole-water column sample was placed in a 16-ounce plastic cup, mixed, and then transferred into a 60-ml plastic bottle. Use of a plastic cup was necessary because the 60-ml bottle was too small to receive a sample from a whole-water column sampler. Excess water in the plastic cup was poured back into the wetland near the sampling point. All of the

60-ml sample containers were labeled to identify date collected, location, and project identification. The samples were then stored in ice or commercial ice substitute and transported to the laboratory in the custody of a TVA RM employee. All samples received from the test site were handled in accordance with TVA's chain of custody procedure. Upon receipt at the laboratory, the samples were kept refrigerated until analyzed for bromide by ion chromography.

3.8 Field Data Collection Procedures

The water quality field data collected included pH, DO, temperature, EC, and redox potential. The data was collected with YSI 600 and YSI 6000 probes. The YSI 600 sondes were used to take one measurement of pH, DO, temperature, and EC in water samples taken during each sampling event. The YSI 6000 sondes were used to automatically obtain daily cycles of pH, DO, temperature, EC, and redox by measuring these parameters every 6 hours.

Before being taken to the field, both the YSI 600 and YSI 6000 sondes were calibrated according to the procedures outlined by the manufacturer of the probes. The hand-held YSI 600 sonde was calibrated in the lab before each trip to the field to measure pH, DO, temperature, and EC. The YSI 6000 sondes were removed from locations 8-15 and brought to Building K-9 to allow for downloading of the measured data onto a laptop computer. After downloading two weeks of data, the sondes were recalibrated according to manufacturer's specifications and re-deployed for the next two-week period (see Appendices A-6 and A-7).

3.9 Laboratory Procedures

Analytical procedures for data collected in the laboratory, including those for determining the explosive content of sediment and plant samples, are provided in Appendixes A and B.

3.10 Sampling Equipment

The equipment used for collecting field and laboratory data is outlined in Table 3-13. Dissolved oxygen, pH, electrical conductivity (EC), temperature, and redox were determined in the field with hand-held instruments. Several types of hand-held instruments are available for

Table 3-13

Equipment Used for Data Collection

Field Data	Equipment
DO, pH, EC, Temperature	YSI 600 Sonde (discrete sampling)
Redox	Orion pH meter
DO, pH, EC, Temperature, Redox	YSI 6000 Sonde (continuous monitoring)
Laboratory Data	
Explosives and Related By-Products	Varian HPLC
TKN, NH_4, NO_3, and PO_4	Lachat Quick Chem 8000 or Technicon AutoAnalyzer II
Organic Carbon	Dohrmann DC 190
BOD-5	Incubation unit and YSI DO probe
COD	Hach DR/2000
Metals	Perkin Elmer or Thermo Jarrel Ash ICP
pH	Orion pH meter
Bromide, Chloride	Dionex ion chromatography system

this type of data collection (Table 3-13). For discrete analysis in time, the YSI 600 sonde was the most convenient since it measures DO, pH, EC, and temperature in one probe.

The YSI 6000 sondes were used for taking continuous measurements of water quality. Twenty YSI 6000 monitoring sondes were used. These sondes are capable of monitoring and recording five parameters, including DO, pH, temperature, redox potential, and conductivity. Each sonde was programmable and was equipped with an independent data logger with battery pack so that it could be deployed for up to 30 days. These sondes were used to provide water quality information and were placed at different locations within the demonstration cells to correlate effects from spatial and temporal differences in diurnal cycles. Other environmental information, such as rainfall and air temperature, was available from the University of Tennessee's Milan Agriculture Experiment Station.

Explosive and explosive by-product concentrations were determined in water, sediments, and plants with a high performance liquid chromatography system. Total Kjeldahl Nitrogen (TKN), NH_4-N, NO_3-N, and PO_4-P were determined colorimetrically via an automatic analyzer. Chemical oxygen demand was determined by a colorimetric analysis. Metals were determined by inductively coupled plasma (ICP) spectrophotometry. Bromide and chloride were measured by ion chromatography. The pH of water samples taken to the laboratory was analyzed with a glass electrode and pH meter. (All procedures are referenced in Appendix A.)

SECTION 4.0
CONSTRUCTION OF FACILITY

4.1 Construction Experience

Construction of the demonstration facility involved the following tasks:

- Excavation of soil
- Installation of foundations
- Installation of a building housing the GAC unit
- Installation of cell berms (installation of prefabricated panel walls, installation of panel braces, and back-filling the panels with earth)
- Installation of synthetic cell liners
- Installation of process piping and instrumentation
- Placing gravel in the gravel-based cells
- Placing soil in the lagoon-based cells
- Planting emergent and submergent plant species
- Checking system preoperational performance

Construction began on March 4, 1996, with site excavation. Excavation was accomplished with a track loader and a four-wheel-drive backhoe. The track loader was equipped with a four-in-one bucket. All excavated soil was reused as berm and fill material. Small pumps were used to keep the excavated cell areas dewatered during construction. However, rain events did delay construction by one week.

While installing site foundations, it was found that the soil underneath the lagoons was strong enough to support the prefabricated walls. As a result, the concrete foundations originally proposed for the lagoon were not installed. All other foundations were placed as originally designed.

No major difficulties were encountered in the installation of the GAC building and related system.

A minor difficulty was encountered in constructing the earthen berms which supported the insulated prefabricated cell wall panels. The plot of land chosen had physical obstructions which limited the spacing between the four cells to about 12 feet between cell walls. With the extension of the cell panel knee braces, the accessible space between the cells for earth-moving equipment was reduced to about 8 feet. This restriction made berm construction more difficult than if a wider spacing between cells had been possible. For future reference, a minimum spacing of 20 feet between cell walls is recommended for cells of this type.

A 20-mil polyethylene synthetic liner was used for both the primary and secondary containment. The liners were installed as single pieces–no field joints were required. Originally, a 45-mil Ethylene Propylene Diene Monomer (EPDM) liner had been specified; however, this was changed as a cost-savings measure. The primary and secondary liners were not joined. The liners were delivered folded into large bundles and were heavy and cumbersome. The liner bundles were placed in each cell with a hydraulic crane. Six to eight workers were required to unfold and position the liners. Some final adjustment to liner position was possible after unfolding. Field joints were required to seal piping penetrations. These utilized threaded bulkheads, gaskets, and sealant. In all locations where the synthetic liner came into contact with the soil or gravel, a layer of geotextile fabric was installed to minimize the possibility of puncture by sharp objects.

After the secondary liners were installed, but prior to installing the soil or gravel in the wetland basins, the secondary liners were leak-tested by filling the wetland basins with potable water and checking the leak detection systems. The basins were not completely filled, rather they were filled to the point that the water level was above the highest points where piping penetrated the liners. No leakage was detected.

Placement of the 4 feet of gravel fill, required for the gravel-based cells, was the most labor- and time-intensive portion of the construction phase. To accomplish this task, gravel was procured from a local vendor, delivered to the site, and stockpiled. A bucket loader was used to load the gravel into a 1½-yard concrete bucket equipped with a bottom-trip unloading door. To facilitate bucket loading, a trough was fabricated and fitted to the concrete bucket. A 22-ton hydraulic crane was used to lift the bucket over the cells and place the gravel into the

appropriate area. To provide rough leveling, a backhoe was positioned outside the cells. The backhoe could reach over the cell walls and level excessively high areas. Final leveling was accomplished by hand.

Soil used in the lagoons was excavated from MAAP and stockpiled near the lagoon cells. From here, it was placed in the cells with the four-in-one track loader and backhoe with some utilization of the concrete bucket and hydraulic crane. As with the gravel, a backhoe was used for leveling with finish leveling by hand. A one-foot-thick layer of soil was placed in the lagoon-based cells.

All piping, headers, and cell sample wells were fabricated with PVC. Most of the headers and cell sample wells were prefabricated in a TVA RM shop and transported to the site for final installation. Generally, piping was installed prior to soil or gravel placement.

On June 3, 1996, after the soil and gravel were installed in the wetland basins, the wetland cells were again checked for leaks. To conduct the leak test, the wetland basins above the secondary liner were filled with potable water and the leak-detection systems were checked. All of the cells except cell A1 passed the leak test. Cell A1 was leading a small amount of water through the secondary (top) liner into the leak-detection system. The construction crew removed the gravel along the liner seams and found several small openings in the factory-installed seams of this cell. The faulty seams were repaired per manufacturer's recommendation and the system was rechecked on June 10, 1996. Again, the cell's secondary liner was found to be seeping water. At this point, a pump was installed to allow water in the leak-detection system to be pumped out. The pump discharges the leakage to the surface of cell A1 near the inlet. Operational procedures were also put in place to monitor the leakage and drain the detection system. Within approximately three months, the seeping appeared to stop. It is believed that the leaks were plugged with a buildup of sediments. Based on this experience, the design and construction team recommended that any future work be completed with liners specifically specified for environmental use and that all field joints be tested with an air sparger. These recommendations were incorporated into the conceptual design and cost analysis provided in Sections 8 and 9 for a commercial system.

4.2 Planting of Vegetation

4.2.1 Initial Planting

The gravel- and lagoon-based cells were first planted in April 1996. The A1 and A2 gravel beds were planted from mid-to-late April 1996. Commercially available bacteria were added to cell A1 on April 19, 1996. Prior to planting, water was added to A1 and A2 to a level approximately 8 inches below the surface. MRS was added to A1 and the water was recirculated. The order of planting from north to south was canary grass (*Phalaris arundinacea*), sweetflag (*Acorus calamus*), wool grass (*Scirpus cyperinus*), and parrotfeather (*Myriophyllum aquaticum*). This planting order, tallest plant to shortest plant, was designed to avoid shading of shorter plants by taller plants. The canary grass and sweetflag were planted on 2-foot centers. The wool grass was planted on 1-foot centers. For canary grass, sweetflag, and wool grass, a hole approximately 6 inches deep was dug in the gravel, a plant was set in the hole, and the roots were then covered with gravel. For the parrotfeather, trenches were dug approximately 6 inches deep and spaced 2 feet apart. Strands of parrotfeather were then planted, one by one, with the roots in the bottom of the trenches. The trenches were back-filled with gravel to cover the roots. After planting was complete, both A1 and A2 were filled to operating levels with water.

The B1 and B2 lagoons were planted during the week of April 30, 1996. The order of planting from north to south was parrotfeather (*Myriophyllum aquaticum*), elodea (*Elodea canadensis*), sago pond weed (*Potamogeton pectinatus*), and water star grass (*Heteranthera dubia*). All vegetation in the lagoons was planted on 1-foot centers. Planting depth ranged from 2 to 4 inches. For the parrotfeather, two to three strands were planted together on each square foot with the roots placed approximately 2 to 4 inches in the soil. For the elodea, sago pond weed, and water star grass, two to three strands were planted together to at least the second node in each square foot. To prevent dehydration of the plants, the soil was kept moist during planting. Plants were sprinkled on an as-needed basis and the lagoons were flooded with potable water after planting was completed. Muddy conditions inside the lagoons during planting made access and maneuverability very difficult.

Muddy water began blocking sunlight to the plants shortly after the lagoon-based cells were filled to their normal water depth. Soybean meal and superphosphate were broadcast into the lagoons to aid flocculation and settling. The lagoons began to clear in about two weeks.

Plants used at the Milan facility were collected from the TVA RM wetlands facility in Muscle Shoals, collected near Milan, Tennessee, or were purchased from commercial nurseries. Canary grass, sweetflag, and a portion of the parrotfeather and wool grass were collected from the TVA RM wetlands facility. The remainder of the parrotfeather was obtained from a natural wetlands near the Milan site. A portion of the wool grass, as well as the elodea and sago pond weed, were obtained from a commercial nursery. Water star grass was supplied by the Agricultural Ecosystems Research Facility in Lewisville, Texas.

4.2.2 Replanting History

Operations with contaminated groundwater began on June 17, 1996. By June 24, 1996, the plants in cell B1 of the lagoon system began to defoliate and die. In addition, a bloom of a green filament-type algae began to appear and a die-off of phytoplankton and insects was observed. By July 30, 1996, the plants in B1 and B2 appeared to be recovering from severe defoliation and a replanting did not appear necessary. The plants in the gravel-based system did not appear to be affected.

By August 14, 1996, a heavy tadpole infestation resulted in severe plant defoliation in cell B2 and minor defoliation in B1. The sago pond tubers were completely destroyed. The water star grass, elodea, and parrotfeather also suffered some damage. In an effort to control the tadpoles, large-mouth bass fingerlings were added to the lagoon on August 27, 1996. In addition, fifteen mature large-mouth bass were added to the lagoons on August 28, 1996 (Four 6- to 8-inch bass and one 12-inch bass were added to B1 and ten 6- to 8-inch bass were added to B2). Parrotfeather was also replanted in cell B2. The parrotfeather was added by dropping the water level as low as possible, leaning over the side of the boat, and pushing the roots into the soil. By August 30, 1996, MAAP personnel reported that the tadpoles were gone and the bass appeared to be in good health. In early September 1996, sago pond weed tubers were replanted in B1 and B2 by broadcasting the tubers into the lagoons from a boat. In late October 1996, it was observed that all of the plants in B1 and B2 were growing and that the

algae was returning to the lagoons. The parrotfeather was growing better in B1. The elodea and water star grass were growing better in B2. The bass remained healthy.

In November 1996, TVA received two buckets of winter plant seeds from WES. The type of seeds received was not specified. The "seeds" consisted of two buckets of what appeared to be soil. Per WES's instructions, one bucket of seeds was broadcast into each of the lagoons on November 5, 1996.

Due to diminishing explosive concentrations from the water in well MI-146, well MI-051 was activated on November 21, 1996, and use of well MI-146 was discontinued. All contaminated water entering the demonstration site from November 21, 1996, forward was obtained from well MI-051. Well MI-051 is located approximately 300 meters north of the demonstration facility and was found to contain an average nitrobody concentration of 9,200 ppb. By early December 1996, the color of the lagoon water turned dark red as a result of photodegradation of TNT. The water change had no immediately noticeable effect on either the submergent or emergent plants.

By April 2, 1997, TVA observed that the plants in the gravel-based systems had begun their spring growth, but the rate of regrowth in the lagoon-based system was slow. By April 8, 1997, plant growth had improved in the lagoons. Parrotfeather was growing; however, the growth of all other plants appeared to be slow. By April 17, 1997, it was evident that while some parrotfeather was alive and growing in the lagoon-based system, only a few elodea remained and the water stargrass and sago pond weed were dead. In addition, it was clear that the seeds broadcast into the lagoons in November 1996 did not germinate.

In contrast, the plants in the gravel-based system were doing well. Growth of canary grass, sweetflag, and wool grass was good in cell A1. Parrotfeather was growing only near the side of cell A1. Growth of canary grass and sweetflag was also good in cell A2; however, wool grass growth was slow and parrotfeather was evident only at the sides and ends of the cell.

On May 5-12, 1997, parrotfeather was replanted in cells A1, A2, B1, and B2; and stargrass was replanted in B1 and B2. The vegetation was replanted in accordance with the following plan:

- Parrotfeather was taken from stock at TVA Wetlands in Muscle Shoals and replanted in deficient areas in B1 and B2. The planting was accomplished by planting a cutting (12 inches in length or larger) in a peat moss cup containing fertilized clay soil and gravel (added for weight). The cup and plant were then placed in the lagoons at desired locations. The cup would sink to the bottom of the lagoon anchoring the plant to the bottom, while the plant top would rise to the surface. This provided for the roots to be anchored in a fertilized cup while the tops extended to the surface and adequate sunlight. Parrotfeather was replanted in A1 and A2 according to the original planting guide.

- Water star grass was obtained from Waterways Experiment Station. The plants, as received, ranged from less than 1 inch to about 24 inches. About half of the plants were more than 12 inches in size. These were planted in peat moss cups containing fertilized clay and gravel and immediately placed in B1 and B2 lagoons.

The elodea, sago pond weed, and some of the water star grass were not reintroduced during the May replanting. These plants were unlikely to survive in May because the plants were small and the lagoon's dark red color would have restricted their access to sunlight and ability to engage in photosynthesis. To enhance the plants' ability to survive, these plants were placed in water-filled containers at TVA's wetlands facility in Muscle Shoals and allowed to grow. They were carried to MAAP and planted in the B1 and B2 lagoons on July 17, 1997.

By May 20, the parrotfeather appeared to be doing well in the lagoon cells. In contrast, the water star grass appeared to be alive, but no growth was evident.

On June 17, 1997, TVA discovered that a hailstorm had seriously damaged the parrotfeather in both lagoons. Plants in the gravel beds sustained some damage, but appeared to be recovering.

On July 17-22, 1997, the water star grass, elodea, and sago pond weed retained in May were planted in cells B1 and B2 according to the following general procedure:

- Prior to planting, the small stargrass was allowed to grow to about 18 inches at TVA's facilities in Muscle Shoals, Alabama. The mature plants were transported to MAAP, planted in peat moss cups containing fertilized clay and gravel, and placed in B1 and B2 lagoons.

- The elodea originated from a commercial nursery. One- to two-inch sections of the plants were planted in peat moss cups filled with fertilized clay and gravel and then placed in a wetland located at Muscle Shoals. The plants were allowed to grow to a length of about 18 inches, then carried to MAAP and placed in the B1 and B2 lagoons.

- Sago pond weed originated from a commercial source as tubers or corms. The corms were planted in peat moss cups containing fertilized clay and gravel. The cups were placed in 24" x 48" x 12" containers filled with river water and the plants were allowed to grow to about 12 inches. Upon maturing, the plants were transported to MAAP and placed in the B1 and B2 lagoons.

No planting activities were conducted after July 22, 1997.

SECTION 5.0
FACILITY OPERATIONS (PHASE II)

5.1 Description of Facility Operations

Both wetland demonstration systems were run with limited operator intervention. TVA RM personnel based in Muscle Shoals, Alabama, were responsible for facility operations. On occasion, MAAP personnel were called upon to inspect the facility and, after consulting with TVA RM personnel, made minor adjustments. MAAP personnel activity was usually initiated by high-water-level alarms, which sounded when water levels were above specified levels.

Operator duties were generally limited to inspecting the system, cleaning all headers, feeding MRS, and initiating repairs (header blockage, GAC replacement, pump failures, burst pipes, instrument failures, etc.). In the absence of an alarm, operational activities were conducted once every two weeks. Other operational visits were initiated if the alarm system was activated, if onsite MAAP personnel indicated a problem existed, or if repairs could not be completed during a regularly scheduled visit.

Specific operator duties included:

- Checking and adjusting water levels. (Levels in cells A1, B1, and B2 were adjusted by raising or lowering exit standpipes; the level in A2 was adjusted with float control switches connected to a sump pump.)
- Checking incoming and outgoing flow rates.
- Mixing and feeding MRS to A1 (see description of duties in Section 2.3).
- Collecting samples and data.
- Checking flow rates through the GAC drums and, if needed, backwashing the GAC units.

- Replacing activated carbon when analysis indicated nitrobody breakthrough at the GAC outlet.

- Cleaning/backwashing the outlet header from cell A1 and the inlet header to A2.

- Initiating system repairs.

- Reviewing the dissolved oxygen or oxidation reduction potential readings to ensure that the gravel-based system's anaerobic cell was operating properly.

If the flow rate through the GAC drums was low, the GAC units were backwashed by opening the drums and directing potable water upwards through the carbon bed to remove adhering solids (algae, MRS, plant debris, tadpoles, insects, sediment, etc.).

A GAC drum's effectiveness at removing nitrobodies was determined by chemical analysis. When the total nitrobody concentration in the water leaving the drums began to approach 50 ppb, the drums were opened, the old carbon removed, and fresh carbon installed. During the duration of the demonstration, the granular activated carbon was replaced three times for the gravel-based system and four times for the lagoon-based system. On some occasions, the GAC drums were replaced due to the buildup of fine particulate within the drum rather than due to nitrobody breakthrough. Replacement was often necessary due to the buildup of solid particulate within the drums. The particulate tended to interfere with the carbon's ability to absorb explosives.

For aesthetic purposes, the grass surrounding the system was mowed twice during the summer season. The demonstration cells did not require weeding. However, one invasive vine was found in A1 and was sprayed with a herbicide in October 1997.

5.2 Operational Problems and Solutions

The wetlands experienced a few operational setbacks; however, none of the issues encountered were overwhelming in nature. Some of the problems encountered included:

- Well pump failure
- Flow meter failures
- Lightning strikes
- Reduced explosive concentrations in well MI-146
- Blockage of the A1 and A2 outlet headers
- Blockage of A1's inlet header
- A misaligned float switch at the A2 outlet
- Flooding of cells A2 and B2 due to flow reductions and line breaks in the GAC units
- Poor plant growth in the lagoon-based system

A general discussion of each of these issues follows.

5.2.1 Well Pump Failure

The pump in well MI-146 began operating in December 1995. The pump was originally used to supply water to another project.

During the startup of the MAAP demonstration facility in June 1996, MI-146's well pump shut down four times during the first week of operation. The pump was also experiencing a drop in outlet pressure due to sand-induced erosion of the pump blades. The pump was replaced with a new unit on June 27, 1996. However, shutdown incidents persisted through July (three incidents over a month's time). A review of the problem indicated that nearby lightning strikes were periodically causing the pump's microprocessor to shut down the unit. To address this problem, the facilities' operating procedures were altered to have MAAP personnel manually restart the pump when this happened.

5.2.2 Flow Meter Failures

The demonstration facilities' original electronic flow meters were unable to withstand local operating conditions. Consequently, the metering system was extensively modified. On October 29, 1996, operating personnel noted that the electronic flow meters located at the A1, B1, and B2 outlets were inaccurate and producing inconsistent results. By December 9, 1996, it was evident that these meters could not be repaired in the field. On January 14, 1997, the meters were removed and sent to the manufacturer for repair.

The manufacturer indicated that moisture had leaked into the meter's waterproof electronic well. It was unclear how this had happened. Plans to repair the meters were abandoned on February 18, 1997, when the cost to repair these units appeared excessive compared to alternative approaches.

Between March 27 and April 2, 1997, it became evident that A2 outlet's electronic meter was beginning to fail. Therefore, all the electronic meters were replaced with mechanical meters between April 8 and April 17, 1997. Those lines which did not have a source of pressurized water (i.e., A1 outlet, B1 outlet, and B2 outlet) were connected to demand-type pumping systems. The new meter layout was as follows:

- At the A1 outlet, a pump was installed in a plastic 30-gallon barrel located at the bottom of the A1 outlet sump. This unit pumped water intermittently from the A1 outlet sump to the A2 inlet header. A one-inch meter was installed between the pump and header to record flow. The header in A2 was modified slightly to allow for the reversion to gravity flow in case of pump failure or loss of electrical power.

- Similar systems were installed at both B1 outlet and B2 outlet. Each system consisted of a small sump (30-gallon drum) being placed inside the larger, existing sump. Incoming water from the lagoon was directed into the smaller sump, then intermittently pumped through a one-inch meter into the larger sump where it was discharged by gravity flow. In the event of a pump failure or loss of electrical power, the smaller sump would overflow into the larger sump, thus, reverting the entire system to gravity flow.

- One-inch turbine meters were installed at the A1 and B1 inlets. Gate valves were also installed to aid in the adjustment of incoming flows.

- At the A2 outlet, a 1½-inch flow meter was installed in the line leading from the A2 outlet sump to the GAC drums. The existing A2 sump pump was capable of providing sufficient pressure to facilitate meter operation.

5.2.3 Lightning Strikes

There were three lightning-related incidents during the demonstration.

- As described previously, lightning strikes periodically caused the pump in well MI-146 to shut down. The facilities' operating procedures were changed to have MAAP personnel manually restart the pump.

- On October 18, 1996, a high-water-level alarm was tripped in A2. Investigation by MAAP personnel indicated that a lightning strike tripped the breaker to cell A2's discharge pump. The breaker was reset and no other actions were necessary. The problem did not reoccur.

- On June 30, 1997, lightning hit the electrical conduit line entering Building K-9. The strike caused the conduit to fuse with the incoming electrical lines, thereby, short-circuiting the electrical system. All of the demonstration subsystems were left without power. By July 4, power to well MI-051 and the carbon source study cells was restored through Building K-100. Flow to the lagoon-based system was restored under a gravity flow arrangement that day. The gravel-based system remained shut down. On July 8, power was restored to the demonstration system's primary circuits and the gravel-based system was restarted that day. However, the circuitry to the demonstration system's telephone alarm system was destroyed. A replacement was ordered and installed. In addition, it was discovered on July 15, 1997, that one of the aerobic cell's internal pumps had also been damaged by the strike. As a temporary measure, the pump was replaced with one of the pumps from the MRS mixing systems. On July 22, 1997, the temporary pump was replaced with a new pump. No other damage to the facility was discovered.

5.2.4 Reduced Explosives Concentration in Well MI-146

During September 1996, operating personnel noted that well MI-146's explosives concentration and water pressure were slowly dropping. A search for a replacement well was initiated in October 1996. On November 21, 1996, well MI-051 was activated. It replaced well MI-146 as the facilities' contaminated water source. Well MI-051's explosive concentrations were higher than those in well MI-146 and the effects of this higher concentration temporarily impacted the wetland's ability to remove explosives (see Section 6.1.2 for a discussion on the impact).

5.2.5 Blockage of Cell A1 and A2 Outlet Headers

On January 4, 1997, operating personnel received a high-water-level alarm from cell A2. Investigation indicated that the A2 outlet header was partially blocked. The gravel-based system was shut down that evening. A crew returned on January 6, 1997, and removed the blockage by back-flushing the A2 outlet header. The cause of the blockage was not identified. The gravel-based system was restarted that day.

On January 14, 1997, operating personnel noted a buildup of slimy solids at the bottom of cell A1's sampling wells. The solids buildup has been attributed to the buildup of excess MRS and dead microorganisms in the winter months. Typically, MRS consumption is reduced in the winter months as the microbial activity is reduced. To remove the buildup, MRS addition was discontinued starting that day.

MRS addition was resumed on February 11, 1997; however, ponding was observed over parts of the gravel bed in cell A1. In hindsight, the ponding observation was the first indication that cell A2's inlet header was beginning to experience blockage. However, the ability to recognize this possibility was obscured by the occurrence of heavy rainfall just prior to the observation.

On February 25, 1997, a large volume of the solid scum was seen on the surface of the A1 outlet sump and the A2 inlet header was partially blocked. Furthermore, it was observed that the A2 outlet header was not level and, as a result, the majority of the water was discharging to

the south side to A2. Both the A1 outlet and A2 inlet headers were cleaned and plans were made to level the inlet header.

On March 1 and 3, 1997, ponding was observed over the gravel beds shortly after a heavy rainfall event. By March 11, 1997, the flooding became severe in cell A1. To address the problem, the A1 outlet and A2 inlet headers were back-washed to remove the scum and MRS addition was temporarily discontinued. In addition, two or three small carp (*Cyprinus carpio*) were placed in A1's outlet sump to scavenge solids entering the sump. By March 25, 1997, the carp were no longer needed and MRS addition resumed. An attempt to remove the carp was made; however, the carp could not be found because murky water conditions in the sump limited visibility.

After March 25, 1997, the system's operating procedures were modified to include a cleaning of the A1 outlet and A2 inlet headers during every biweekly visit and the A2 inlet header was leveled. The gravel-based system experienced no further problems after the header cleaning policy was put in place. It was also observed that the solids buildup diminished as ambient temperature increased.

On April 8, 1997, carp remains were discovered while cleaning the inlet header. The cause of death was not clear.

5.2.6 Blockage of Cell A1 Inlet Header

An analysis of the May 1997 bromide tracer test suggested that cell A1 was short-circuiting. A partial blockage of the A1 inlet header was cited as a possible cause. Plant roots were thought to be the most likely source of obstruction. However, it was not possible to verify the blockage because cells for the alternate carbon source and higher flow rate study were located atop the inlet header. The carbon source study was ongoing and the cells could not be disturbed. (For a description of this study, see Section 11.3 "Recommendation for Future Work" and the study test plan in Appendix C.)

In an attempt to remedy this problem, a new A1 inlet header was installed on August 18, 1997. The new header was positioned at the gravel surface. Water flowed from the header to five

2-inch-slotted PVC pipes dug into the gravel bed to a depth of 2 feet. The 2-inch pipes were positioned equal distances across the header. Each of the 2-inch pipes was equipped with a valve and flow meter. The valve/metering system was installed to allow closer monitoring of the injection process and permit greater control over feed injection.

Hydraulic tracer analysis conducted in late August 1997 suggested the channeling observed during the May 1997 hydraulic tracer test was likely the result of local channeling within the gravel. So, it is possible that the original header was not blocked (see discussion in Section 6.2.3).

5.2.7 Misaligned Float Switches at the A2 Outlet

During a scheduled visit on February 5, 1997, operating personnel observed that the discharge pumps at the A2 outlet were running continuously causing the water level in cell A2's second basin to drop well below normal. It was determined that the float switches which control the A2 outlet pump were out of alignment. Consequently, water was being directed out of cell A2 without full aerobic treatment. The switches were realigned and the system was returned to normal operation. It is believed that the float switches may have been out of alignment since January 4, 1997, when the A2 outlet sump pumps were removed to facilitate cleaning of the outlet header (see discussion in Section 5.2.5). Apparently, the switch settings were not realigned when the pumps were reinstalled.

5.2.8 Flooding Due to Flow Reduction and Line Breaks in the GAC Unit

Both the gravel- and lagoon-based systems experienced problems with flow backing up in the cells directly behind the GAC drums (cells A2 and B2). The problems were caused by the buildup of solids in the GAC units. These solids would eventually plug the GAC drums resulting in reduced flow from the wetland cells and a buildup of back pressure in the lines leading to the GAC drums. In some instances, the flow reduction was sufficient to cause flooding in the cells upstream of the GAC units.

In general, both systems experienced an equal number of problems. However, the nature of the problems varied. Because the gravel-based system's water contained fine suspended solids,

this system tended to experience slow steady increases in GAC drum back pressure. Consequently, potential system failures were easier to anticipate and prevent. In contrast, the "solids" from the lagoon-based system consisted of a variety of items including: plant debris, tadpoles, insects, and sediment. Generally, blockage of the lagoon's GAC subsystem corresponded to abrupt changes in the lagoon's operating conditions. These changes included: insect die-off, plant defoliation, hailstorms, vegetation planting, sediment sampling, etc. Consequently, it was more difficult to predict when the lagoon-based GAC units would plug. Each wetland experienced seven to eight incidents in which it was necessary to back-flush the GAC unit. Three incidents in each wetland resulted in high water levels in the wetland cells. The remaining incidents led to back-flushing either to facilitate flow or as a precautionary measure. None of these issues will affect commercial-scale operations since GAC units will not be installed in commercial systems.

The primary effect on both the gravel- and lagoon-based systems was an increased water level in cells A2 and B2. While inconvenient, this generally had little impact on the system's performance. The three incidents affecting the gravel-based system were as follows:

- On July 8, 1996, back pressure in the line connecting the A-side GAC unit and the A2 outlet pump blew off a hose connecting the pump to the line. This caused water to accumulate in cell A2. The GAC unit was back-flushed and the line reconnected.

- On April 22, 1997, cell A2 experienced a high-water-level alarm. The A-side GAC unit was back-flushed and the problem was solved.

- On June 9, 1997, back pressure between the A-side GAC unit and the A2 outlet pump blew off a hose connecting the pump to the line. This caused water to accumulate in cell A2. The A2 high-water-level alarm failed to signal a problem and cell A2 was flooded. The GAC unit was back-flushed, solving the low flow problem. The alarm failure was traced to an out-of-order telephone line. MAAP repaired the phone line.

Three similar high-water-level incidents occurred in the lagoon-based system. These incidents are described as follows:

- On August 14, 1996, the lagoon-based system's GAC unit plugged during a tadpole infestation. The GAC unit was back-flushed and bass were placed in the wetlands to remove the tadpoles.

- On August 27, 1996, sediment stirred up during the sampling process plugged the lagoon-based system's GAC unit. The GAC unit was back-flushed and the sampling procedures were altered to minimize sediment disturbance.

- On June 17, 1997, the lagoon-based system's GAC unit was plugged after a hailstorm damaged lagoon vegetation. The GAC unit was back-flushed solving the problem.

SECTION 6.0
EXPERIMENTAL RESULTS (PHASE II)

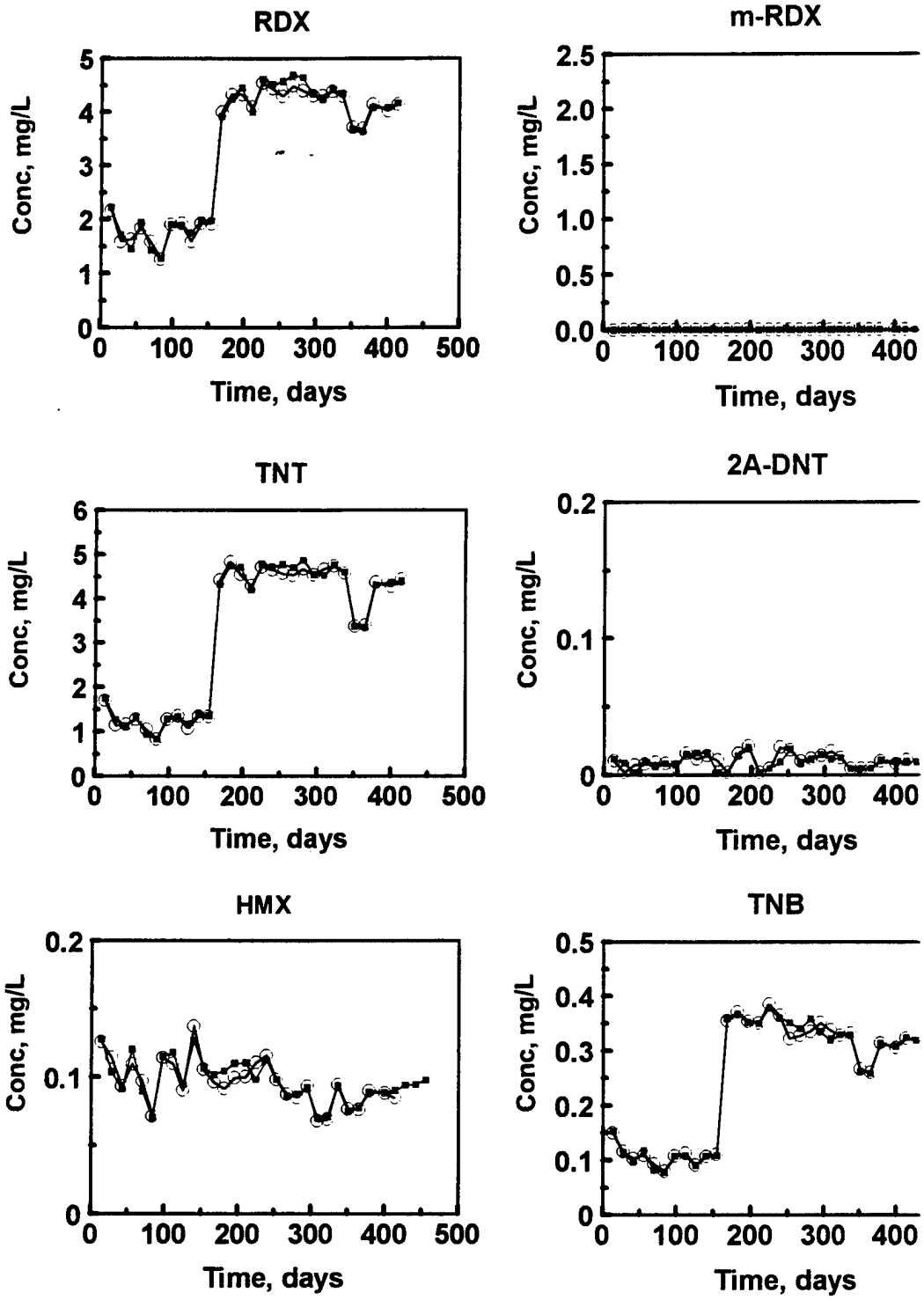
6.1 Routine Sample Test Results

6.1.1 Incoming Explosives Concentrations

The concentration of various explosives entering the demonstration wetlands are shown in Figure 6-1. During the demonstration's first 157 days of operation, to November 21, 1996, the average total nitrobody concentration was 3,200 ppb. From day 157 until the end of the Phase II demonstration, on September 16, 1997, the source of contaminated water was from a well with an average total nitrobody concentration of 9,200 ppb. The concentrations of RDX, TNT, TNB, and 2,4-DNT increased three to four fold when the source of groundwater was changed. Influent concentrations of TNT, RDX, TNB, and HMX were, respectively, 1250, 1770, 110, and 110 ppb before November 21; and respectively, 4440, 4240, 330, and 91 ppb after November 21, 1996. The concentration of HMX remained about the same in the new well. The concentration of 2,6-DNT was always below the detection limit of 5 ppb.

6.1.2 Explosives Removal by the Gravel-Based Wetland

The concentrations of explosives and by-products released from the first (cell A1) and second (cell A2) gravel-based wetlands during the 456 days of the demonstration are shown in Figure 6-2. During most of the demonstration, the concentration of explosives in the effluent of cell A1 was significantly higher than in the effluent of cell A2. However, for a short period after the groundwater wells were changed, some of the explosives concentrations were lower in the effluent of cell A1 as compared to the effluent of cell A2 (Figure 6-2). During this period, it is believed that the microbial population in cell A1 had not yet acclimated to the higher nitrobody concentration, resulting in an increased nitrobody concentration in the discharge. Thus, higher-than-normal concentrations may have been initially released into cell A2. Heavy rainfall during this period may have also been a contributing factor (see Section 6.1.5.2). It is possible that the water level rose above the gravel surface in cell A1, resulting in short circuiting of the influent groundwater from cell A1 to cell A2.



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Note: When a chemical was not detecte

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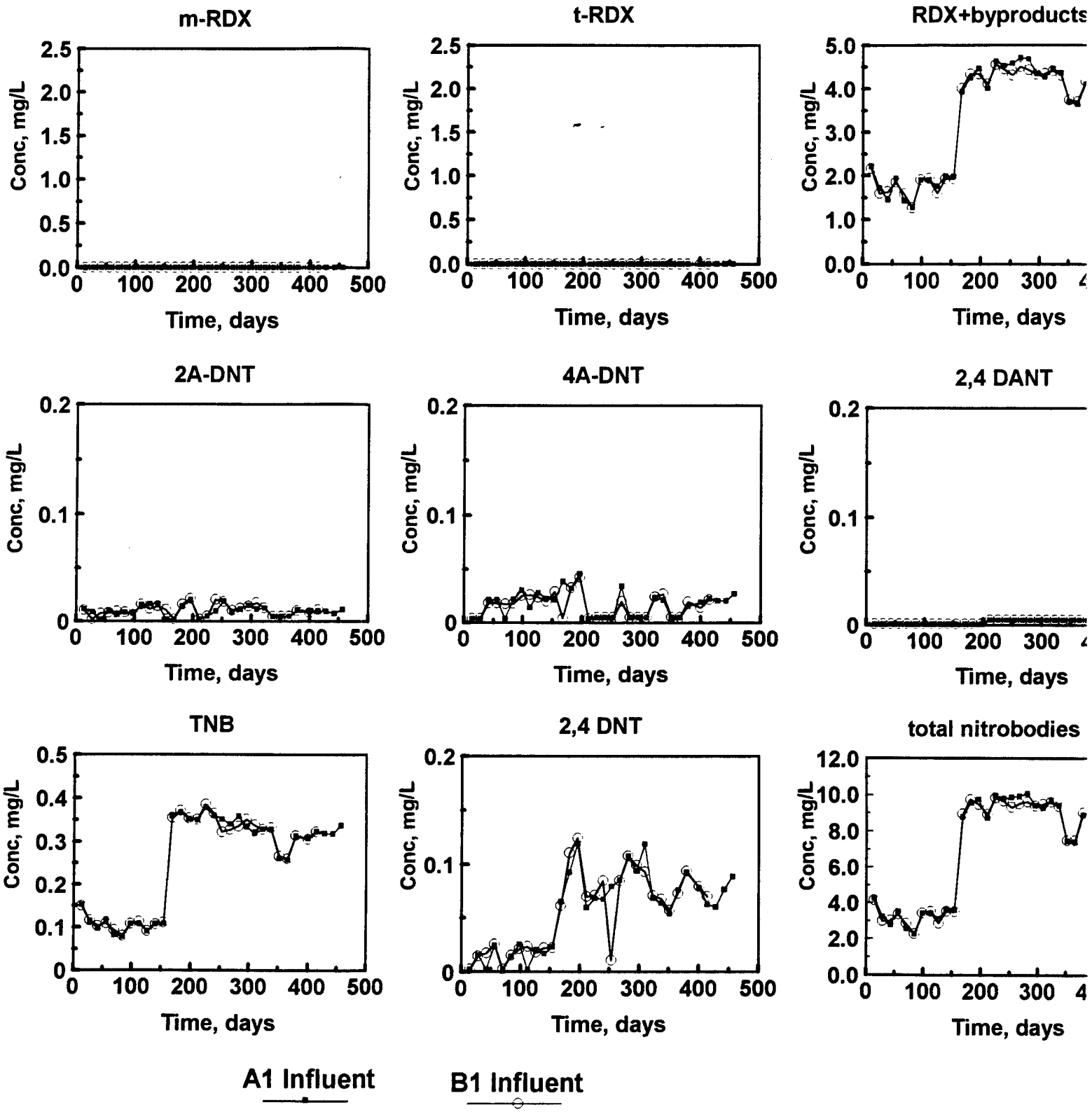
Incoming Explosive and E

From June 17, 19

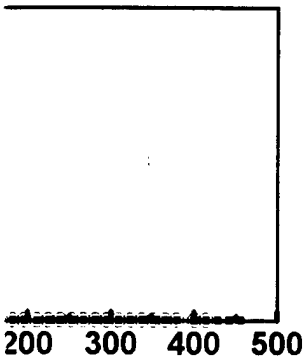


te: When a chemical was not detected, the method detection limit was plotted instead.

Figure 6-1
Incoming Explosive and Explosive By-Product Concentrations
From June 17, 1996, to September 16, 1997

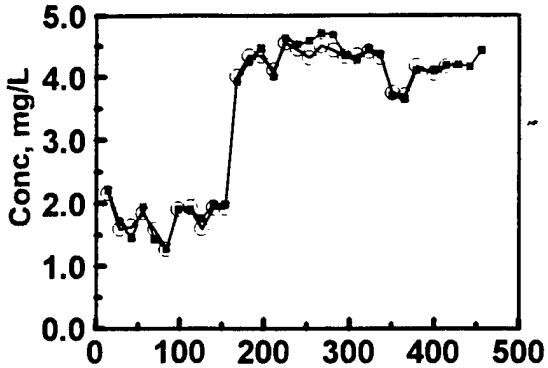
2

t-RDX



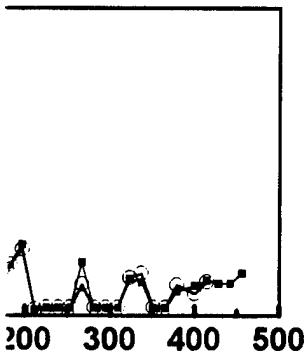
ime, days

RDX+byproducts



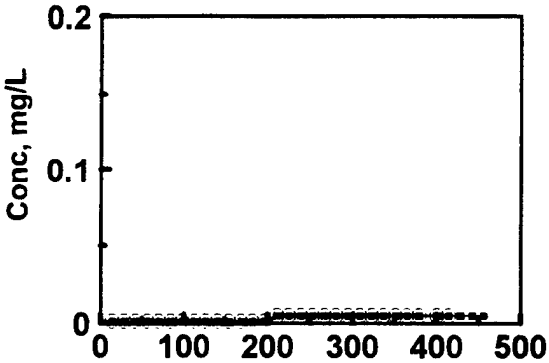
Time, days

4A-DNT



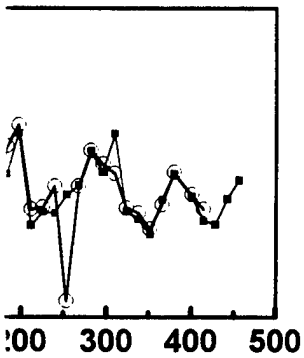
ime, days

2,4 DANT



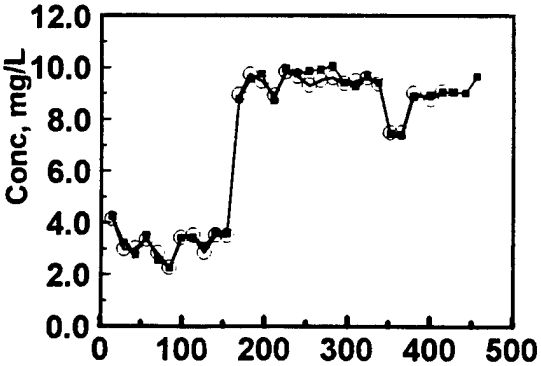
Time, days

,4 DNT



me, days

total nitrobodies



Time, days

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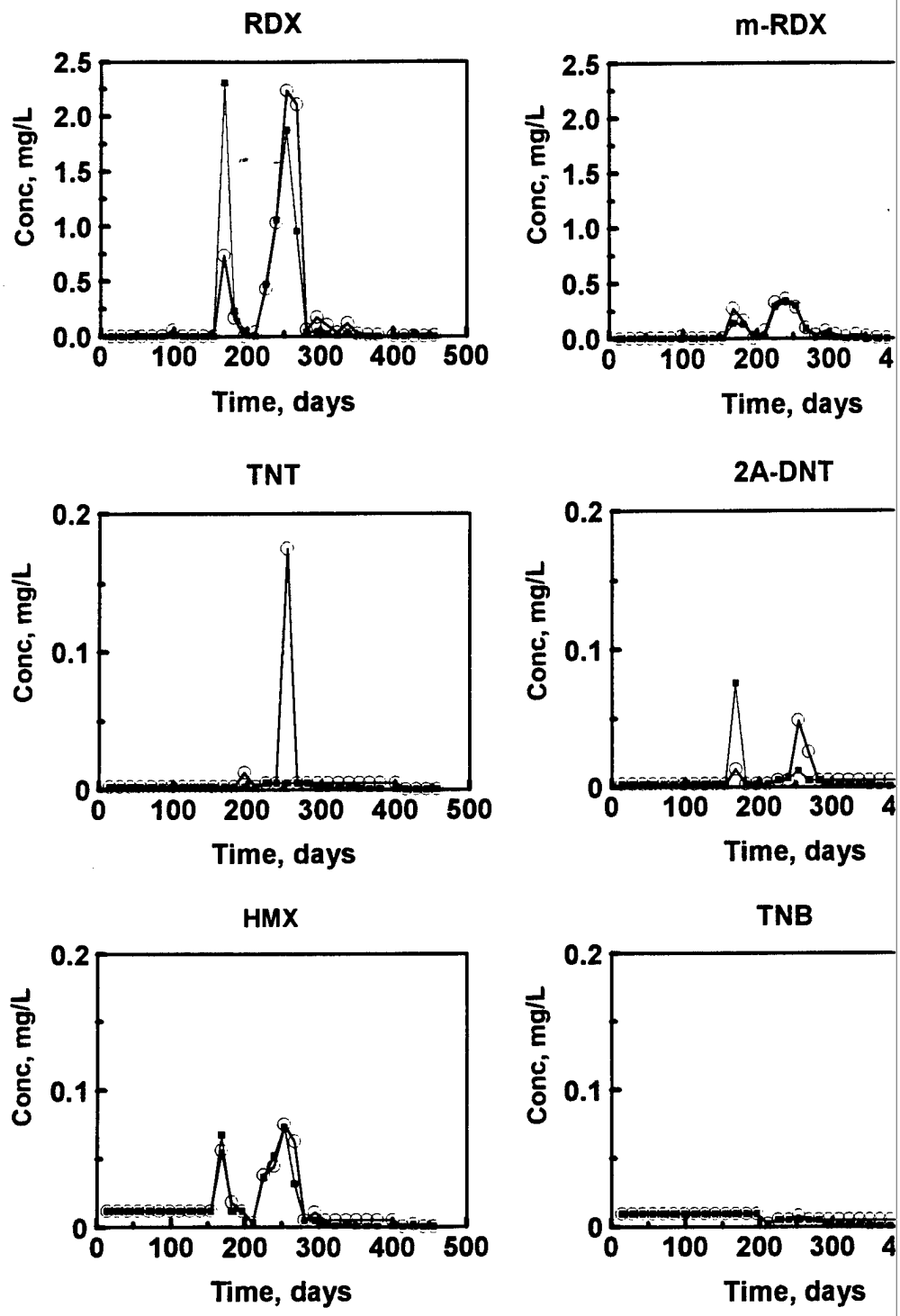

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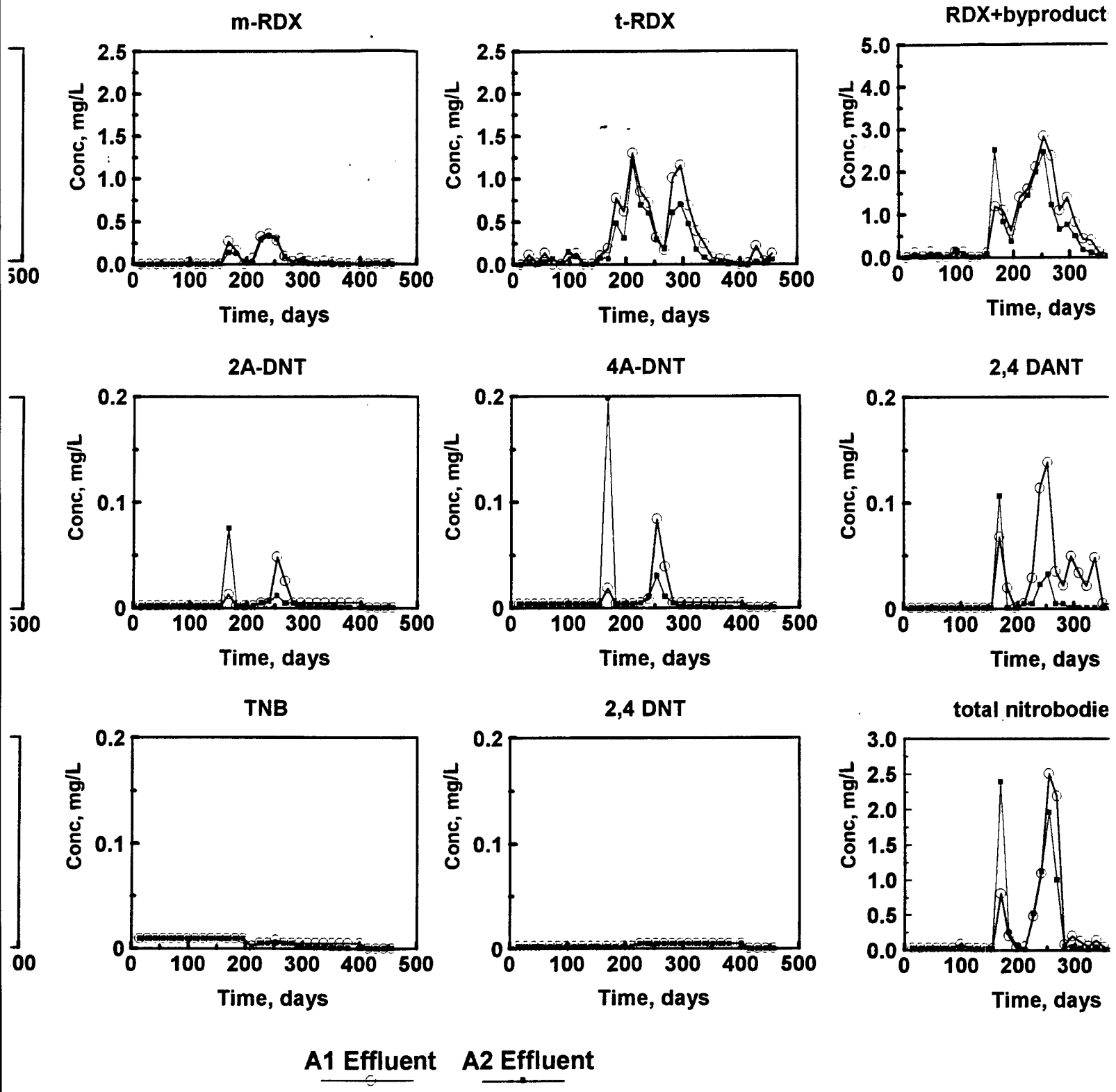
Note: When a chemical was not det

Effluent Explosive and Explosive By-Pr
from June 17,

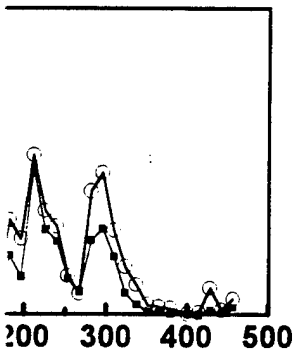


Note: When a chemical was not detected the method detection limit was plotted instead.

Figure 6-2
Explosive and Explosive By-Product Concentrations from the Gravel-Based Wetlands from June 17, 1996, to September 16, 1997

2

t-RDX



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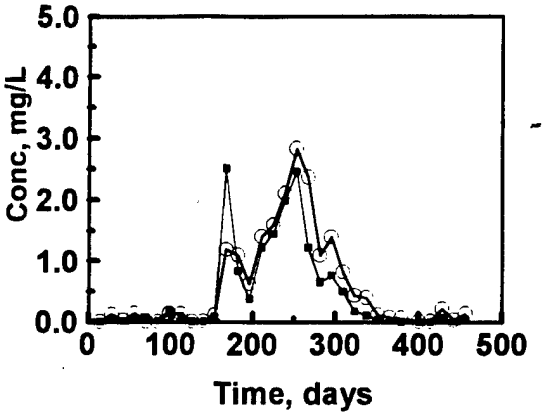
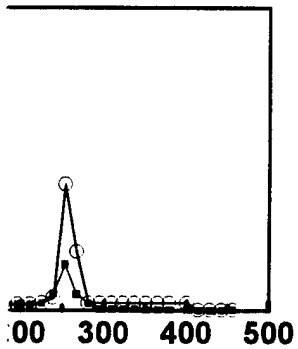
RDX+byproducts

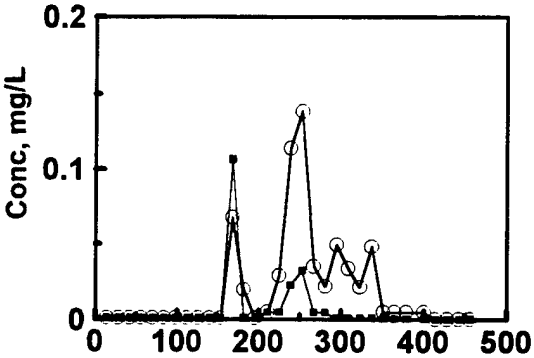


A-DNT

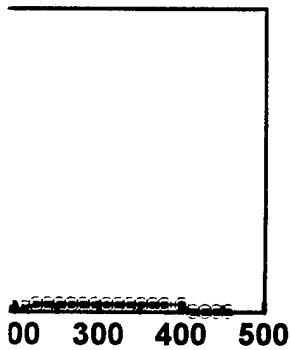


me, days

2,4 DANT



,4 DNT



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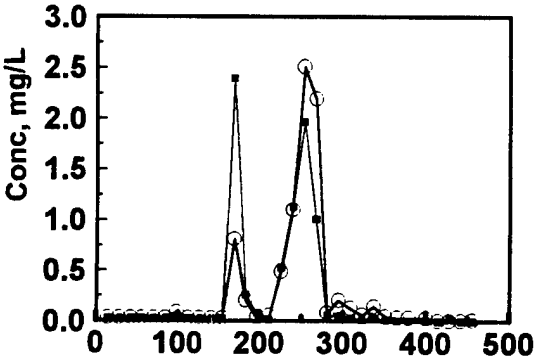
total nitrobodies



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The gravel-based wetland did a very effective job at removing the nitroaromatic explosives (TNT, TNB, and 2,4-DNT) as evidenced by effluent concentrations released from A2 being less than the respective detection limit. By-products of TNT degradation are 2A-DNT, 4A-DNT, and 2,4-DANT. These by-products were observed to be released from the anaerobic cell (cell A1) during the colder winter months around 250 days into the demonstration (to February 22, 1997). When the TNT degradation products were released from the anaerobic cell, they were removed in the aerobic wetland (cell A2) with removal efficiencies at 80% or greater.

The removal of the nitramines, RDX and HMX, was not as effective as the removal of the nitroaromatics. Excluding the peak that occurred shortly after changing to the new well, there was a period from January 28, 1997, to March 11, 1997, in which RDX and HMX were released from both A1 and A2 (see Figure 6-2; days 225 to 267). The release occurred in the colder winter months when water temperatures leaving the gravel-based wetlands were below 13°C (see Section 6.1.5.3).

The concentrations of the RDX by-products, m-RDX and t-RDX, were well above the detection limits from December 4, 1996, to May 20, 1997 (days 168 to 337). Two t-RDX peaks were observed as a result of inadequate t-RDX degradation. During these periods, RDX was being degraded at a faster rate than t-RDX. From January 28, 1997, to March 11, 1997, when RDX was not fully removed, the concentrations of t-RDX declined (Figure 6-2; days 225 to 267). It took a longer period of time for the gravel-based system to effectively remove t-RDX compared to m-RDX when coming out of the winter season. As evidenced by A2 effluent, the removal of m-RDX was adequate from March 25, 1997, (day 281) and beyond. The removal of t-RDX was not completely effective until June 3, 1997 (day 351) and beyond.

The aerobic wetland cell, A2, did not remove nitramines (RDX and HMX) or nitramine by-products (m-RDX and t-RDX) as effectively as the nitroaromatic by-products (2A-DNT, 4A-DNT, and 2,4-DANT) (see Figure 6-2). The removal efficiencies ranged from 0% to 75% for RDX, HMX, m-RDX, and t-RDX removal in the aerobic wetland.

The gravel-based wetland did an effective job of removing explosives during periods of warm temperature. The inability of the gravel-based wetland to completely remove explosives from

the contaminated groundwater during the winter months may have been due to the lower water temperatures experienced during this time period (see Figure 6-8 in Section 6.1.5.3). The lower temperatures are thought to have caused a decrease in the rate at which the explosives were degraded via microbial pathways.

However, the decline in treatment efficiency cannot be solely ascribed to lower temperature. The A1 and A2 influent headers were experiencing blockage problems during this period. (See Section 5.2.5 for a description of the problems encountered.) The blockage problem caused water levels to rise above the surface of the gravel bed, thereby, allowing the contaminated water to flow above the gravel surface (or short-circuit). To minimize blockage, MRS addition was discontinued during the days indicated in Table 6-1. In addition, recirculation was not conducted during days shown in Table 6-1; either because the MRS was not being added or because a tracer study was being conducted at the time. Even after discontinuing MRS addition, the effluent headers had to be periodically flushed to remove solids and prevent the water from rising above the gravel bed. Therefore, the combined impacts of reduced carbon loading (MRS addition), short-circuiting, and low water temperatures are thought to have contributed to the decreased removal efficiency observed during the winter of 1996/1997.

Table 6-1

Exceptions to Milk Replacement Starter (MRS) Addition

Date	Day	No MRS Added	No Recirculation
January 14, 1997	211	X	
January 28, 1997	225	X	X
February 11, 1997	239		X
February 25, 1997	253		
March 11, 1997	267	X	X

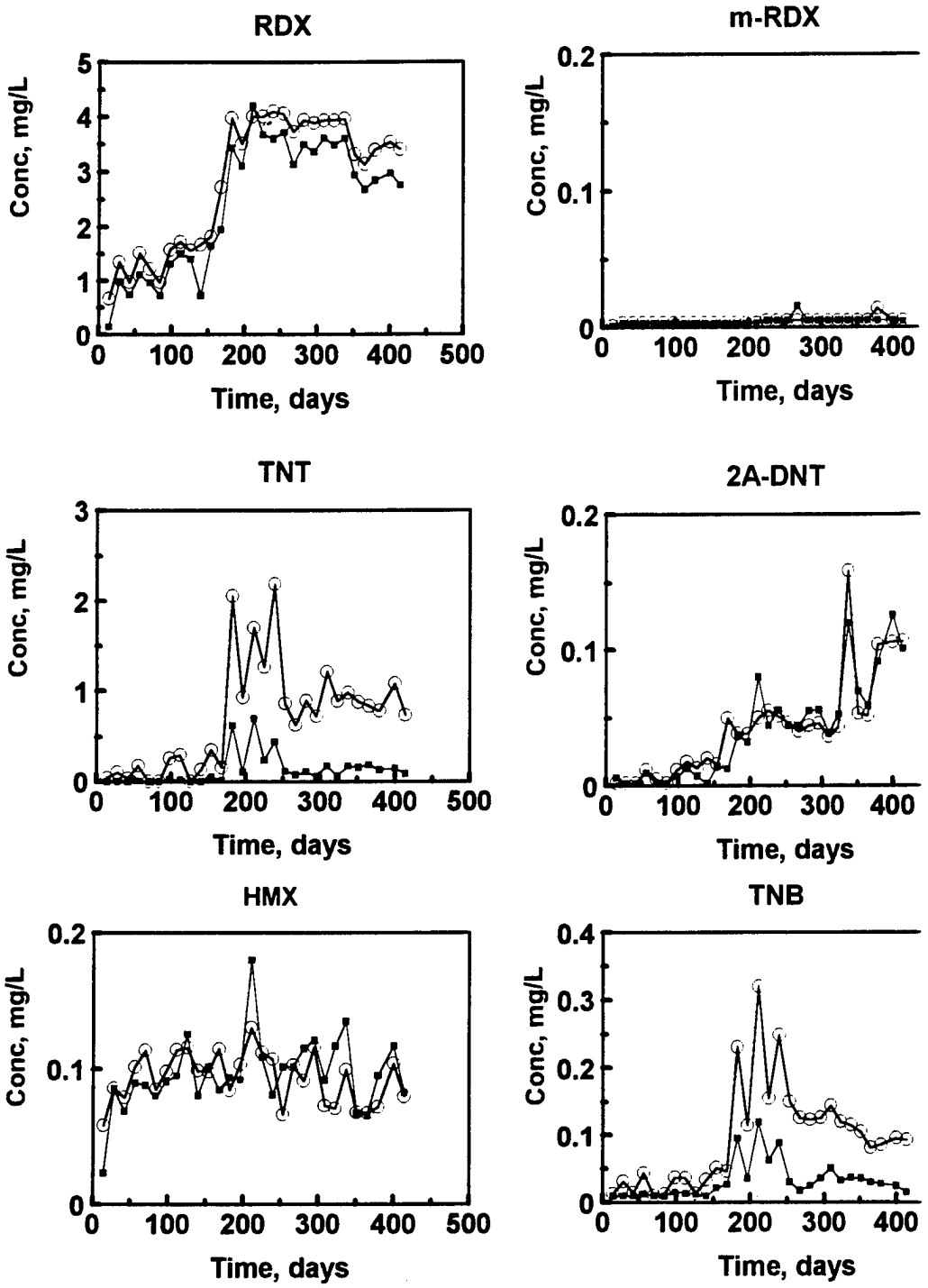
6.1.3 Explosive Removal by the Lagoon-Based Wetland

Both lagoon cells removed nitroaromatics (TNT, TNB, and 2,4-DNT) from the contaminated groundwater influent (Figure 6-3). The nitroaromatic concentrations in the water released from cell B1 were higher than those released from cell B2 which suggest the sequential treatment of the groundwater as the water passed through the lagoon system. The observed reductions in nitroaromatic concentration in both cells are thought to have occurred either by microbial degradation, reaction with nitroreductase enzymes produced by plants, photo-degradation, or a combination of all three. The concentrations of the TNT by-products, 2A-DNT and 4A-DNT, increased continuously throughout the demonstration. Apparently, these by-products are not easily removed once produced resulting in a slow and continuous increase in the effluent concentration of these compounds with time. 2A-DNT and 4A-DNT are produced by the reduction of one nitro TNT group.

The lagoon-based system's ability to remove the nitramines, RDX and HMX, was also very limited (Figure 6-3). Both RDX and HMX require anaerobic conditions for microbial breakdown. Due to the lagoon system's constant high dissolved oxygen conditions and ensuing high redox levels, there was a negligible reduction of RDX or HMX. Consequently, the concentrations of RDX and HMX leaving both B1 and B2 were close to the influent concentrations (Figure 6-1). No RDX by-products were observed in the effluent from B1 and B2 (Figure 6-3), probably due to the system's limited ability to remove RDX.

6.1.4 Comparison of the Gravel- and Lagoon-Based Wetlands

The gravel-based wetland was better at removing nitrobodies from the contaminated groundwater than the lagoon-based wetland (Figure 6-4). The percent removal of all the nitrobodies was 85% or greater in the gravel-based wetlands, except during the winter when treatment efficiencies declined. Reasons for the decline in treatment efficiency are outlined in Section 6.1.2. The lagoon-based system's TNT and TNB removal efficiencies were, for the most part, greater than 85%. However, the removal efficiencies for RDX and HMX were low, averaging 25% and 10%, respectively. The lagoon-based system's 2,4-DNT removal efficiency varied widely during the first 200 days of operation, however, the removal



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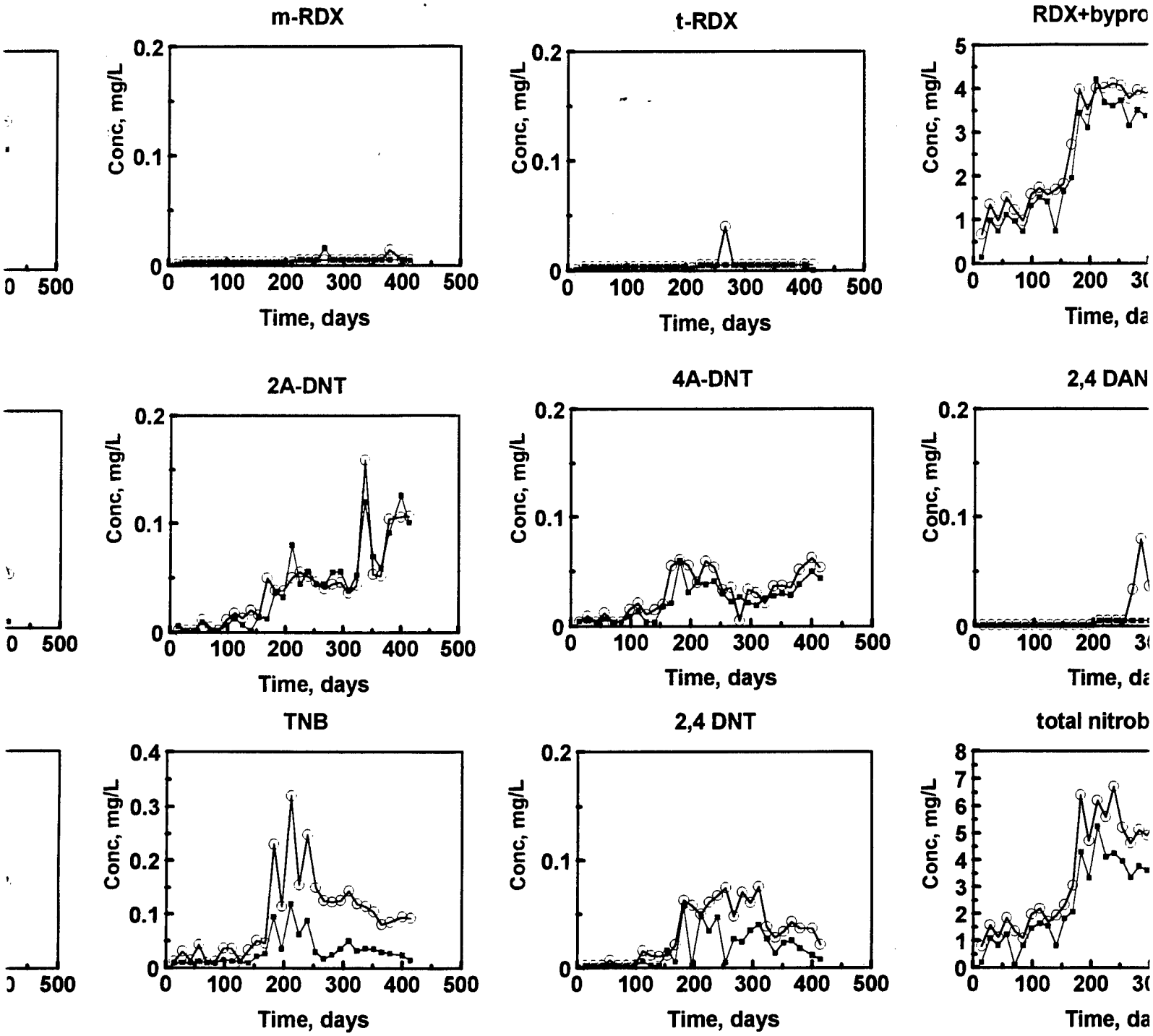
Note: When a chemical was not detect

Effluent Explosive and Explosive By-Produ
from June 17, 19



Note: When a chemical was not detected the method detection limit was plotted instead.

Figure 6-3
nt Explosive and Explosive By-Product Concentrations from the Lagoon-Based Wetlands from June 17, 1996, to September 16, 1997

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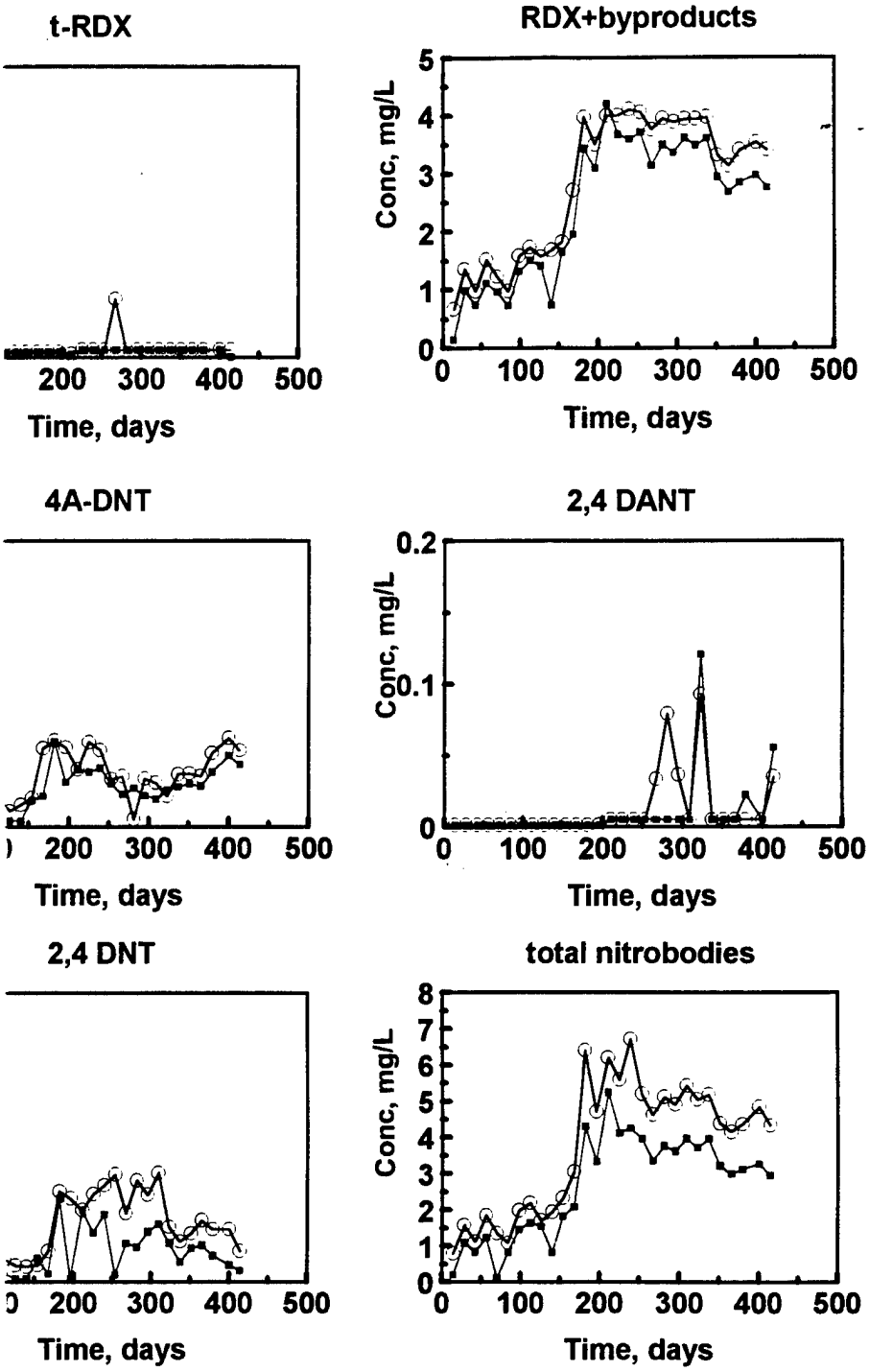

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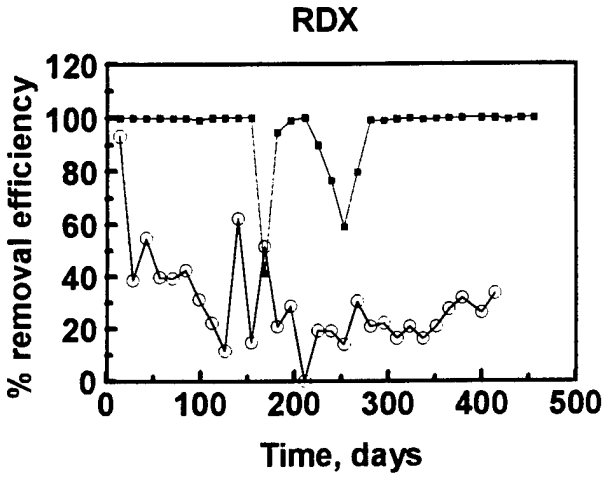

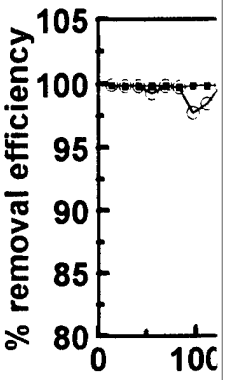

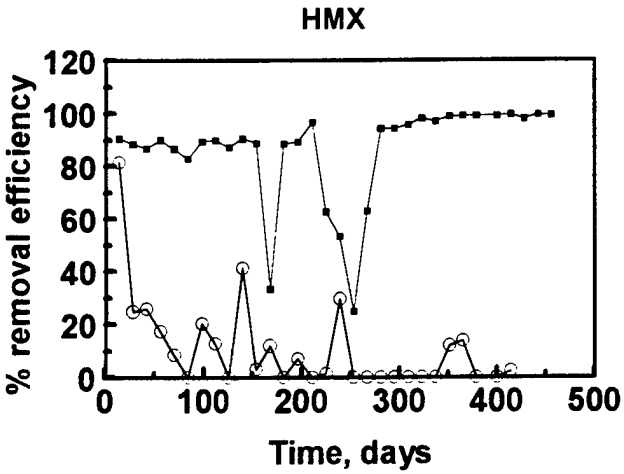

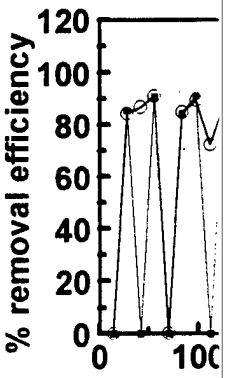

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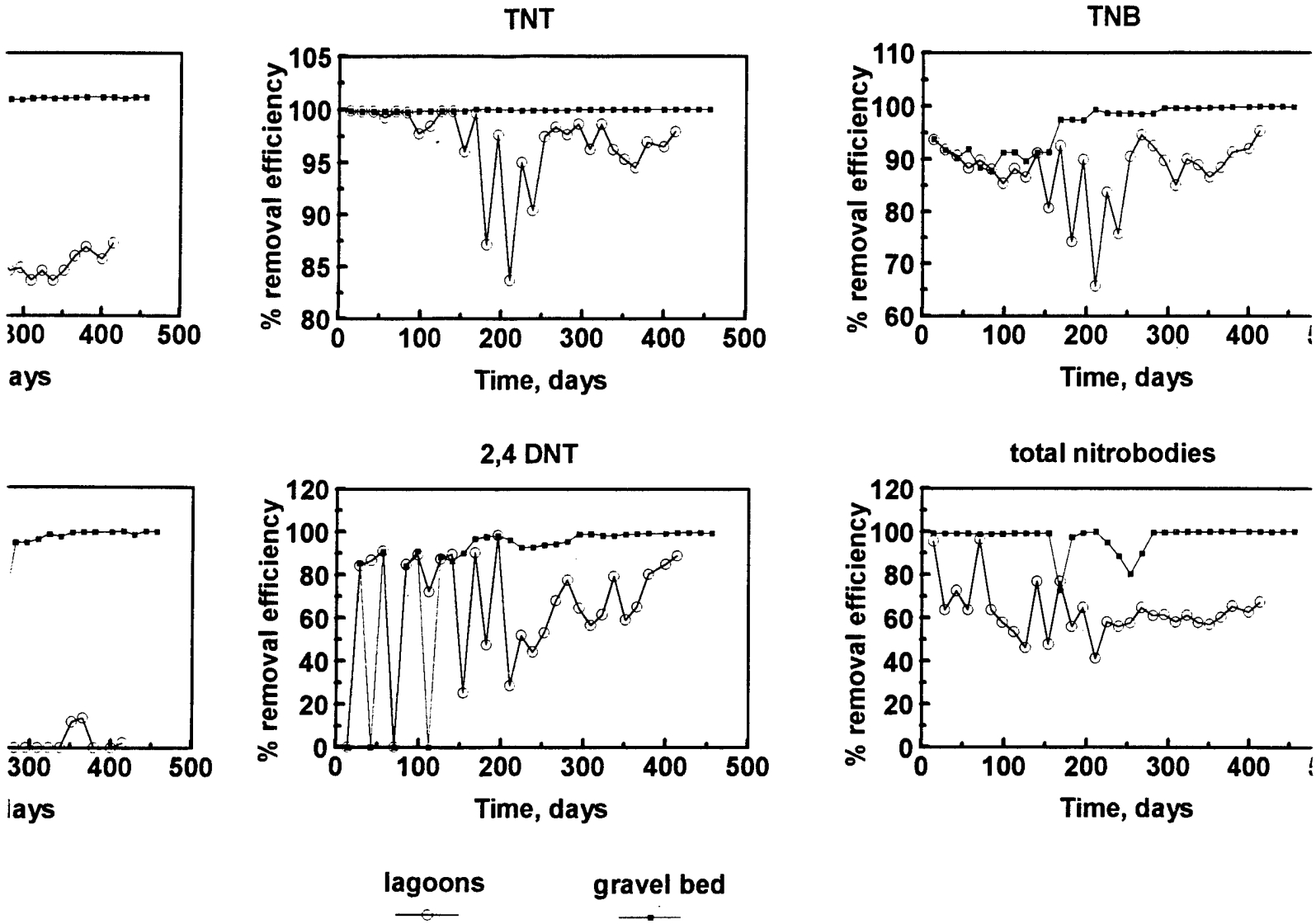

Figure 6-4
Removal Efficiencies of the Gravel- and Lagoon-Based Wetlands
From June 17, 1996, to September 16, 1997

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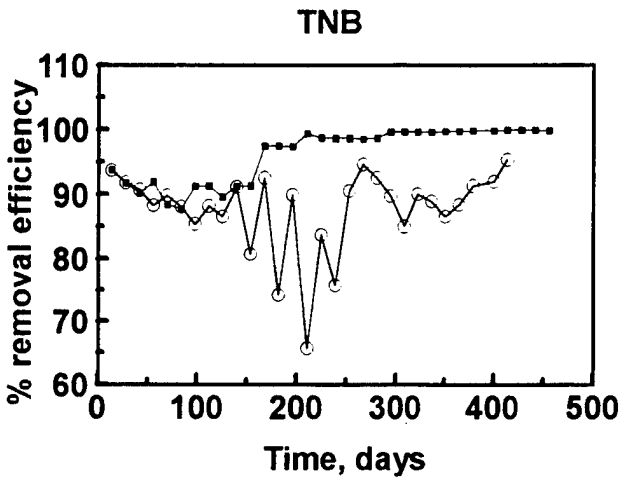

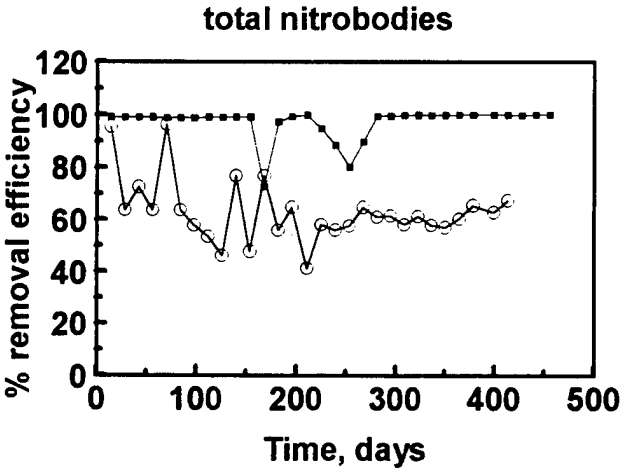

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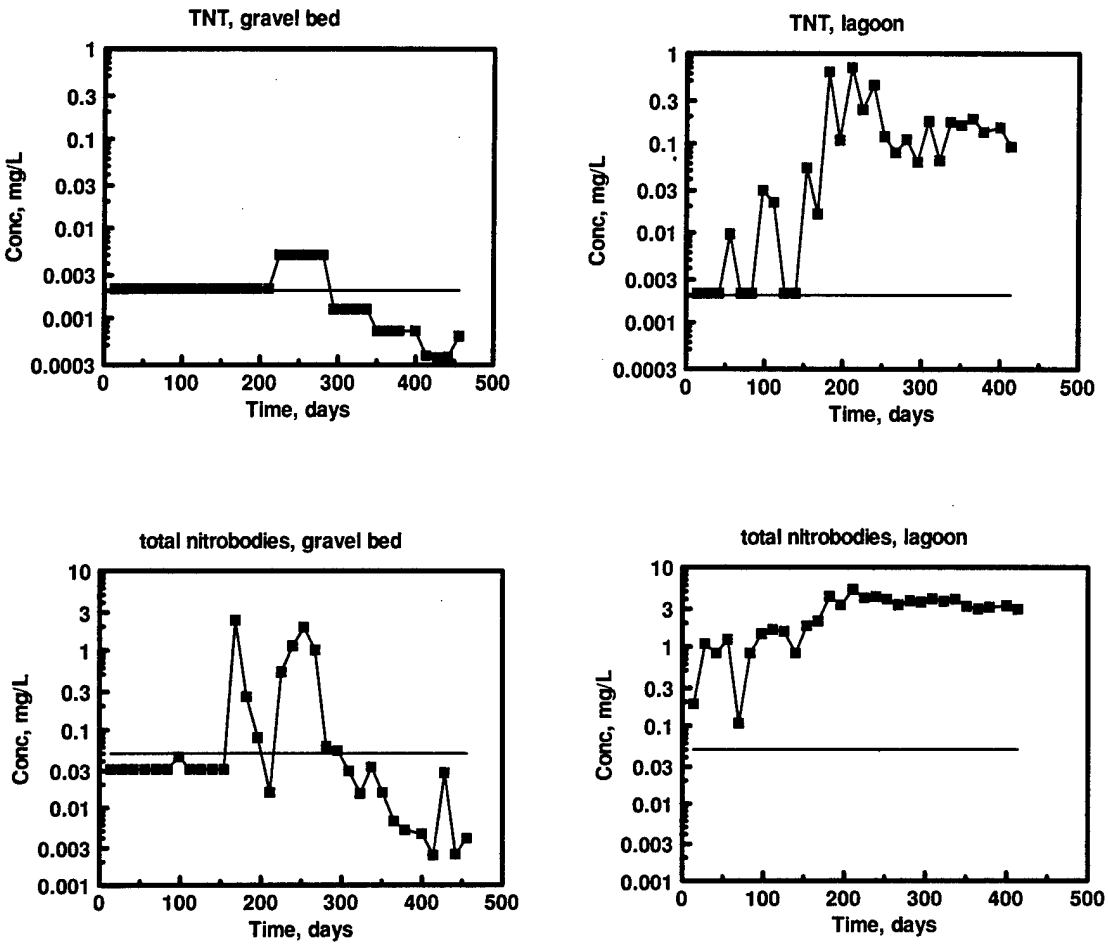
efficiency appeared to stabilize at approximately 30% by January 3, 1997, (day 200) and slowly increased to approximately 90% by September 16, 1997 (day 456). The lagoon-based system's 2,4-DNT removal efficiencies were also low, ranging from 20% to 80%. 2,6-DNT was never found above the 5 ppb detection limit, so is not shown in Figure 6-4. The percent removal figures listed above were calculated based on the formula:

(Influent conc. - Final effluent conc. from wetland system)/(Influent conc.) x 100

A goal of the Milan demonstration was to reduce TNT concentrations to below 2 ppb and total nitrobody concentrations to below 50 ppb. The effluent concentrations from the gravel- and lagoon-based wetlands are shown in Figure 6-5 to display whether or not this goal was met.

The gravel-based wetland was generally able to meet the TNT goal, but did not meet the total nitrobodies goal during winter operations. The effluent concentration of TNT from the gravel-based wetland was always below the detection limit as plotted in Figure 6-5. However, the detection limits were briefly above 2 ppb from January 28, 1997, to March 19, 1997, (days 225 to 275) due to a laboratory instrument column failure. In December 1997, the HPLC column began to deteriorate and had to be replaced. About mid-January, after installing the new column, the explosive detection limits were reassessed. A careful review of the January data suggested that additional measures needed to be taken before a detection limit of 2 ppb could be claimed. Consequently, a detection limit of 5 ppb was set until such time as the analytical procedure could be refined. Once the procedure was refined, the detection limit was lowered to 2 ppb (or lower).

Other than having the detection limit above 2 ppb from January 28, 1997, to March 19, 1997, a satisfactory meeting of the TNT goal was documented. In contrast, the total nitrobodies concentration in the effluent leaving cell A2 was not consistently below the goal of 50 ppb. Two peaks were observed, the first peak occurring between December 2 and Dec 30, 1996, (days 168 to 196) after changing to well MI-051 on November 21, 1996. As discussed previously, this peak has been mainly attributed to the increase in the influent's explosive concentration. The second peak occurred between January 28, 1997, and April 8, 1997, (days 225 to 295) and has been attributed to the combined impacts of reduced MRS addition,



Notes:

- Horizontal Line = TNT remediation goal of <2 ppb (<0.002 mg/liter) or a total nitrobody remediation goal of <50 ppb (<0.05 mg/liter).
- When a chemical was not detected, the Method Detection Limit was plotted instead.

Figure 6-5
Comparison of the Gravel- and Lagoon-Based Wetland's Ability to Meet Demonstration Goals (From June 17, 1996, to September 16, 1997)

short-circuiting, and low water temperature; all of which contributed to decreased removal efficiency during the winter of 1996/1997. In spite of these circumstances, 72% of samples taken from the gravel-based wetland met this performance goal.

In contrast, the lagoon-based wetland consistently failed the performance criteria for both TNT and total nitrobodies (Figure 6-5). Except for some samples collected in the first 150 days of the demonstration (to November 14, 1997), TNT concentrations were above the 2 ppb TNT goal. Total nitrobodies in the effluent of the lagoon wetlands was always above the 50 ppb goal.

6.1.5 Flow Rate, Meteorological, and Water Quality Data

The following discussions relate to Figures 6-6 to 6-17 concerning various meteorological and water quality data that were collected during the Phase II demonstration. Data summaries, illustrated by box or scatter line plots, represent data collected over the sampling period between June 1996 and September 1997. The line within an individual box-plot represents the mean (middle of distribution), while the lower and upper ends of the box represent the first and third quartiles, respectively. The lower and upper T-bars represent the first and ninth deciles, respectively; and the open circles represent data points lying beyond the first and ninth deciles. The relative position of the mean line within the box indicates degree and direction of skewness. The scatter line plots have a data point representing the average and a line representing the standard deviation. With respect to figures in this series, sample positions 1 through 7 represent as follows:

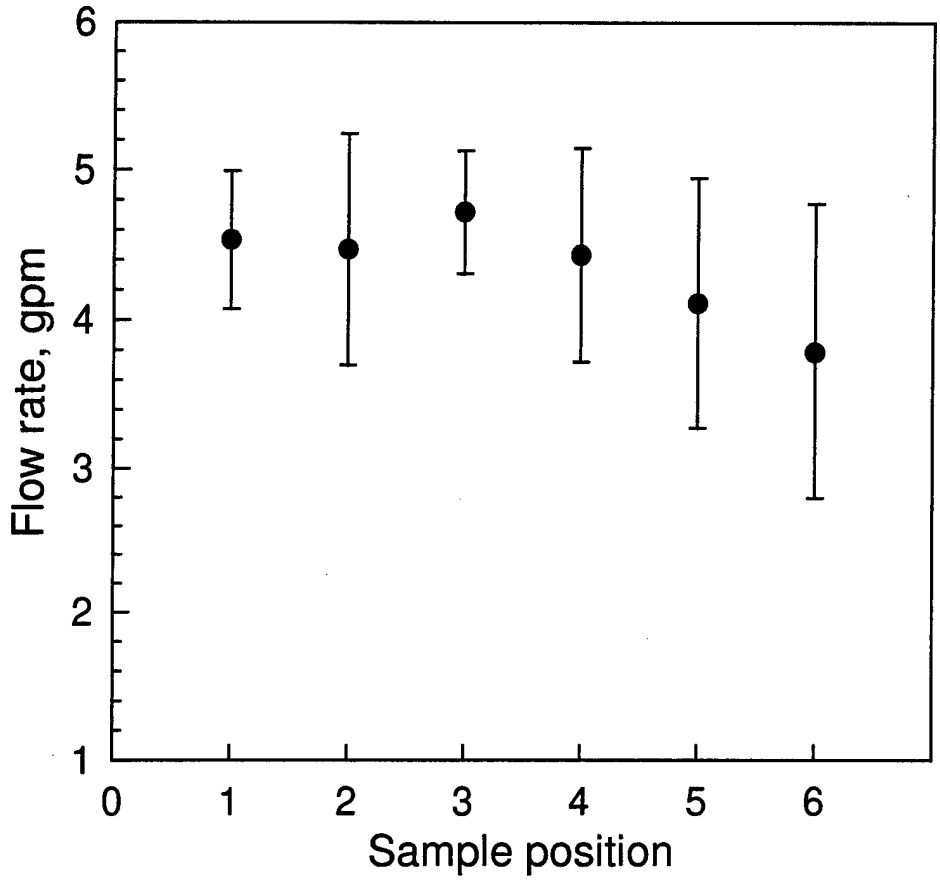
(1) influent values for gravel bed A1
(2) effluent values from gravel bed A1
(3) effluent values from gravel bed A2
(4) influent values for lagoon B1
(5) effluent values from lagoon B1
(6) effluent values from lagoon B2
(7) effluent values from activated carbon drums

Data values for sample positions 16-29 represent water quality for samples collected from interior positions along the lengths of the gravel- and lagoon-based systems, respectively (see Figures 3-1 and 3-2 for relative positions). It should also be noted that samples prior to November 21, 1996, were based on influent from well MI-146, while samples collected after November 21, 1996, were based on influent from well MI-051.

6.1.5.1 Influent and Effluent Flow Rates

Figure 6-6 illustrates influent and effluent flow rates (gpm) for all cells (sample points 1-6). The data is based on biweekly sampling events for the period July 1996 to September 1997. Inlet flow rates into the gravel-based (sample point 1) and lagoon-based (sample point 4) systems averaged slightly less than the design flow rate of 5 gpm. With respect to the gravel-based system, there was very little difference between the inlet and outlet flow rates. This is reasonable given the water-conserving nature of gravel-based wetlands. In contrast, data for the free water surface lagoon system revealed a downward trend in flow rates resulting primarily from high evaporation rates. Evaporation rates in free water surface systems, such as ponds and lagoons, are primarily dependent on temperature, but are also influenced by solar radiation, humidity, and wind. In the mid-south, monthly water losses to evaporation from open ponds can range from approximately 1 inch in January to 6 inches in June. On an annual basis, monthly water losses average approximately 3.7 inches.[Ref. 7] Based on a real evaporation rate, this is equivalent to 3,300 gallons/surface-acre-day (0.12"/day = 0.30 cm/day). Converting these values to the area of one lagoon cell results in an estimated water loss of 0.1 gpm in each lagoon cell.

As mentioned earlier, both treatment systems were lined with two 20-mil reinforced synthetic liners to prevent loss of water due to seepage. During the course of the demonstration, there was no indication of water loss due to seepage through the leak detection system (i.e., the liner at the bottom of the leak detection system was not leaking), and therefore, any net losses of water to the system were attributed to either evaporation (lagoons) or evapotranspiration (gravel-based system).



The sample positions above are located at the:

(1) A1 Influent (inlet to anaerobic gravel bed)

(2) A1 Effluent (outlet from the anaerobic gravel bed)

(3) A2 Effluent (outlet from the aerobic gravel bed)

(4) B1 Influent (inlet to the first lagoon)

(5) B1 Effluent (outlet from the second lagoon)

(6) B2 Effluent (outlet from the second lagoon)

Figure 6-6

Wetland Influent and Effluent Flow Rates
(From June 17, 1996, to September 16, 1997)

The rather wide ranges of variation in influent and effluent flow rates, as reflected by the error bars (+/- one standard deviation), were due to the cumulative effects of several sources of variation including: pump flow variation, mechanical flow meter variation, precipitation, evaporation, and evapotranspiration. As noted earlier, evaporation and evapotranspiration are very dynamic and are influenced by diurnal, daily, and seasonal changes in plant physiology, plant density, solar radiation, wind, humidity, and temperature.

6.1.5.2 Meteorological Data

Figure 6-7 illustrates average monthly meteorological data based on daily measurements from the University of Tennessee's Milan Agricultural Experimental Station. Box plots of rainfall data (inches) for the period June 1996 to September 1997 are provided at the top of Figure 6-7. The data indicates a wide range of rainfall events during the year with above-normal rainfall during the summer of 1996, a relatively dry winter (1996/1997), and a very wet spring and early summer (1997).

Box-plot data for maximum and minimum temperatures (°F) for the period June 1996 through September 1997 are provided in the third and fourth charts in Figure 6-7. Mean minimum and maximum monthly temperatures followed an expected diurnal regime for temperate climates at this latitude with highest mean daily temperatures recorded during the June to September timeframe (82 to 83°F) and lowest mean daily temperatures recorded during January (22°F). It should be noted that temperature is a key variable in remediation and can influence community respiration, photosynthesis, solubility of dissolved oxygen, redox potential, biochemical reaction rates, and ensuing treatment efficacy.

6.1.5.3 Water Temperature

Figures 6-8 and 6-9 summarize water temperature data related to the two treatment systems, as well as influent groundwater temperatures, for the period June 1996 through September 1997. Seasonal variation in temperatures are depicted in the chart in Figure 6-9. Mean groundwater influent temperatures ranged from a high of 20°C in August to approximately 10°C during the months of January and February 1997. The ten-degree variation in pumped groundwater temperature over this period of time was influenced by annual changes in soil temperature.

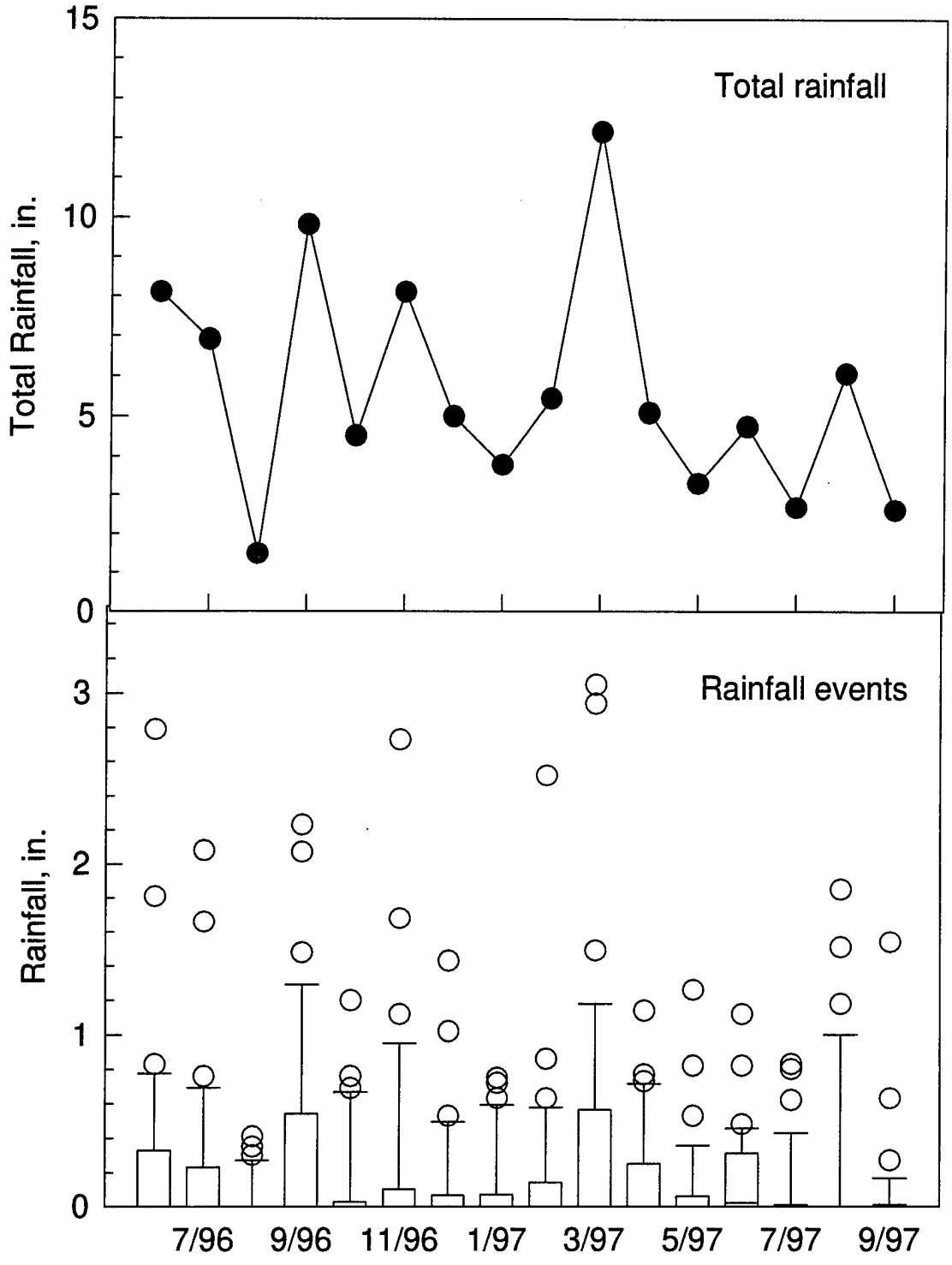


Figure 6-7
Weather Conditions From June 17, 1996, to September 16, 1997

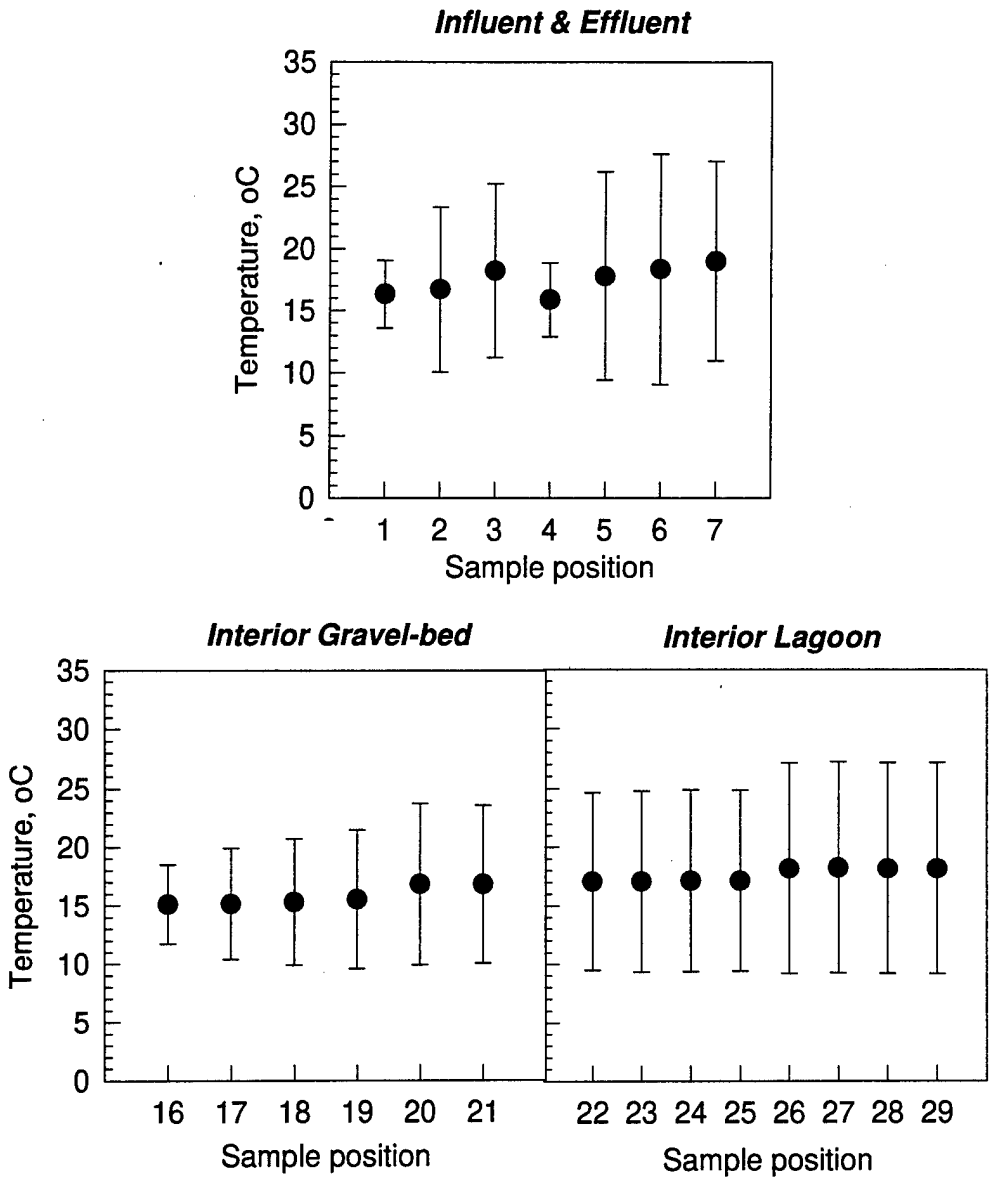


Figure 6-8

Average Wetland Water Temperatures From June 17, 1996, to September 16, 1997

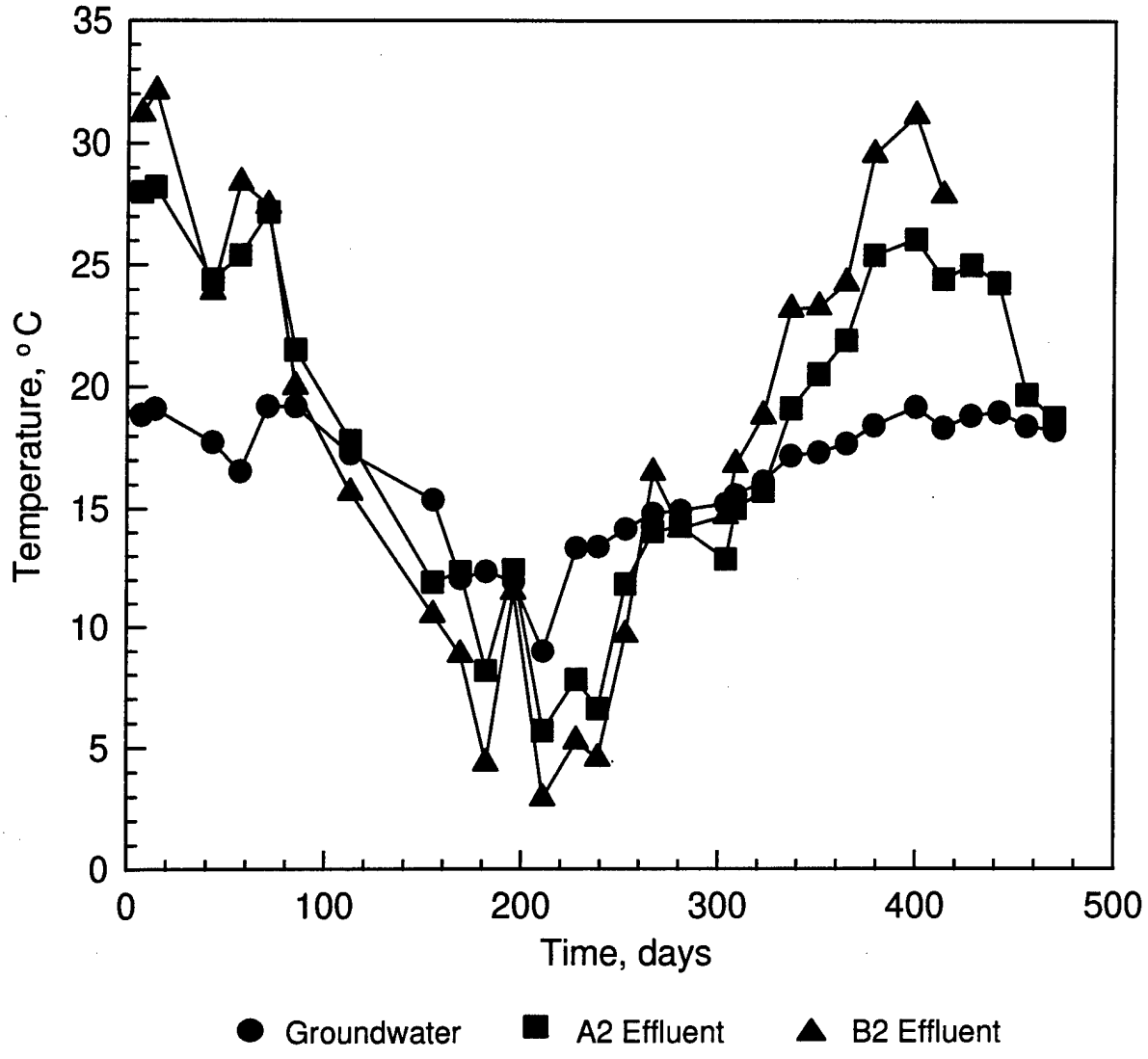


Figure 6-9

Annual Variation of Water Temperatures From June 17, 1996, to September 16, 1997

Groundwater temperature at this latitude is a near-constant 14-15°C. However, as the water was pumped from the well to the demonstration site, water temperature was moderated by ambient surface soil temperatures. This figure also illustrates the greater seasonal variation in lagoon-effluent temperatures as compared to the gravel-based effluent. The gravel serves as a heat sink, and thus, tends to moderate diurnal changes in temperature.

The chart at the top of Figure 6-8 summarizes the mean temperatures and variation around the means for influent and effluents from the two treatment systems. Mean annual temperatures for the two systems were very similar, ranging from 16 to 17.5°C. However, annual variation was slightly greater for the lagoon system than for the gravel-based treatment system. This was due to the temperature-moderating effect of the rock substrate (i.e., the substrate was acting as a heat sink).

The two charts at the bottom of Figure 6-8 illustrate temperature data for various locations within the gravel- and lagoon-based treatment systems. As in the previous illustrations, the mean temperatures were very similar across locations within both systems while variation around the means were higher for the lagoons than for the gravel-based systems. As the water traveled the length of the treatment cells, the mean temperature and temperature variation in both systems increased. For the lagoon-based system, variation around the means was very uniform, reflecting the well-mixed nature of shallow lagoons. In the gravel-based system, the mean water temperature increased as the water passed through the gravel-based systems (see chart at lower left), again reflecting the cumulative heat-holding capacity of the gravel.

6.1.5.4 Electrical Conductivity

Electrical conductivity (EC) is a measure of salt concentration which can be correlated with total dissolved solids. The chart at the top of Figure 6-10 depicts the changes in EC (mS/cm) as a function of influent and effluent for gravel-based wetland (sample positions 1-3), lagoon-based wetland (sample positions 4-6), and effluent from the GAC drums (sample position 7). In the gravel-based system, there was a significant increase in mean EC values when comparing influent and effluent values of A-1 (0.35 vs 0.64 mS/cm). This can be accounted for by several additive factors, such as addition of minerals in the organic fertilizer

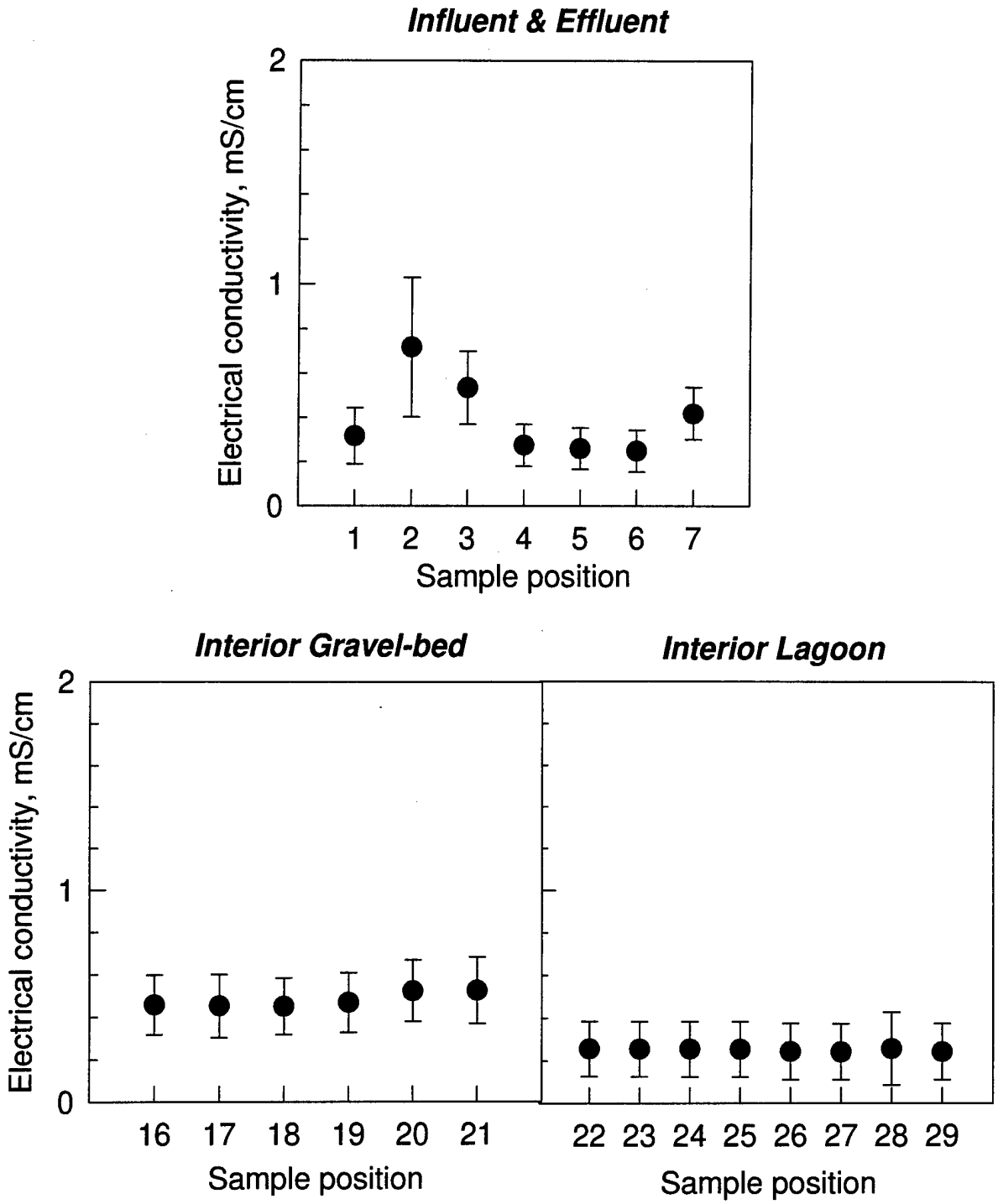


Figure 6-10

Average Electrical Conductivity of Wetland Waters From June 17, 1996, to September 16, 1997

(the MRS carbon source), evapotranspiration, and the dissolution of compounds in the gravel matrix, such as calcium carbonate ($CaCO_3$). A decrease in mean EC in the effluent of A2 (aerobic cells; 0.64 vs 0.48) can be accounted for by the aerobic process which both reoxygenates the pore water and removes supersaturated gasses, such as CO_2. Subsequent changes in redox potential and pH-buffering systems, as a result of the aerobic process, can also effect removal of several ionic compounds, such as manganese and iron, due to oxidation. Furthermore, significant off-gassing of supersaturated CO_2 and a subsequent shift in the carbonate alkalinity system results in precipitation of $CaCO_3$ and co-precipitation of other compounds.[Ref. 8]

Mean EC values in the lagoon system (approximately 0.28 to 0.30) were very stable with little change from influent to effluent (Figure 6-10, sample positions 4-6). Mean EC for effluent from the GAC unit (0.40, sample position 7) was intermediate to effluent values for A2 and B2.

The chart in Figure 6-11 illustrates a scatter diagram for EC data representing effluent values for the effluent from cells A1, A2, and B2 over the period from June 1996 to September 1997. There are two noteworthy trends: 1) the initial wide scatter of values for A1 and A2, probably resulting from the initial high dissolution rate of $CaCO_3$ from the gravel matrix, and 2) the general upward trend in EC for all three effluents, which may have been influenced by a change in groundwater source, such as seasonal dynamics in evaporation and evaportraspiration.

The two charts on the bottom half of Figure 6-10 illustrate mean EC values for several interior sample positions within the gravel- and lagoon-based treatment systems, respectively (sample positions 16-29). Mean EC values in both systems tended to be very stable with little change in electrical conductivity from location to location. This was especially true for the lagoon system, which is typical for shallow lagoons, in which there is strong convective diurnal mixing.

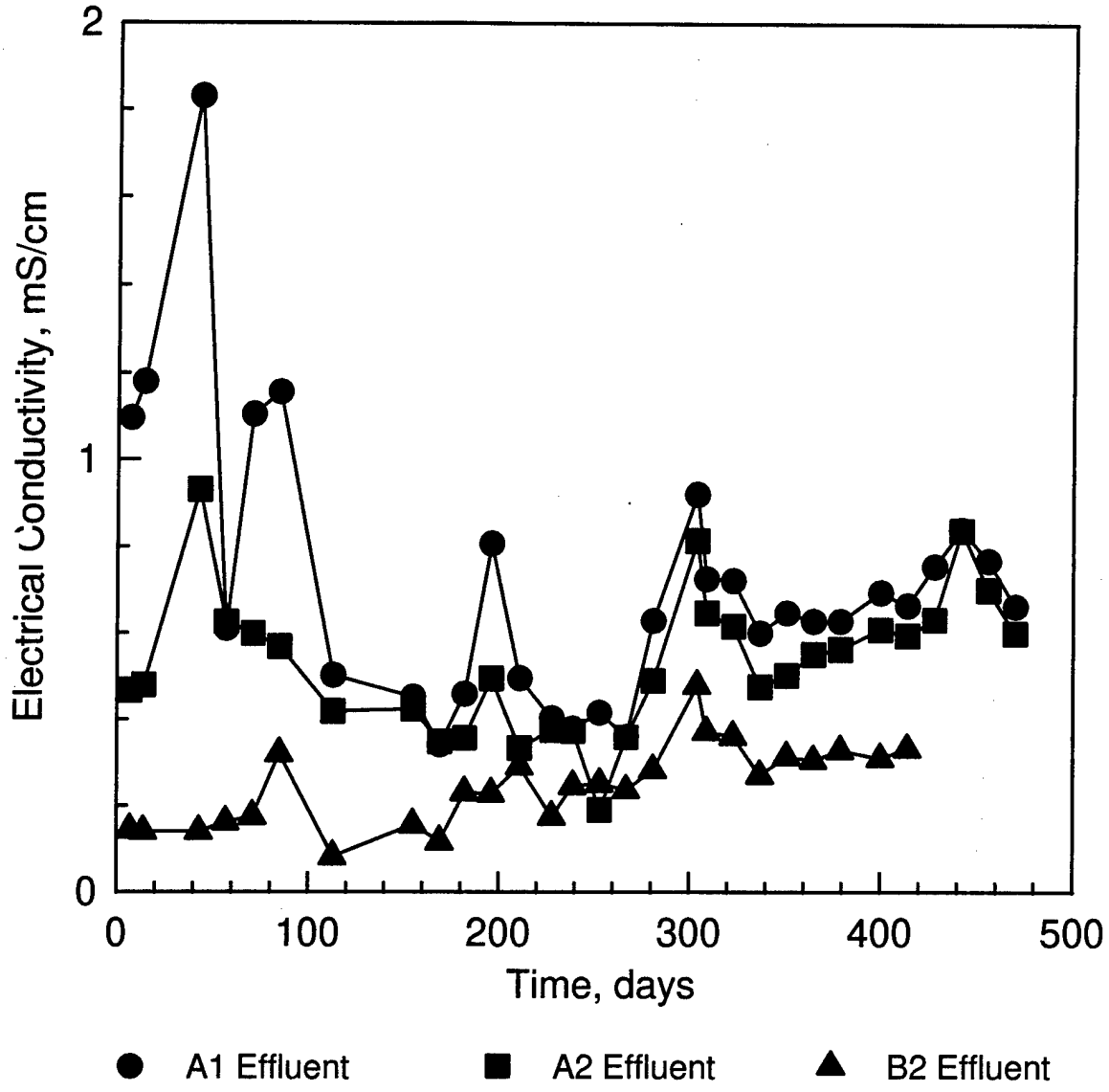


Figure 6-11

Annual Variation of Electrical Conductivity of Wetland Waters

From June 17, 1996, to September 16, 1997

6.1.5.5 Dissolved Oxygen Concentration

The data in Figures 6-12 and 6-13 summarize dissolved oxygen (DO) correlations for the influent, effluent, and interior locations for both the lagoon- and gravel-based systems. The chart at the top of Figure 6-12 depicts mean DO concentrations (mg/liter), calculated over all sample dates, as a function of sample position. The mean influent DO concentration was approximately 5.5 mg/liter.

Mean concentrations for effluents from A1 (anaerobic gravel-based cell) and A2 (aerobic gravel-based cell) were approximately 1.5 and 6.5 mg/liter, respectively. The significant difference in mean DO concentration between effluents from A1 and A2 was due to high community respiration rate in A1 resulting from organic fertilization and re-aeration of water in A2.

Mean DO concentrations for lagoon effluents from B1 (position 5) and B2 (position 6) were approximately 9.5 and 10.5, respectively. These relatively high mean DO concentrations were due to relatively high levels of net primary productivity (high photosynthetic rates coupled with low community respiration rates). No supplemental carbon (MRS) or nutrients were added to the lagoon system, and as a result, community respiration rates were low. The soil contained adequate nutrients for plant growth in the sense that limited plant productivity and resulting daytime oxygen evolution were sufficient to maintain high DO concentrations, especially in B2.

The chart in Figure 6-13 illustrates the annual variation in DO concentration (mg/liter) for the period June 1996 through September 1997. Significant seasonal changes in DO concentrations are due to several interacting factors: 1) changes in community respiration as a function of temperature (high respiration in the summer; low respiration in the winter), 2) changes in DO solubility as a function of temperature (higher solubility at low temperatures; lower solubility at high temperatures), and 3) changes in light intensity (high in spring and summer; low in fall and winter).

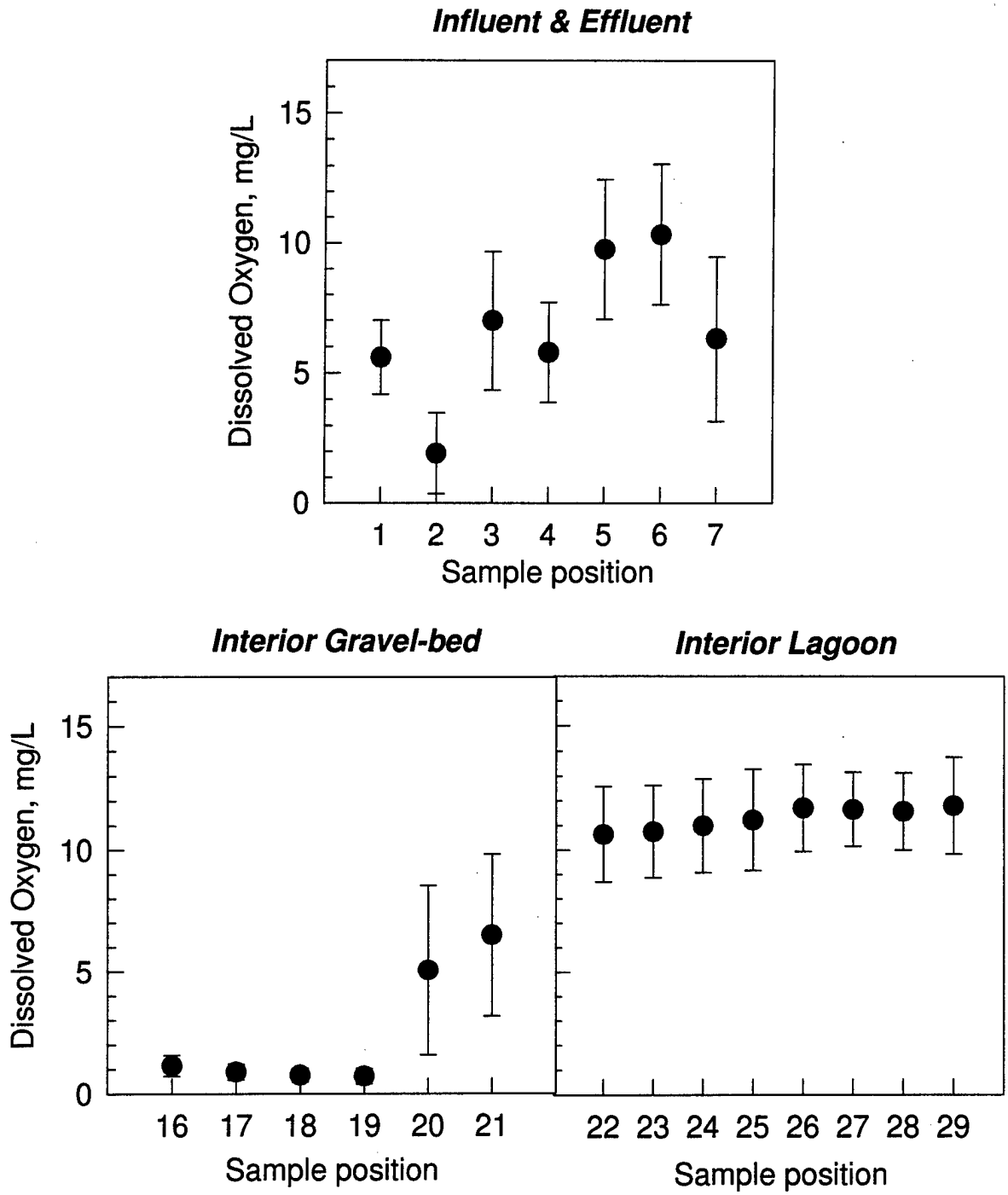


Figure 6-12

Average Dissolved Oxygen Content of Wetland Waters From June 17, 1996, to September 16, 1997

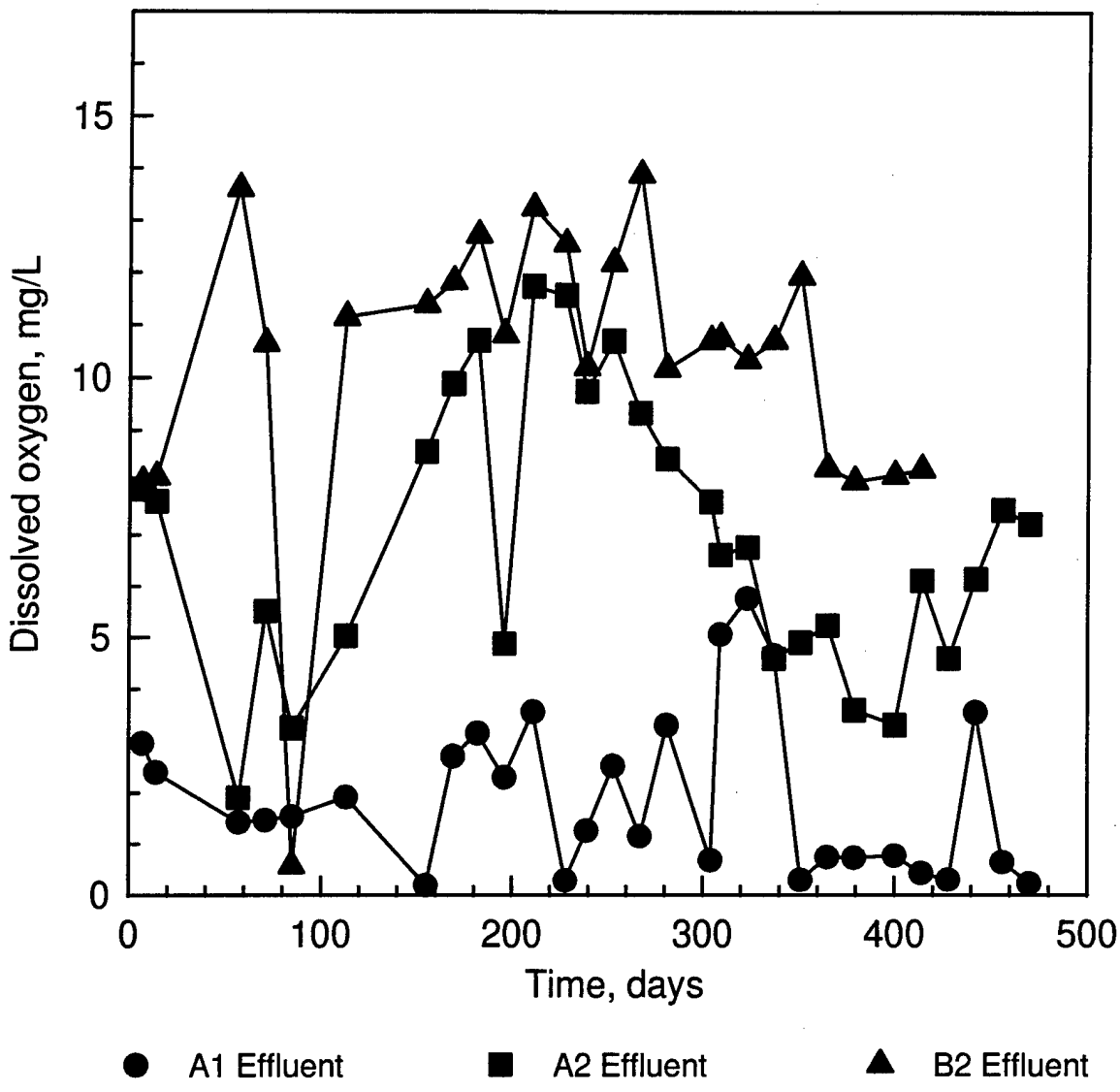


Figure 6-13

Annual Variation of the Wetland Water's Dissolved Oxygen Content From June 17, 1996, to September 16, 1997

The rather high effluent DO values (>10 mg/liter) from the lagoon system (B2) were due to daytime photosynthetic evolution of dissolved oxygen. A1 effluent dissolved oxygen levels (DO, mg/liter) were comparatively low for the duration of the demonstration as a result of high organic fertilization rates (MRS, average loading = 203 lbs/acre/day) and ensuing high microbial and root respiration rates. Moderate to high DO concentrations for A2 effluent resulted from the aeration process in which atmospheric oxygen was added to the water via mechanical aeration. The aerobic cells provided atmospheric oxygen, thereby, enhancing removal of residual organic matter as quantified by significant reductions in BOD_5 and COD.

The lower left hand chart in Figure 6-12 illustrates mean DO concentrations (mg/liter) and respective measures of variation for interior positions of the gravel-based system (positions 16-19) and the paired aerobic cells (positions 20 and 21). Mean DO concentrations for the sample positions within the anaerobic gravel-based cell were very low (<1.0 mg/liter). Low values, with relatively little variation around the mean, were due to: 1) high intermittent organic fertilization, 2) high microbial and plant root respiration rates (community respiration), and 3) marginal re-aeration at the air-water interface resulting from subsurface flow and low surface-to-volume ratio.

Mean DO concentrations for sample positions 20 and 21 (aerobic cells) were significantly higher than concentrations in the anaerobic cell (positions 16-19) due to active aeration, which provided atmospheric oxygen at rates in excess of community respiration needs. The rather large amount of variation around the mean values for positions 20 and 21 was due to temperature-induced changes in oxygen solubility and community respiration rates, which are additive in their effects (for example, see seasonal variation in DO concentration for A2 effluent in Figure 6-13).

Mean DO concentrations and respective standard deviations are illustrated for sample positions in lagoons B1 and B2 (lower right hand chart of Figure 6-10). Mean values were uniform across all sample positions, ranging from 10.0 to 10.2 mg/liter. The uniformly high DO concentrations, often near saturation or in excess of saturation, are indicative of relatively high photosynthetic rates, coupled with low community respiration rates. In this particular instance, plant nutrients for the submerged aquatic plants were available from the soil substrate. Carbon for photosynthesis was provided by atmospheric CO_2, which was replenished at the air-water

interface on a daily basis. Low soil organic carbon limited microbial respiration. Thus, nutrients and carbon were available to sustain relatively high rates of photosynthesis while community respiration rates remained low because of limited organic carbon.

6.1.5.6 Redox Potential

Figures 6-14 and 6-15 summarize the redox potential data (standardized against a hydrogen electrode) for influent and effluent streams and for interior sample positions, respectively. The chart at the top of Figure 6-14 illustrates mean redox values for influents and effluents of the various gravel- and lagoon-based treatment cells (sample positions 1-6, respectively). Addition of organic carbon to the anaerobic gravel-based cell (A1) significantly reduced the mean redox potential from +450 (influent, sample position 1) to near zero (A1 effluent, sample position 2). Subsequently, the mean redox value was restored to near ambient conditions in the A2 effluent, +450, as a result of oxidation of organics (BOD_5) and re-aeration of the water. Sample positions 5 and 6, representing mean effluent values for the two lagoons B1 and B2, respectively, were positive and in the range +360 to +450.

Annual variation (Figure 6-15) for effluent from the anaerobic gravel-based cell (A1) varied considerably from -240 to +300, while redox values for effluent from the gravel-based aerobic cells (A2) ranged from +50 to +800. There did not appear to be any clearly defined seasonal trends and values were highly variable over the treatment period for both A1 and A2 effluents. High levels of variability in redox measurements often occur for several reasons (microbial fouling of probe, sensitivity to rapidly changing conditions; e.g., convective currents and associated mixing of oxygen-rich and oxygen-depleted water due to changes in temperature, etc.). Because redox is known to be highly variable, it is often viewed as a qualitative rather than a quantitative variable. However, mean redox values still provide valuable information regarding the relative degree of oxidation/reduction of the treatment environment and the impact of divergent environments on remediation of natural and man-made compounds.

The bottom chart in Figure 6-14 illustrates redox as a function of sample position within the gravel-based wetland system, with position 16 being proximate to the influent, 19 being distant

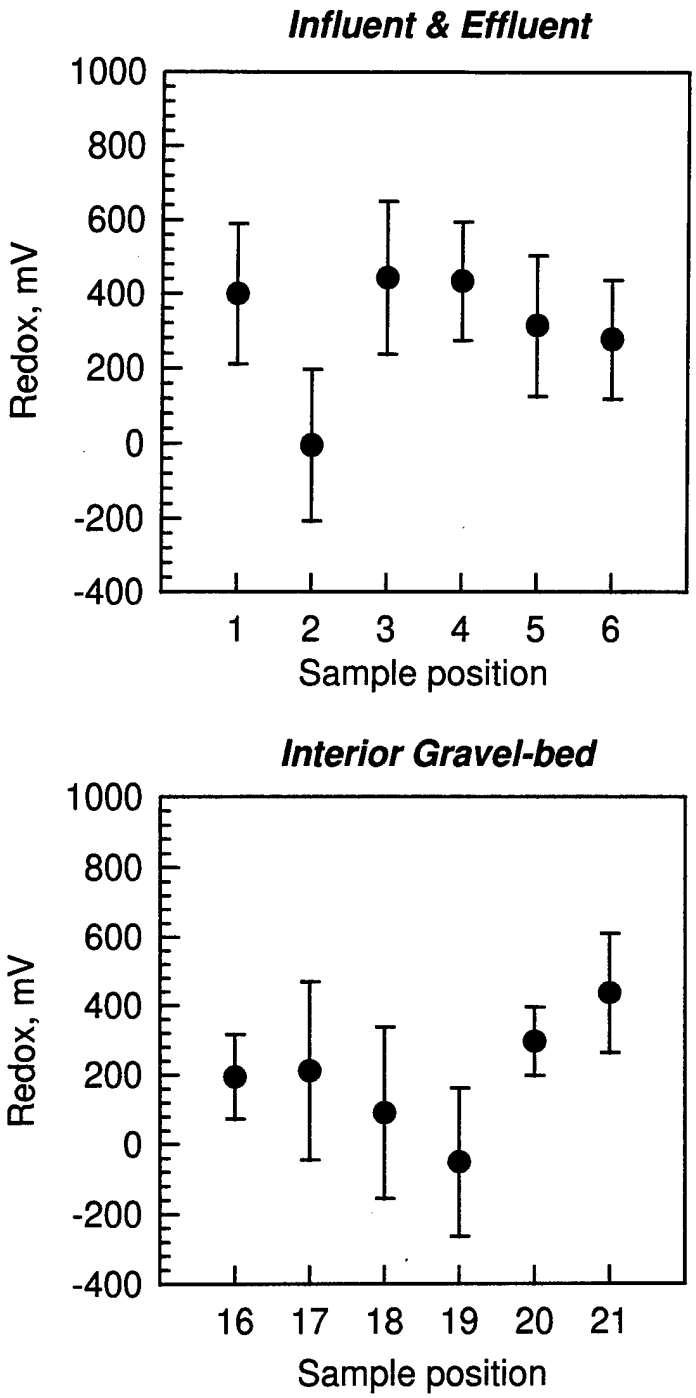


Figure 6-14

Average Redox Potential of Wetland Waters From June 17, 1996, to September 16, 1997

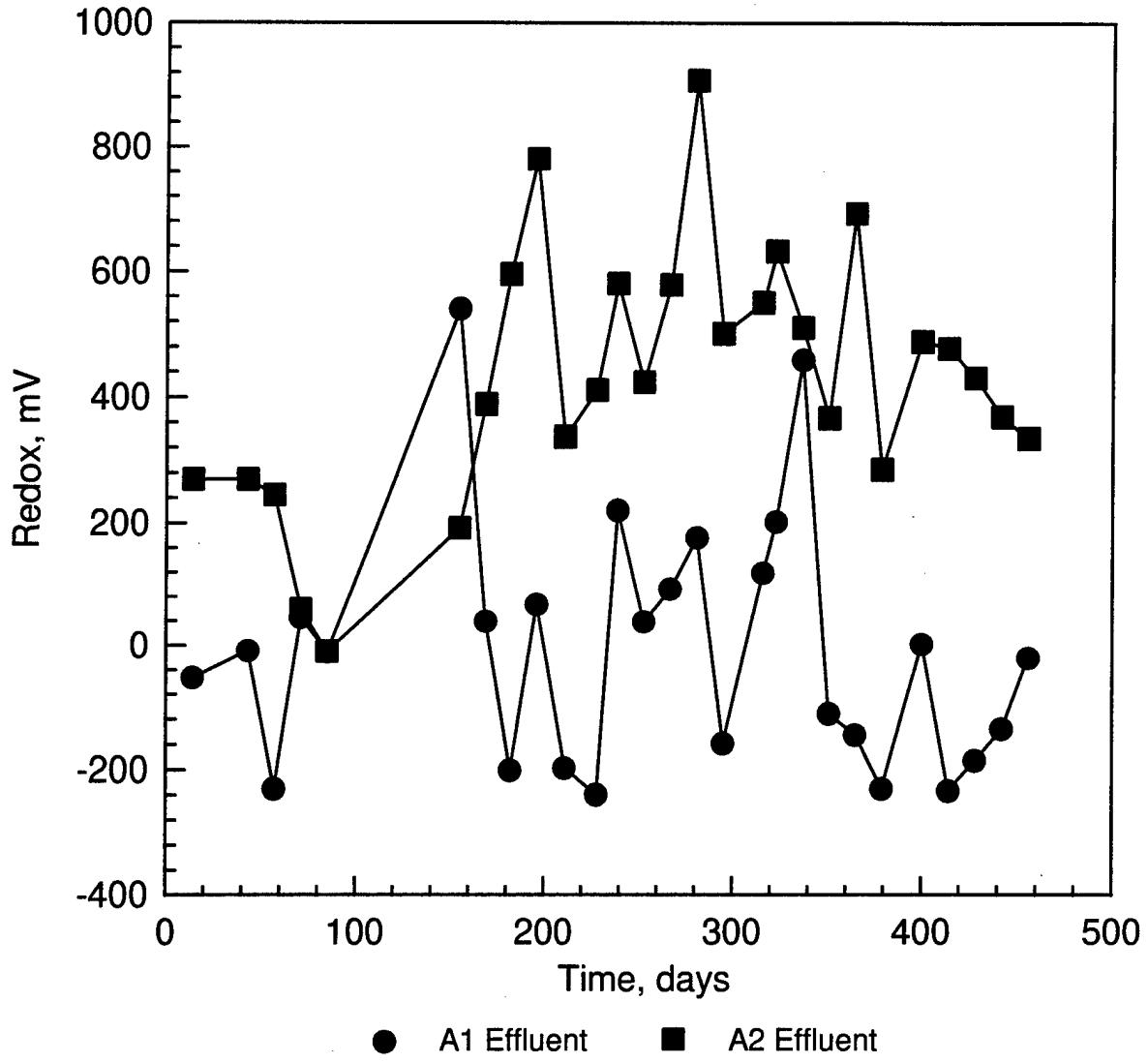


Figure 6-15

Annual Variation of Redox Potential of Wetland Waters From June 17, 1996, to September 16, 1997

from the influent and proximate to the discharge, and positions 20 and 21 representing sampling points in the two aerobic cells. The stair-step pattern exhibited for mean redox values representing sample points 16-19 can be explained by the plug-flow nature of water moving through the gravel cell (A1) and the related stepwise reduction of oxygen, nitrate, sulfate, and carbon dioxide (CO_2). The relatively high redox values near the A1 inlet can be explained by the continuous input of dissolved oxygen (DO) and nitrate (NO_3) from the groundwater (DO = 5 mg/liter, NO_3 = 30 mg/liter) into the inlet portion of A1, while the relatively low redox values near the discharge end of A1 can be explained by plug flow and the progressive reduction of the other compounds (nitrate, sulfate, etc.), culminating in the potential reduction of CO_2 to methane.

Cell A1 was "fertilized" every 14 days with an organic carbon source to reduce redox potential to near anaerobic levels. Treatment efficacy for degrading recalcitrant compounds, such as RDX and HMX, is greatest at very low redox conditions, such as those required for reducing sulfate and CO_2.[Ref. 7, 8]

Effluent leaving A1 and entering A2 (aerobic cells) was devoid of oxygen, nearly anaerobic, and enriched with organics, ammonium, and phosphorus from the mineralization of the organic fertilizer (MRS). The aerobic cells increased redox potential and also provided a sequential anaerobic-anoxic-aerobic continuum, which was favorable for microbial removal of residual organics, explosive by-products, total nitrogen, and total phosphorus.

6.1.5.7 pH

Figures 6-16 and 6-17 provide pH data with respect to influent and effluent, annual variation, and as a function of sample position in gravel- and lagoon-based systems. Mean influent pH values for gravel- and lagoon-based treatment systems were approximately 5.0 and 5.1, respectively. The mildly acidic pH values in the respective influents were probably due to high ambient dissolved CO_2 concentrations, which are typical for many groundwater sources. The rather significant increase in pH for A1 effluent was due to increases in total alkalinity resulting from calcite dissolution (river gravel) and anaerobic processes (e.g., fermentation, nitrate reduction, sulfate reduction, and methanogenesis) in the gravel bed. Further increases

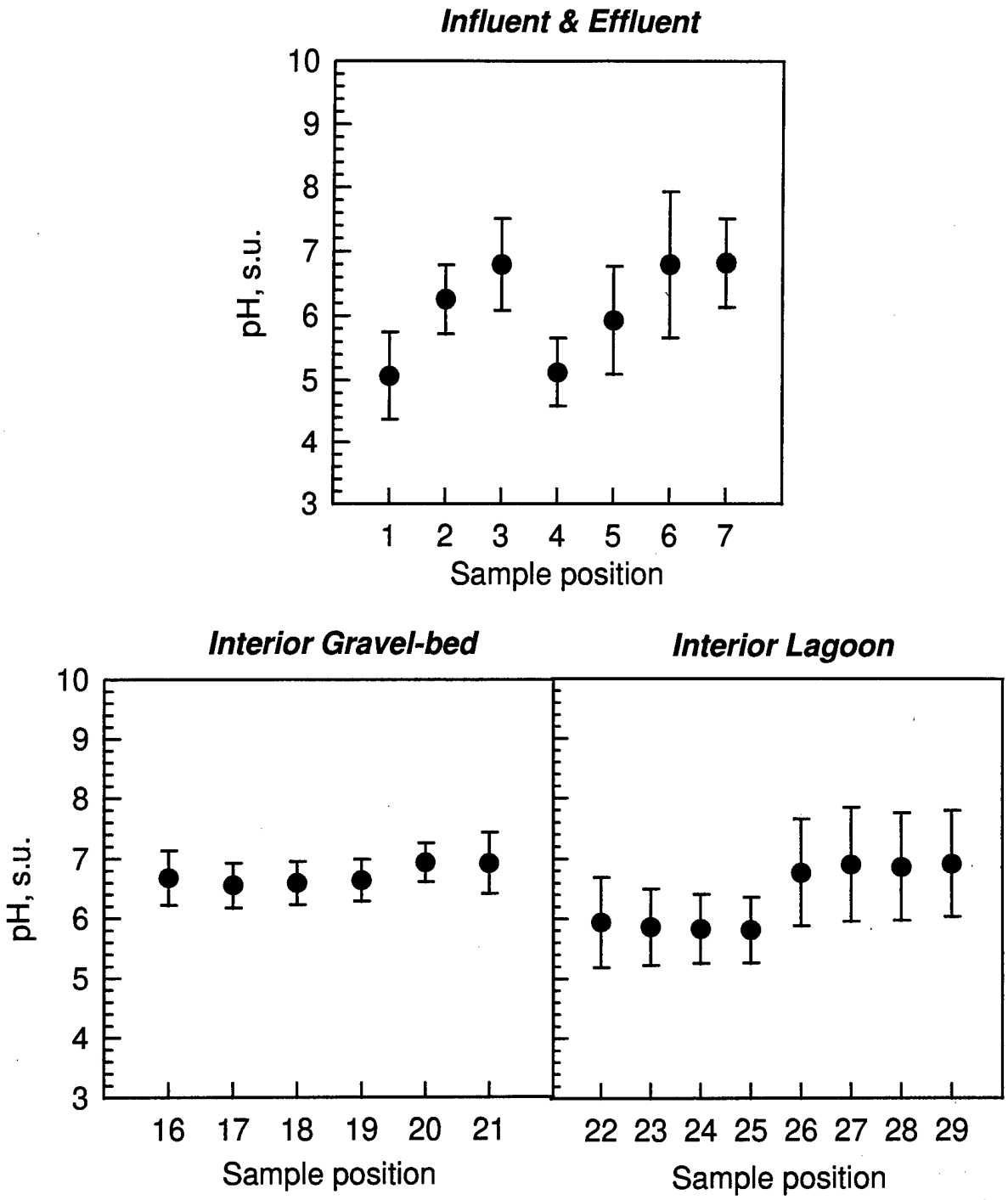


Figure 6-16

Average pH of Wetland Waters
From June 17, 1996, to September 16, 1997

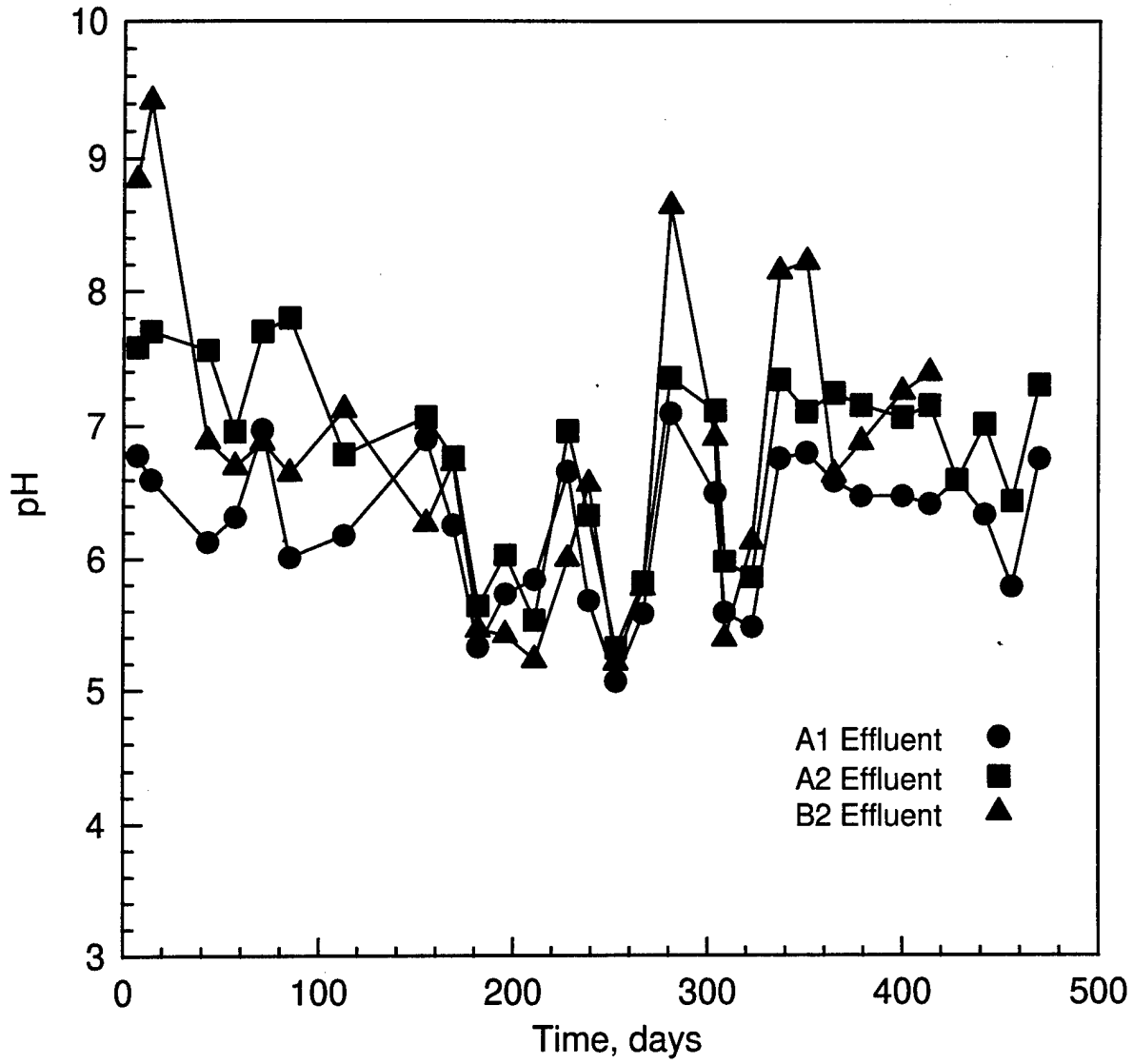


Figure 6-17

Annual Variation of pH of Wetland Waters From June 17, 1996, to September 16, 1997

in pH for water exiting cell A2 (chart at top of Figure 6-16, sample position 3) were due primarily to significant degassing of CO_2 during the aerobic process. These same phenomena have been observed and quantified in other coupled anaerobic/aerobic wetland treatment systems in which organic matter and aeration were used to manage wetland treatment processes.[Ref. 8] The rather significant increases in pH in the lagoon system (positions 4-6) can be explained on the basis of CO_2 being extracted from the water as a result of photosynthesis by the submerged aquatic plants. Water exiting the GAC drums (position 7) had a mean pH value similar to effluents exiting the gravel- and lagoon-based treatment systems.

Annual variation of pH (Figure 6-17) is most pronounced for the lagoon system (range = 5.2 to 9.5), which was strongly influenced by photosynthetic extraction of CO_2. During winter months when ambient light and temperature regimes were reduced, pH was also reduced due to low rates of photosynthesis. During summer months, pH values were elevated due to enhanced photosynthesis resulting from higher ambient light and temperature regimes.

The lower left hand chart in Figure 6-16 illustrates mean pH values for interior positions of the gravel-based system. Mean values were very similar with little variation around the means within the gravel-based system. The pH's ranged from 6.6 to 6.9 (positions 16-19) and were only slightly elevated in the two aerobic cells (positions 20 and 21).

Within the two-cell lagoon system, mean pH values ranged from 6.0 to 6.8, with a slight increase in values from cell B1 to B2 (see lower right hand chart in Figure 6-16). There was also a significant increase in variability of pH values in cell B2 as compared to B1, since increased photosynthetic rate leads to increased pH values. Explosives toxicity and reduced light penetration may have hindered photosynthesis in cell B1 to a greater extent than in B2.

6.1.5.8 Metals

Tables 6-2 and 6-3 summarize average metals and trace metals concentration data (mg/liter) for influent and six sample positions for two wells, respectively. Well MI-146 provided water to the wetland and lagoon system from June 17 to November 21, 1996, while well MI-051 provided water to both systems subsequent to November 21, 1996.

Table 6-2

Wetland Metals Concentrations for Well MI-146 From June 17, 1996, to November 21, 1996

		Concentration (mg/L) at Sample Point[1]																				
		Gravel-Based Wetland									Lagoon-Based Wetland									GAC System		
Sample Point		1			2			3			4			5			6			7		
Total Number of Samples Taken		11			11			11			11			11			11			11		
Metal	Detection Limit	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.
Ca	0.03	5.3	2.2	11	87	49	11	65	8	11	4.5	0.6	11	5.1	0.5	11	4.7	0.9	11	39	9	11
Mg	0.2	1.7	0.23	11	5.7	3.1	11	6.2	2.5	11	1.6	0.2	11	1.9	0.2	11	1.9	0.2	11	4.5	1.6	11
Fe	0.001	0.21	0.38	5	14	11	11	0.10	0.08	10	0.037	0.028	9	0.054	0.03	8	0.085	0.085	8	0.098	0.054	10
Mn	0.008	0.05	0.03	11	13	6.2	11	0.92	0.92	8	0.031	0.007	11	0.029	0.01	11	0.017	0.008	10	0.18	0.18	10
Cu	0.02	BDL	NA	NA	0.01	0	1	0.04	0	1	0.03	0	1	0.02	0	1	0.03	0	1	0.02	0	1
Pb	0.3	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	0.04	0	1	BDL	NA	NA	BDL	NA	NA	0.04	0	1
Ni	0.07	0.62	0	1	0.35	0.34	2	0.31	0.24	3	0.23	0.23	4	0.23	0.23	4	0.23	0.23	4	0.27	0.27	3
Cd	0.03	BDL	NA	NA	0.01	0	1	0.04	0.042	2	0.01	0	1	0.01	0	1	0.01	0	3	0.01	0	2
Zn	0.009	0.02	0.01	8	0.01	0	3	0.024	0.024	7	0.019	0.009	7	0.016	0.008	5	0.01	0	5	0.76	0.76	11

1) Avg. = Average.
SD = Standard deviation.
Num. = Number of observations in which the metal was above the detection limit.
BDL = All samples below detection limit.
NA = Not applicable.

Table 6-3

Wetland Metals Concentrations for Well MI-051 From November 21, 1996, to September 16, 1997

		Concentration (mg/L) at Sample Point [1]																				
		Gravel-Based Wetland									Lagoon-Based Wetland									GAC System		
Sample Point		1			2			3			4			5			6			7		
Total Number of Samples Taken		20			20			20			17			17			17			20		
Metal	Detection Limit	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.
Ca	0.03	23	1.1	11	68	12	20	70	10	20	22	1	17	22	2	17	22	4	17	46	11	20
Mg	0.2	8.7	0.4	20	7.5	1.4	20	8.0	1.7	20	8.5	0.6	17	8.5	0.9	17	8.5	1.4	17	8.2	1.7	20
Fe	0.001	0.045	0.029	15	8	4	20	0.14	0.11	19	0.048	0.038	12	0.06	0.06	13	0.036	0.017	14	0.096	0.096	18
Mn	0.008	0.24	0.02	20	4.5	2.0	20	0.03	0.03	14	0.25	0.11	17	0.22	0.05	17	0.15	0.13	17	0.046	0.046	19
Cu	0.02	0.02	0	2	0.09	0.03	3	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	0.03	0	1	BDL	NA	NA
Pb	0.3	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Ni	0.07	BDL	NA	NA	0.15	0	1	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Cd	0.03	BDL	NA	NA	0.08	0.03	3	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Zn	0.009	0.014	0.006	17	0.03	0.03	11	0.01	0	3	0.011	0.003	12	0.01	0	11	0.014	0.009	11	0.12	0.12	15

1) Avg. = Average.
SD = Standard deviation.
Num. = Number of observations in which the metal was above the detection limit.
BDL = All samples below detection limit.
NA = Not applicable.

Average levels of calcium (Ca) in the influents ranged from 4.5 to 5.3 mg/liter (well MI-146) and 22 to 23 mg/liter (well MI-051). There were significant increases in average concentrations of Ca and magnesium (Mg) in the gravel-based system resulting from both heavy rates of organic fertilization (MRS) and the dissolution of calcium carbonate and dolomite contained in the gravel matrix. There were also significant increases in average concentrations of iron (Fe) and manganese (Mn). These increases were due primarily to the frequent and heavy rates of organic fertilizer (MRS) applied to maintain near anaerobic conditions. However, average effluent concentrations of Fe and Mn from the aerobic cells (A2, position 3) returned to near-ambient conditions. Similar results have been reported regarding metals removal from acid mine drainage.[Ref. 8] Mn and Fe are removed as the oxides and hydroxides when exposed to alkaline and oxidizing environments. The aerobic cells produced a highly oxidized environment with near neutral pH.

Average concentrations of Ca, Mg, Fe, and Mn, and their respective dynamics under conditions of lagoon treatment (positions 4-6), are summarized in Tables 6-2 and 6-3. In general, average concentrations of Ca and Mg were relatively low (<22 and 9 mg/liter, respectively), very stable, and deviated little from influent concentrations.

Average concentrations of Fe and Mn in the lagoon-based system, although less than 0.3 mg/liter, appeared to be fairly dynamic. For example, average concentrations of Fe tended to increase in the lagoon system from 0.037 mg/liter (influent) to 0.085 in the effluent of B2. Conversely, average concentrations of Mn tended to decrease as water moved through the lagoon system (Tables 6-2 and 6-3). However, these trends were not statistically significant given the relatively large standard deviations (Tables 6-1 and 6-2). Metals concentrations (Ca, Mg, Fe, and Mn) exiting the GAC drums (position 7) were generally intermediate to concentrations exiting A2 and B2.

Trace metals, including copper (Cu), lead (Pb), nickel (Ni), cadmium (Cd), and zinc (Zn) were also monitored (Tables 6-2 and 6-3). Average trace metal concentrations were generally low (0.5 mg/liter) and often below detection limits. Addition of MRS increased average trace metal concentrations, but only temporarily. Both the gravel- and lagoon-based treatments tended to remove trace metals to near or below their respective detection limits. Effluent from the GAC drum (position 7) had relatively high concentrations of Zn, suggesting that the GAC

drums either contained Zn or retained and then released Zn. The mean effluent values from the GAC contained Zn at significantly higher concentrations than effluent concentrations from A2 and B2.

6.1.5.9 Nutrients and Water Quality

Tables 6-4 and 6-5 summarize average nutrient and water quality data (mean and standard deviation, mg/liter) for influent (two groundwater supply wells) and six sample positions. These positions being the groundwater influent to the anaerobic gravel bed A1, effluent from the A1 anaerobic gravel bed, effluent from the A2 aerobic bed, groundwater influent to the B1 lagoon, effluent from the B1 lagoon, effluent from the B2 lagoon, and effluent from the GAC unit. Groundwater well MI-146 provided water to the wetland and lagoon systems from June 17, 1996, to November 21, 1996, while groundwater well MI-051 provided water to both treatment systems subsequent to November 21, 1996.

With either well being used, TKN, NH_4-N, PO_4-P, NPOC, COD, and BOD-5 were significantly increased in the effluent of A1 (position 2) (Tables 6-4 and 6-5). This was due to the heavy and frequent fertilization of the pore water with MRS. However, effluent water quality leaving the paired aerobic cells (position 3) was restored to near influent quality, underscoring the aerobic gravel bed's ability to remove residual organic carbon and nutrients.

Relatively high mean NO_3-N concentrations contained in the influent groundwater were denitrified in the anaerobic gravel bed (A1) accordingly: 6.4 to 0.24 mg/liter, with well MI-146 and 28 to 2.6 mg/liter, with well MI-051. In contrast, mean nitrate levels leaving the aerobic cell increased to 4.4 and 6.2 mg/liter. This increase was due to the aerobic conversion of ammonium (NH_4) to nitrate. More NH_4 can be removed in the aerobic cell by further optimizing the size of gravel substrates and the frequency, depth, and duration of aeration.

Nitrate removal in the lagoon system (positions 4-6) was slight (6.3 to 4.4 mg/liter, with well MI-146 and 26 to 24 mg/liter, with well MI-051). Denitrification in the lagoon system was probably impaired due to high oxygen concentrations. Limited removal was probably accomplished by a combination of plant uptake of NO_3-N and denitrification at the sediment-water interface.

Table 6-4

Nutrient Concentrations and Water Quality for Well MI-146 From June 17, 1996, to November 21, 1996

		Concentration (mg/L) at Sample Point[1]																				
		Gravel-Based Wetland									Lagoon-Based Wetland									GAC System		
Sample Point		1			2			3			4			5			6			7		
Total Number of Samples Taken		11			11			11			11			11			11			11		
Analysis	Detection Limit	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.
TKN	0.05	0.63	0.20	11	17	12	11	1.6	1.6	11	0.62	0.18	11	0.74	0.38	11	0.69	0.26	11	2.2	2.2	11
NH_4-N	0.02	0.55	0.14	11	17	11	11	1.5	1.5	8	0.51	0.20	11	0.29	0.17	11	0.18	0.14	10	2.0	2.0	10
NO_3-N	0.04	6.4	0.7	11	0.24	0.24	11	4.4	2.8	11	6.3	0.8	11	5.2	1.1	11	4.4	1.6	11	4.0	1.6	11
PO_4-P	0.01	0.04	0.04	11	0.06	0.06	9	0.04	0.04	9	0.02	0.01	8	0.02	0.01	10	0.02	0.02	9	0.02	0.01	9
Cl	0.1	4.7	0.4	11	13	11	11	9.1	4.5	11	4.8	0.4	11	4.4	0.4	11	4.6	0.5	11	7.9	3.9	11
NPOC	0.9	3.2	1.4	10	54	54	9	3.4	1.7	9	2.5	1.1	9	3.4	1.6	10	5.8	4.5	9	5.0	4.9	9
TSS	2.0	BDL	NA	NA	37	37	11	13	13	6	BDL	NA	NA	15	15	2	6.9	6.9	3	16	16	4
COD	1.0	1.7	0.8	5	158	158	9	3.9	3.3	8	3.6	2.7	5	4.0	4.0	10	5.0	2.6	11	9.4	9.4	8
BOD-5	0.1	0.40	0.26	6	91	91	11	1.2	1.1	10	0.40	0.35	7	1.2	0.9	10	1.6	1.1	9	5.9	5.9	8

1) Avg. = Average.
SD = Standard deviation.
Num. = Number of observations in which the nutrient was above the detection limit.
BDL = All samples below detection limit.
NA = Not applicable.

Table 6-5

Nutrient Concentrations and Water Quality for Well MI-051 From November 21, 1996, to September 16, 1996

		Concentration (mg/L) at Sample Point[1]																				
		Gravel-Based Wetland									Lagoon-Based Wetland									GAC System		
Sample Point		1			2			3			4			5			6			7		
Total Number of Samples Taken		20			20			20			17			17			17			20		
Analysis	Detection Limit	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.
TKN	0.05	0.63	0.24	20	8.6	3.4	20	0.61	0.61	20	0.92	0.28	17	0.92	0.28	17	1.1	0.4	17	0.62	0.49	20
NH_4-N	0.02	0.46	0.14	20	7.3	3.0	20	0.34	0.34	13	0.45	0.11	17	0.31	0.08	15	0.23	0.11	14	0.32	0.32	15
NO_3-N	0.04	28	1	20	2.6	2.6	19	6.2	4.6	20	26	3	17	26	3	17	24	4	17	15	3	20
PO_4-P	0.01	0.02	0.01	11	0.07	0.06	20	0.01	0.01	17	0.02	0.01	5	0.02	0.01	5	0.01	0.01	9	0.02	0.02	12
Cl	0.1	2.6	0.4	20	5.3	2.4	20	5.5	2.0	20	2.6	0.3	17	2.6	0.3	17	2.8	0.6	17	4.1	1.4	20
NPOC	0.9	4.1	0.2	20	25	22	20	2.1	0.3	20	4.5	0.9	17	4.5	0.9	17	4.6	1.0	17	1.6	0.4	20
TSS	2.0	BDL	NA	NA	20	10	20	2.8	0.3	2	3.1	1.2	7	3.1	1.2	7	4.9	2.2	9	3.4	1.6	8
COD	1.0	7.1	3.8	15	63	63	20	5.4	3.9	7	5.5	3.5	4	8.5	4.4	17	9.3	5.0	18	3.2	2.3	13
BOD-5	0.1	0.46	0.46	13	42	39	20	0.89	0.67	18	0.60	0.60	9	1.4	1.4	16	1.6	1.2	16	1.2	0.7	20

1) Avg. = Average.
SD = Standard deviation.
Num. = Number of observations in which the nutrient was above the detection limit.
BDL = All samples below detection limit.
NA = Not applicable.

Anaerobic mineralization of proteins in the organic fertilizer (MRS) resulted in relatively high concentrations of NH_4-N in the effluent of A1, with averages ranging from 7.3 to 17 mg/liter (Tables 6-4 and 6-5). Removal of NH_4-N in the gravel-based aerobic system was excellent (averaging greater than 90% removal). Nitrification, the microbial oxidation of NH_4 to NO_3, requires approximately 4.5 mg/liter DO per mg NH_4 oxidized. The high specific surface area of the aerobic system, coupled with effective sequential reoxygenation of the fixed biofilm, resulted in NH_4-N removal rates equivalent to 1.8 to 4.1 g/m^2 per day for wells MI-146 and MI-051, respectfully.

Because there was no organic fertilization of the lagoon system, average concentrations of NH_4-N (mg/liter) were less than 1 mg/liter (Tables 6-4 and 6-5). NH_4-N dynamics in the lagoon system (positions 4-6, Table 6-5) indicated small but significant reductions in concentration. Reduction of NH_4-N in the lagoon system was probably due to a combination of processes including: 1) off-gassing of NH_4-N to the atmosphere due to high pH and diurnal convective mixing of the shallow water column, 2) uptake of NH_4-N by aquatic macrophytes and phytoplankton, 3) adsorption of NH_4-N to the soil sediments, and 4) limited nitrification.

TKN is a measure of reduced nitrogen forms. It is the sum of organic-N and ammonia-N, but does not contain NO_3-N. In the gravel-based system, TKN was highly correlated with NH_4-N because most of the organic nitrogen had been mineralized to NH_4-N. However, in the lagoon system, TKN tended to increase as NH_4-N decreased (Tables 6-4 and 6-5, positions 4-6). This can be explained on the basis of uptake of NH_4-N by planktonic organisms (phytoplankton, zooplankton, and bacteria), which would register as an increase in TKN (organic-N).

For both treatment systems, average ortho-phosphorus concentrations (PO_4-P) exiting the wetland were always less than 0.01 mg/liter (Table 6-5). These low levels were due in part to the low concentrations of PO_4-P in the groundwater influent (lagoon and gravel system) and the high microbial demand for supplemental phosphorus added as organic fertilizer (gravel system only). Furthermore, in aquatic systems, PO_4-P can be reduced to relatively low concentrations via adsorption to soil or gravel matrixes (not a sustainable process) and complexation with calcium carbonate and subsequent precipitation. Microbial phosphorus removal is also an important and sustainable pathway, especially in sequential aerobic/anaerobic systems. Uptake by aquatic macrophytes can remove limited amounts of

phosphorus on a seasonal basis; but, relative to other removal mechanisms, plant removal of P is limited by plant biomass, seasonality, low plant biomass P concentrations (0.1% on a dry matter basis), and biological recycling of P within the plant.

6.2 Intensive Sampling Test Results

6.2.1 Sediment Quality

To determine if explosives accumulated in the gravel and sediments of the wetlands, gravel and sediment samples were taken during bimonthly sampling events and analyzed for extractable explosives (Section 3.3). Data from the extractions are summarized in Tables 6-6 and 6-7 as an average of the demonstration program's seven bimonthly sampling events. The average is presented with the standard deviation and number of samples in which the analyte was detected above the detection limit. Positions 30 through 33 in the gravel-based wetlands and positions 34 through 37 are identified in Figure 3-2.

A higher concentration of nitrobodies (TNT, RDX, HMX, TNB, 2,6-DNT, and 2,4-DNT) and a greater number of samples above the detection limit were observed in gravel from the front end of the first gravel-based wetland (A1) closest to the influent header (position 30). The gravel nearest the influent is exposed to a higher concentration of nitrobodies before they are degraded by microbial action. So, we expect a higher concentration of nitrobodies to be sorbed onto the gravel surface closest to the influent.

Since TNT degradation is rapid in the gravel-based wetland (see Figure 6-30 in Section 6.2.4.1), TNT concentrations were very low on gravel in the second half of the anaerobic wetland (A1) and in the aerobic wetland (A2). The concentration of TNT by-products in the gravel also decreased down the length of the gravel-based wetlands.

The concentration and frequency of observing RDX on the gravel decreased down the length of the anaerobic gravel-based wetland (Table 6-6). The first samples in which RDX was observed in the aerobic gravel-based wetland (positions 32 and 33) were taken in December

Table 6-6
Explosives and Explosive By-Products in the Gravel of the Gravel-Based Wetlands
(June 17, 1996, to September 16, 1997)

		Concentration (ppb) at Sample Point[1]											
		Anaerobic Cell						Aerobic Cell					
Sample Point		30			31			32			33		
Total Number of Samples Taken		7			7			7			7		
Analysis	Detection Limit (ppb)[2]	Avg. (ppb)[2]	SD	Num.	Avg. (ppb)[2]	SD	Num.	Avg. (ppb)[2]	SD	Num.	Avg. (ppb)[2]	SD	Num.
Explosives													
2,4,6-Trinitrotoluene (TNT)	2	41	30	3	2	NA	1	BDL	NA	NA	BDL	NA	NA
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	2	136	136	6	30	24	5	80	80	4	98	92	3
Trinitrobenzene (TNB)	2	5	1	4	4	NA	1	6	1	2	8	1	2
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2	15	6	3	8	NA	1	10	NA	1	BDL	NA	NA
2,4-Dinitrotoluene (2,4-DNT)	2	11	NA	1	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
2,6-Dinitrotoluene (2,6-DNT)	2	4	NA	1	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
TNT By-Products													
2-Amino-4,6-dinitrotoluene (2A-DNT)	2	69	69	6	13	3	3	7	4	4	8	4	3
4-Amino-2,6-dinitrotoluene (4A-DNT)	2	37	37	5	8	5	2	5	3	2	7	NA	1
2,6-Diamino-4-nitrotoluene (2,6-DANT)	2	20	7	2	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
2,4-Diamino-6-nitrotoluene (2,4-DANT)	2	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Azoxy Compounds													
Tetranitro-2,2'-azoxytoluene (TN-2,2-AZT)	2	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Tetranitro-2',4-azoxytoluene (TN-2,4-AZT)	3	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Tetranitro-4,4'-azoxytoluene (TN-4,4-AZT)	3	32	NA	1	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
Dinitro-4,4'-azoxytoluene (DN-4,4-AZT)	4	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA	BDL	NA	NA
RDX By-Products													
Mononitroso RDX (m-RDX)	2	16	6	5	13	8	4	17	14	2	12	7	2
Trinitroso RDX (t-RDX)	2	25	11	6	21	14	5	21	19	4	20	13	3

1) Avg. = Average; BDL = All samples below detection limit; NA = Not applicable; Num. = Number of observations in which the explosive was above the detection limit; SD = Standard deviation.
2) Micrograms per kilogram on a dry weight basis.

Table 6-7
Explosives and Explosive By-Products in the Sediment of the Lagoon-Based Wetlands
(June 17, 1996, to September 16, 1997)

		Concentration (ppb) at Sample Point[1]											
		Cell B1						Cell B2					
Sample Point		30			31			32			33		
Total Number of Samples Taken		7			7			7			7		
Analysis	**Detection Limit (ppb)[2]**	**Avg. (ppb)[2]**	SD	Num.	**Avg. (ppb)[2]**	SD	Num.	**Avg. (ppb)[2]**	SD	Num.	**Avg. (ppb)[2]**	SD	Num.
Explosives													
2,4,6-Trinitrotoluene (TNT)	2	42	*NA*	*1*	30	*NA*	*1*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	20	1030	*856*	*6*	1370	*1010*	*6*	1080	*794*	*6*	1380	*930.5*	*5*
Trinitrobenzene (TNB)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	25	144	*61*	*5*	157	*59*	*5*	153	*77*	*5*	169	*80*	*4*
2,4-Dinitrotoluene (2,4-DNT)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
2,6-Dinitrotoluene (2,6-DNT)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	40	*NA*	*1*
TNT By-Products													
2-Amino-4,6-dinitrotoluene (2A-DNT)	25	137	*87*	*3*	167	*62*	*3*	53	*28*	*3*	61	*19*	*3*
4-Amino-2,6-dinitrotoluene (4A-DNT)	25	125	*95*	*4*	188	*57*	*3*	65	*26*	*3*	63	*31*	*4*
2,6-Diamino-4-nitrotoluene (2,6-DANT)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
2,4-Diamino-6-nitrotoluene (2,4-DANT)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Azoxy Compounds													
Tetranitro-2,2'-azoxytoluene (TN-2,2-AZT)	25	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Tetranitro-2',4-azoxytoluene (TN-2,4-AZT)	47	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Tetranitro-4,4'-azoxytoluene (TN-4,4-AZT)	40	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
Dinitro-4,4'-azoxytoluene (DN-4,4-AZT)	59	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*	BDL	*NA*	*NA*
RDX By-Products													
Mononitroso RDX (m-RDX)	25	132	*129*	*4*	123	*66*	*5*	82	*28*	*4*	65	*34*	*5*
Trinitroso RDX (t-RDX)	25	57	*44*	*2*	26	*NA*	*1*	BDL	*NA*	*NA*	BDL	*NA*	*NA*

1) Avg. = Average; BDL = All samples below detection limit; NA = Not applicable; Num. = Number of observations in which the explosive was above the detection limit; SD = Standard deviation.
2) Micrograms per kilogram on a dry weight basis.

1996 when higher RDX concentrations were observed in the water (Figure 6-2). The concentration of RDX by-products on the gravel was lower than the RDX concentration in the gravel and remained fairly constant down the length of the wetland.

Only one sample was observed to contain an azoxy compound above the detection limit (Table 6-6). This sample was in the front half of the first gravel-based wetland (A1). All other gravel samples collected had less than 2 to 4 ppb of azoxy compounds. The absence of azoxy compounds in the gravel indicated that it was unlikely that the degradation of TNT formed nitrosoamine groups that could couple to form toxic azoxy compounds.

The concentration of explosives in the lagoon sediments is presented in Table 6-7. As with the majority of explosives in the gravel from the gravel-based wetlands, TNT concentrations were higher in sediments closest to the influent. Compared to gravel, higher concentrations of TNT by-products were found in the sediments with highest concentrations in the latter half of the first lagoon cell (B1).

The concentrations of the nitramines, RDX and HMX, were also higher in the lagoon sediments than in the gravel from the gravel-based wetlands. The greater concentrations were probably due to higher concentrations of nitramines in the water due to the limited degradation of these compounds in the lagoons and to the higher sorptive capacity of soil versus gravel. The concentrations of nitramines in the sediments were fairly constant at all sampling locations.

RDX by-products, m-RDX and t-RDX, were found in the sediments of the lagoon-based wetlands. M-RDX was found at all sampling locations. T-RDX was only observed in sediment from the first lagoon wetland. The absence of RDX by-products in the water raised a question--whether or not RDX degradation occurred via reduction of the nitroso groups to form m-RDX and t-RDX. The presence of the degradation products in the sediment may mean that either the degradation products were formed in the water and quickly sorbed onto the sediment or that they were formed from the reduction of RDX that was sorbed onto the sediment and reduced via microbial processes. If the degradation occurred within the sediment, the predominance of m-RDX over t-RDX indicates the reducing potential of the sediment was not

that great since the formation of the by-product with one nitroso group (m-RDX) predominated over the formation of the by-product with three nitroso groups (t-RDX).

Using the data in Tables 6-6 and 6-7, calculations were made to determine the quantity of explosives found on the gravel and sediment compared to the total quantity of explosives fed into the wetland systems. These calculations were made assuming:

- The explosive concentrations found in the top gravel and sediment layers would be found throughout the four-foot-deep gravel matrix.

- The explosive concentrations found in the sediment would be found only in the first six inches of the sediment matrix.

Equal explosive concentrations were assumed to be found throughout the gravel matrix because flow occurred throughout the gravel bed. Equal explosive concentrations were assumed to be present in only 6 of the 12 inches of soil depth because most of the interaction between explosives and sediment would occur at the water-sediment interface. The gravel-based system contained approximately 992 metric tons (1,090 short tons) of gravel. The lagoon-based system contained approximately 86 metric tons (95 short tons) of soil. These assumptions may not have been entirely accurate, but their use allowed for a rough estimate of the potential accumulation of explosives via sorption onto wetland media.

Data for explosives in the gravel of the gravel-based wetland is shown in Figure 6-18. The data are presented in a cumulative bar chart where total percentage of explosives found in the gravel for a particular time period is a summation of all the smaller bars representing four sampling locations. The quantity of total nitrobodies (RDX, TNT, TNB, HMX, 2,4-DNT, and 2,6-DNT) and total explosives (nitrobodies plus measured by-products) on the gravel were always less than 1.3% of the mass of nitrobodies entering the wetlands. The percentage of nitrobodies on the gravel decreased to less than 0.1% of influent nitrobodies during the summer of 1997. This was probably an indication of greater degradation of nitrobodies during warmer summer months. The percent of RDX and TNT found in the gravel followed a pattern

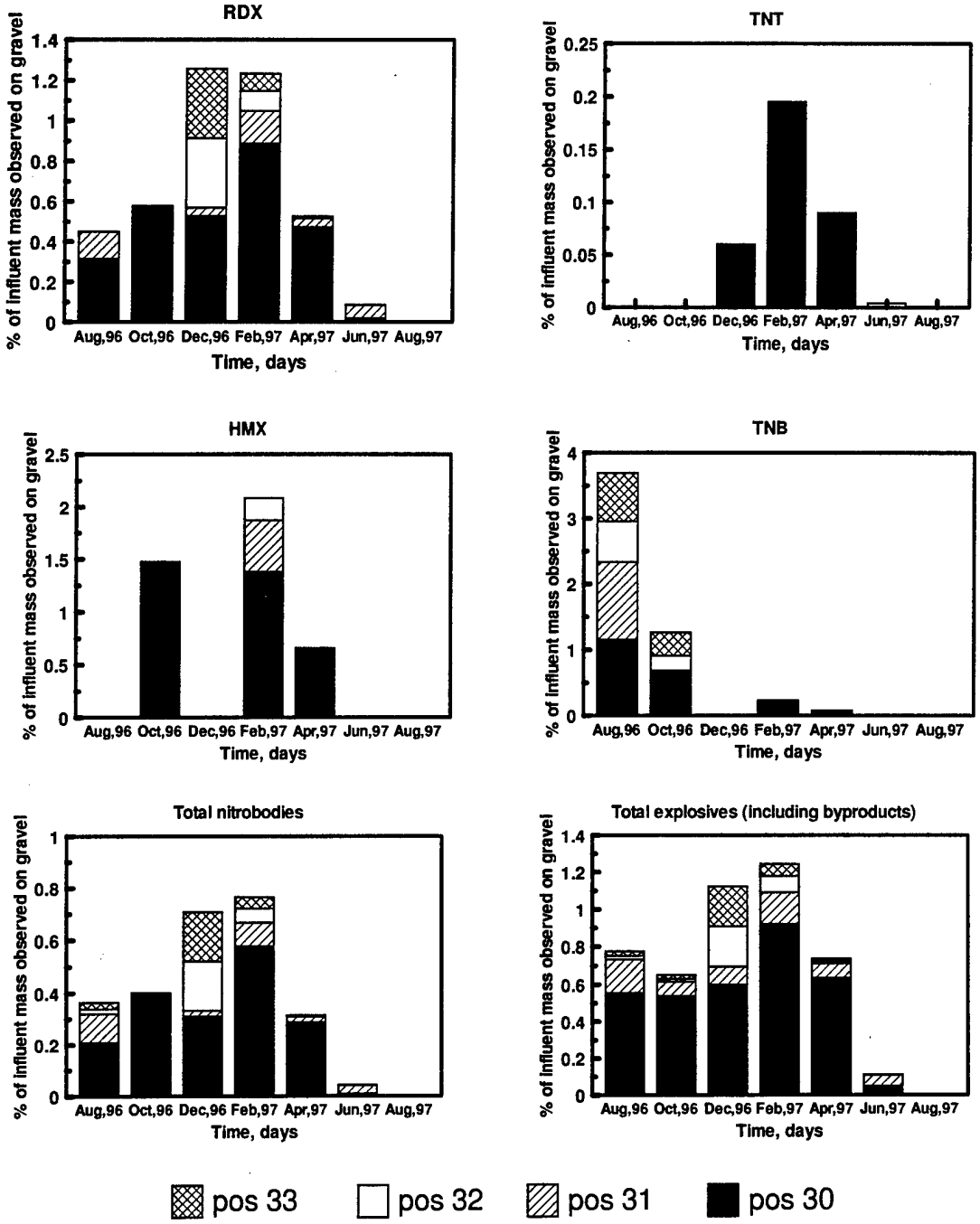


Figure 6-18

Percent of Explosive and Explosive By-Products Found in the Gravel of the Gravel-Based Wetlands From June 17, 1996, to September 16, 1997

where greater percentages of explosives were observed during colder winter months. The accumulation of the explosives on the gravel correlated well with the decreased degradation rate of RDX and TNT in the water phase during the colder winter months (Figure 6-2).

Like the gravel-based wetlands, the percent of nitrobodies and total explosives found in the sediment in the lagoon wetland cells were always less than 1.3% of the mass of nitrobodies entering the lagoon wetland (Figure 6-19). The mass of RDX, HMX, nitrobodies, and total explosives were all greatest during the winter. There was very limited removal of RDX and HMX in the water going through the lagoon wetlands (Figure 6-2). Any RDX and HMX that was sorbed onto the sediment was degraded more readily during the warmer temperatures experienced in the fall, spring, and summer as opposed to the winter.

For both the gravel- and lagoon-based wetlands, a very limited amount of explosives was observed to reside in the wetland's gravel or sediment. This observation indicated that the removal of explosives from the water was not due to sorption of explosives onto the substrate, but due to biological degradation of the explosives.

6.2.2 Toxicity Testing

Toxicity testing of influent and effluent water and wetland substrates (gravel and soil), was conducted to evaluate the relative toxicity of aqueous and substrate samples as a function of treatment, location within the treatment systems, and time (seasonal influences and/or wetland maturation influences). Toxicity tests were conducted according to EPA Methods. Details of methods, operating procedures, and QA used to conduct the toxicity tests are available in Appendices A and B.

The primary intent of the toxicity studies was to determine which system variables (treatments, locations within treatments, season, and/or wetland maturation time) resulted in significant changes in toxicity of the contaminated groundwater. It should be noted that the results of toxicity testing, as reported here, provided quantitative and relative measures of toxicity. However, in mixed-contaminant situations (e.g., TNT, RDX, HMX, and by-products) toxicity test results generally do not provide conclusive evidence as to which toxicant, or combination

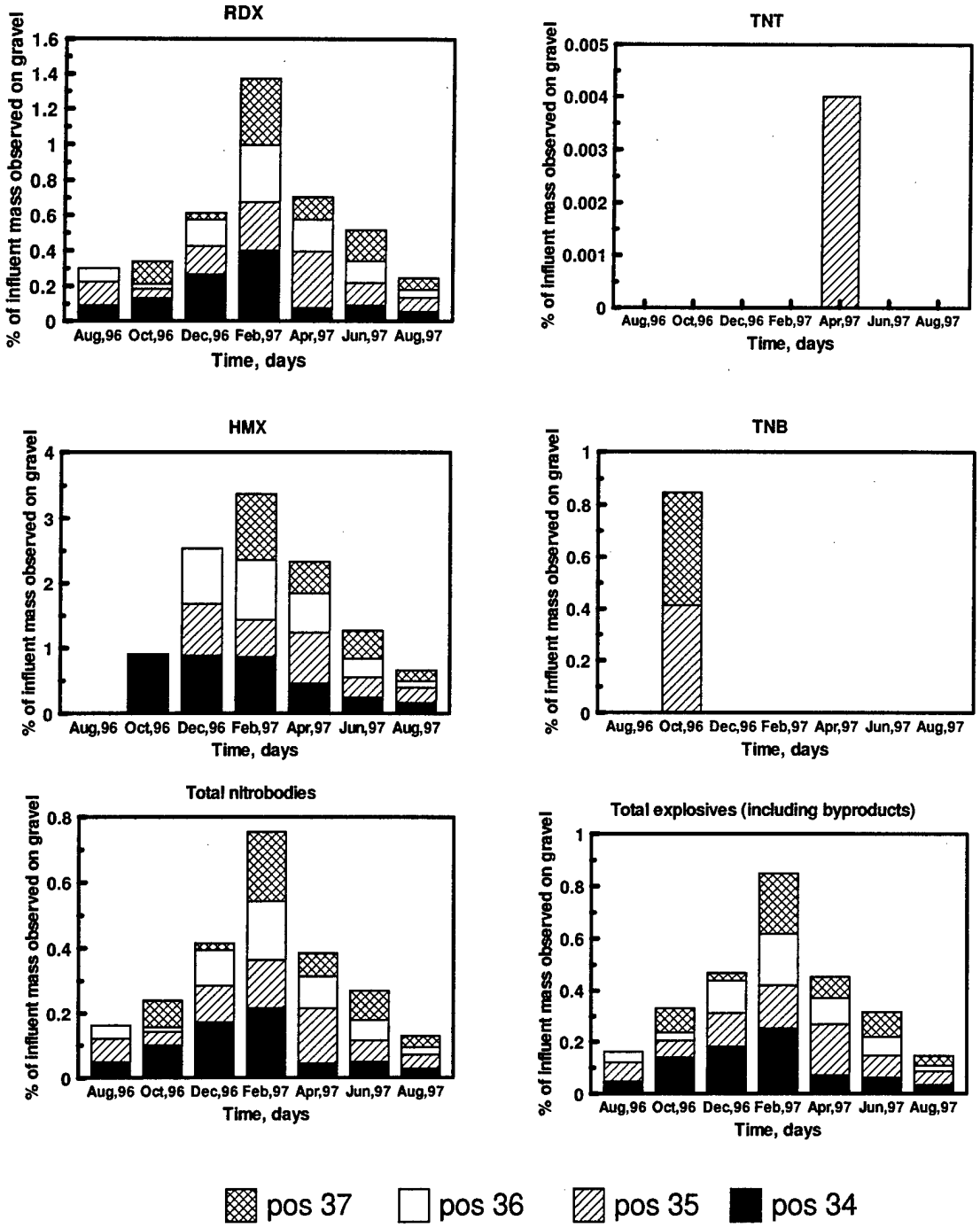


Figure 6-19

Percent of Explosive and Explosive By-Products Found in the Sediment of the Lagoon-Based Wetlands From June 17, 1996, to September 16, 1997

of toxicants, and/or their respective interactions, may have caused toxicity. However, it may be reasonable to infer which of the compounds may have caused toxicity based on supporting literature and careful analysis of the results.

6.2.2.1 Toxicity of Influent and Effluent Water Samples

Two independent toxicity tests involving fathead minnows, *Pimephales promelas*; and daphnid water fleas, *Ceriodaphnia dubia,* were conducted on three dates: January 15-22, 1997; February 26 to March 5, 1997; and August 6-13, 1997. The tests were used to evaluate toxicity of influent and effluent aqueous streams from the gravel- and lagoon-based treatment systems. Detailed reports of results for all toxicity tests are provided in Appendices B1, B2, and B3.

The results of the water-based toxicity tests revealed two important trends (Table 6-8).

1) Within toxicity testing dates, there were significant reductions in toxicity as a result of wetland treatment, both in the gravel- and lagoon-based systems.

2) There were significant improvements in toxicity reduction with time.

The second trend indicated that toxicity reduction was either influenced by seasonal changes (e.g., temperature), that wetland treatment processes were improving with time (maturation effects), or that both seasonal and time effects were impacting toxicity.

Referencing the appended toxicity reports (Appendix B), during the January 1997 toxicity tests, aqueous toxicity was manifested in the influent well water as expressed by complete fish mortality and reduced daphnid reproduction. However, measures of toxicity were reduced after passing through either of the treatment systems. Average toxicity was more greatly reduced after treatment in the gravel wetlands (fish survival averaged 16.5%; daphnid reproduction averaged 33.3 young) as compared to the lagoon system where fish survival averaged 0% and daphnid reproduction averaged 17.7 young. Under controlled conditions, fish survival averaged 98% and daphnid reproduction averaged 34.1 young.

Table 6-8

Summary of Water Toxicity Tests

Sample Location	Test Date		
	January 15-22, 1997	**February 26 - March 5, 1997**	**August 6-13, 1997**
Influent			
Survival, minnows (%)	0	NA[4]	0
Change in minnow weight (%)[2]	-100[1]	NA[4]	-100[1]
IC_{25} (minnows)[3]	19.6	NA[4]	NA[4]
Decrease in daphnid reproduction (%)[2]	-100[1]	NA[4]	-100
IC_{25} daphnid reproduction[3]	13.6	NA[4]	NA[4]
Lagoon Effluent			
Survival, minnows (%)	0	98	100
Change in minnow weight (%)[2]	-100[1]	0	+18
IC_{25} (minnows)[3]	NA[4]	>100	>100
Change in daphnid reproduction (%)[2]	- 48	-18	-8
IC_{25} daphnid reproduction[3]	NA[4]	>100	>100
Gravel Effluent			
Survival, minnows (%)	16.5	73	99
Change in minnow weight (%)[2]	-31	-12	+10
IC_{25} (minnows)[3]	NA[4]	>100	>100
Change in daphnid reproduction (%)[2]	-5	NA[4]	-13
IC_{25} daphnid reproduction[3]	NA[4]	>100	>100

1) 100% mortality due to extreme toxicity.

2) Change in minnow weight and daphnid reproduction expressed as a % of control values.

3) IC_{25} represents the % of influent water added to non-toxic (control) water to elicit a 25% reduction in weight of minnows and/or a 25% reduction in reproduction of daphnids. IC_{25}, which have values >100, indicates no significant measure of toxicity.

4) NA = Not applicable.

During the second toxicity test (February 26 to March 5, 1997), effluent showed no toxicity as evidenced by IC_{25} values greater than 100 for both parameters (i.e., a change in minnow weight or change in daphnid reproduction). It should also be noted that there was a significant reduction in toxicity during this test as compared to the January results (Table 6-8).

In the third toxicity test (August 6-13, 1997), influent well water was still highly toxic as demonstrated by 100% mortality of fathead minnows and complete lack of reproduction by daphnid test population. In contrast, the survival rate in the effluent of both the gravel- and lagoon-based systems was substantially better. Survival of fathead minnows in the lagoon-based system's effluent averaged 100%. Fathead minnow survival in a gravel-based system's effluent was 99%. Although average daphnid reproduction was reduced marginally in the gravel- and lagoon-based systems (13% and 8%, respectively), the reductions were not statistically significant ($P<0.05$) when referenced to the control.

In summary, a cursory examination of water toxicity was conducted during the demonstration. The results of this examination suggest that:

- The toxicity of the influent water remained high during the course of the demonstration.
- The gravel- and lagoon-based systems were able to reduce effluent toxicity to acceptable levels.
- Water toxicity of both the lagoon- and gravel-based systems' effluent decreased with time.

Due to limited scope of the toxicity tests, these conclusions should be considered preliminary in nature.

6.2.2.2 Toxicity of Wetland Gravel and Lagoon Sediments

Two independent toxicity tests involving the amphipod (scud, side-swimmer), *Hyalella azteca,* and the midge larvae, *Chironomus tentans,* were conducted on two dates: March 11-21, 1997, and August 15-25, 1997, to evaluate toxicity of: 1) gravel substrate collected from the

gravel-based wetlands and 2) soil-based sediments collected from the lagoon-based treatment system. Detailed reports describing these toxicity tests, including methods, results, and conclusions, are provided in Appendix B-4.

Gravel and Sediments: Toxicity Results for March 11-21, 1997

During the winter testing period, toxicity, as measured by reduced survival of amphipods over a 10-day test period, was demonstrated in gravel samples from cell positions 16 and 17 and in lagoon sediments from cell positions 24 and 28 (Table 6-9). It is noteworthy that in the gravel-based system, gravel samples from cell locations proximate to the influent well water experienced significantly higher mortality than more distant positions (compare data from cells 16 through 21 in Table 6-9). In contrast, sediment from location 28 (more distant from influent) exhibited higher levels of toxicity than location 24 (proximate to influent well water). Toxicity to the midge was also apparent in lagoon sediments from both cells. The midge test was not administered to the gravel cells. Although toxicity adversely affected amphipod and midge survival in several locations, there were no significant reductions in growth.

Gravel and Sediments: Toxicity Results for August 15-25, 1997

During the summer testing period, toxicity results for amphipods revealed no significant toxicity in gravel cell positions 16-20, but significant toxicity (both survival and growth) in gravel cell 21 and sediment positions 24 and 28 (Table 6-10). Detectable concentrations of TNT by-products, RDX, and HMX were found in both sediment samples. However, concentrations of these compounds in gravel samples from cell position 21 were all below detection limits (see supporting tables, Appendix B4). Furthermore, unionized ammonia concentrations in overlying water samples in cell 21 were below potentially toxic concentrations (<200 ug/L). Possible causative agents could not be identified in the gravel samples.

Table 6-9

Survival and Growth Data for Amphipods and Midges Cultured in Gravel and Sediment Samples During March 11-21, 1997[1]

Treatment/Location	Amphipod Data		Midge Larva Data	
	Mean Survival (%)	Mean Growth (mg dry weight)	Mean Survival (%)	Mean Growth (mg dry weight)
Formulated sediment	75.0	0.035	88.8	1.53
Gravel control	86.3	0.029	NA[3]	NA[3]
Gravel 16	23.8[2]	0.071	NA[3]	NA[3]
Gravel 17	73.4[2]	0.064	NA[3]	NA[3]
Gravel 18	92.5	0.098	NA[3]	NA[3]
Gravel 19	97.5	0.070	NA[3]	NA[3]
Gravel 20	80.0	0.069	NA[3]	NA[3]
Gravel 21	78.8	0.056	NA[3]	NA[3]
Sediment 24	70.0[2]	0.048	71.3[2]	0.70
Sediment 28	28.8[2]	0.045	40.0[2]	0.58

1) Each value based on average of eight replicates. The gravel and sediment was obtained from the gravel- and lagoon-based treatment systems.

2) Statistically significant reduction compared to gravel control (gravel treatments) and formulated sediment (sediment treatments), respectively. Vertical comparisons only.

3) NA = Not applicable.

As part of the amphipod toxicity protocol, nutrients may or may not be provided to test organisms, depending upon the water's ammonia concentration. Based on the known high aerobic metabolism of the bacteria in the aerobic cell's gravel matrix (positions 20 and 21) and the extremely high competition for nutrients and organic matter, we hypothesize that the poor survival and reduced growth of amphipods in these particular gravel samples may have been due to starvation.

Conversely, it is also possible that an unidentified, but highly toxic, aerobic metabolite could have been formed from the breakdown of primary explosives and their respective by-products. Ten-day exposure of midge larvae to sediments from positions 24 and 28 resulted in significant reductions in survival. Growth comparisons, although reduced by as much as 50% (Table 6-10), were not statistically analyzed since survival was significantly reduced.

6.2.2.3 Plant Biomass: Emergent Species in the Gravel-Based System

In August 1997, four plant species were subsampled in triplicate to evaluate both vegetative and root biomass as a function of species location within each gravel cell (proximate to influent vs. distant to influent) and between anaerobic and aerobic gravel cells (A1 vs. A2). Fresh biomass subsamples were oven-dried to determine dry matter content per unit of growing area.

Table 6-11 summarizes plant biomass data (shoots and roots) with respect to average standing crop and variation in standing crop within a species and location. Average standing crop data (biomass, dry matter basis) among species varied ten-fold: parrotfeather biomass (shoots plus roots), 319 g/m^2; wool grass, 3376 g/m^2; sweetflag, 921 g/m^2; and canary grass, 2732 g/m^2. There was also considerable variation in species biomass with respect to location. The data indicates strong species and location interactions (Figure 6-20). For example, wool grass biomass (g/m^2) was exceptionally high in the anaerobic cell, but significantly reduced in the aerobic cell, while canary grass biomass was high in the aerobic cell, but reduced by more than 50% in the anaerobic cell.

Table 6-10

Survival and Growth Data for Amphipods and Midges Cultured in Gravel and Sediment Samples During August 15-25, 1997[1]

Treatment/Location	Amphipod Data		Midge Larva Data	
	Mean Survival (%)	Mean Growth (mg dry weight)	Mean Survival (%)	Mean Growth (mg dry weight)
Formulated sediment	85.0	0.051	81.3	1.17
Gravel control	92.5	0.947	NA[3]	NA[3]
Gravel 16	86.4	0.110	NA[3]	NA[3]
Gravel 17	96.3	0.094	NA[3]	NA[3]
Gravel 18	90.0	0.069	NA[3]	NA[3]
Gravel 19	91.3	0.066	NA[3]	NA[3]
Gravel 20	85.0	0.062	NA[3]	NA[3]
Gravel 21	61.3[2]	0.041[2]	NA[3]	NA[3]
Sediment 24	60.0[2]	0.032[2]	63.8[2]	0.61
Sediment 28	63.8[2]	0.023[2]	65.0[2]	0.74

1) Each value based on average of eight replicates. The gravel and sediment were obtained from the gravel- and lagoon-based treatment systems.

2) Statistically significant reduction compared to gravel control (gravel treatments) and formulated sediment (sediment treatments), respectively. Vertical comparisons only.

3) NA = Not applicable.

Table 6-11

Average Biomass (g/m^2) and Respective Measures of Variation as a Function of Species, Location, and Tissue Type

SPECIES	LOCATION	SHOOTS			ROOTS		
		g/m^2	Standard Deviation	cv (%)	g/m^2	Standard Deviation	cv (%)
Parrotfeather	A1 influent half	168.6	150.9	90	96.9	104.3	108
	A1 effluent half	246.3	309.1	125	156.8	218.5	139
	A2	170.3	184.9	109	118.2	113.7	96
Wool grass	A1 influent half	3483.9	659.6	19	1128.2	242.2	21
	A1 effluent half	2878.3	562.4	20	1355.5	984.6	73
	A2	433.2	79.6	18	849.2	361.2	43
Sweetflag	A1 influent half	636.2	243.2	38	227.8	73.5	32
	A1 effluent half	794.1	373.3	47	364.2	58.0	16
	A2	409.1	190.9	47	331.0	163.3	49
Canary grass	A1 influent half	1023.1	96.7	9	1402.9	625.9	45
	A1 effluent half	559.2	144.6	26	816.3	331.8	41
	A2	2816.5	1346.9	48	1579.6	878.8	56

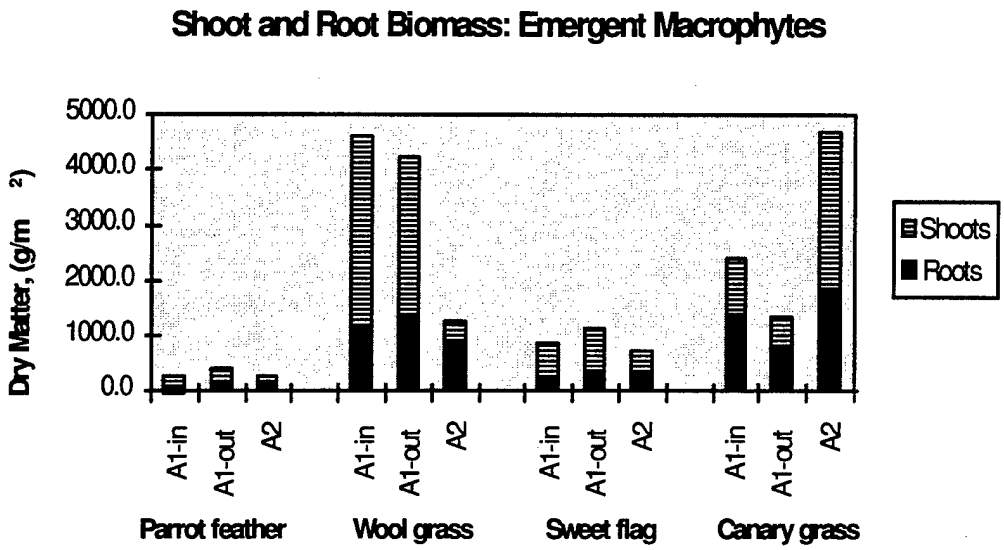


Figure 6-20

Standing Crop Biomass in Gravel-Based Wetlands as a Function of Species and Location

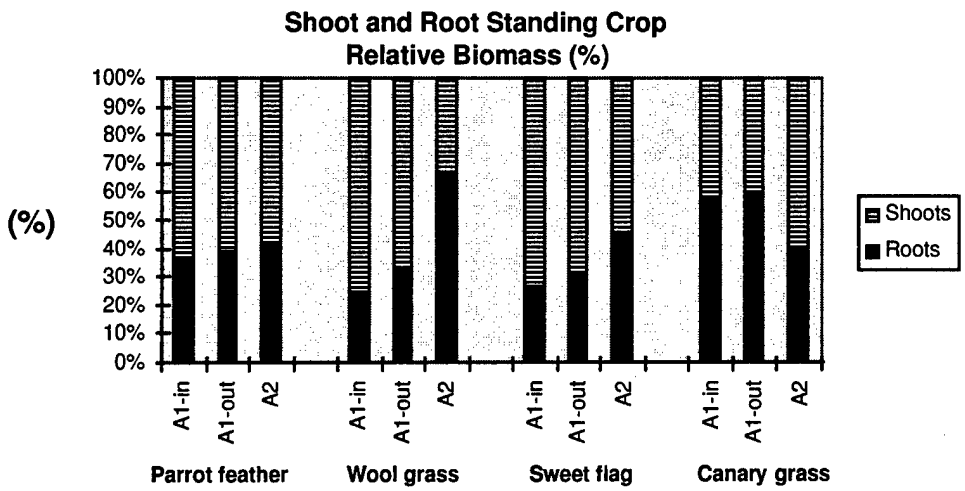


Figure 6-21

Relative Biomass of Shoots and Roots in Gravel-Based Wetlands as a Function of Species and Location

Figure 6-21 reveals the relative percent of biomass contributed by shoot tissue and root tissue as a function of species and location. With the exception of canary grass, there was a tendency for the root biomass, as a percent of the total biomass, to increase from the A1 inlet to the A2 outlet. This may have been influenced by nutrient dynamics since diminished nutrient concentrations may promote greater root biomass. Oxygen dynamics in the root zone may also have been a factor since canary grass is a facultative wetland plant and may prefer an aerated root zone. Similar results, strong species and environment interactions, were evident in preliminary treatability studies.[Ref. 9,10]

Although these species of emergent macrophytes were selected according to their ability to remediate explosive compounds, they also provide several other important functions in a wetland environment. During the growing season, the plants actively uptake nutrients and transpire water, thereby, helping to purify water. The root biomass provides considerable surface area for plant/microbial interactions. These symbiotic relationships facilitate oxidation/reduction reactions, nutrient uptake, and detoxification of metals, explosives, and other toxic compounds.

Dead plant tissues decompose providing nutrients and a carbon substrate for the growth of bacteria and new plants. The contribution of organic carbon by plant biomass can be considerable (root and shoot tissues contain 48%-50% carbon on a dry matter basis). Rapid mineralization of organic matter by microbes can contribute to oxygen depletion, thereby, helping to maintain low redox conditions (anaerobic gravel cell) required for microbial reduction of explosives compounds.

Over the course of this demonstration, a carbon supplement (MRS) was added on an intermittent basis to maintain low redox conditions. As the wetland matures, the contribution of organic matter by plant residues is expected to increase to a level adequate for sustaining redox conditions. This will diminish, if not eliminate, the need for exogenous carbon supplements.

6.2.2.4 Plant Biomass: Submergent Species in the Lagoon-Based System

Due to extreme depredation of submergent plants by grazing tadpoles during the spring of 1996, it was necessary to stock a predatory fish, largemouth bass (*Micropterus salmoides*), into the lagoons. The bass were originally stocked as small fingerlings, but these had little impact on the tadpoles. Subsequently, larger bass were introduced. The larger bass preyed on the tadpoles and significantly reduced their population. Subsequent replanting of the submergent plant species was completed in September 1996. During November 1996, it became necessary to change to a water source (well) which had significantly higher explosive concentrations (see Section 5.2.4). Plant establishment and plant productivity were impaired due to seasonal influences (poor growth during the winter). Furthermore, some TNT was transformed to TNB via sunlight activation and the high concentrations of TNB imparted a deep-red color to the water. Due to the red coloration, sunlight penetration of the water was attenuated and the low light intensity possibly reduced photosynthesis and plant growth.

6.2.3 Hydraulic Tracer Analysis

The mixing characteristics of both the gravel- and lagoon-based wetlands were determined using a bromide (Br) tracer. To conduct the test, sodium bromide was added to the influent of the individual cells at the quantities indicated in Table 6-12. The tracer flowed through the wetlands while water samples were collected from the effluent stream or from internal sampling wells within the wetlands (see Figures 3-3 and 3-4 in Section 3.5.3). The samples were used to determine the concentration of tracer leaving the wetlands.

Tracer tests for cell A1 were conducted in January, May, and August of 1997. During the January test, the pattern of bromide release from the gravel-based cell (A1) was consistent, on days 0 to 14, with that for a combination of plug-flow and complete-mix (Figure 6-22). The vertical bar in Figure 6-22 is one retention time at the flow rates monitored during the tracer tests (Table 6-12). Since gravel-based wetlands typically exhibit combined mixing characteristics,[Ref. 11] this finding was not surprising. However, the continued release of bromide after 14 days, at an approximate concentration of 0.7 mg/liter, was unexpected. Such behavior is not characteristic of gravel-based wetlands. The continued release of bromide

Table 6-12

Summary of Flow Data for Bromide Tracer Studies

Test Date		January 1997[1]		May 1997[2]		August 1997[3]	
Cell	Water Volume (m^3)	Flow (gpm)	Retention Time (days)	Flow (gpm)	Retention Time (days)	Flow (gpm)	Retention Time (days)
A1	205	4.6±0.6	8.2	4.8±0.1	7.8	4.9±0.2	7.7
A2	43	4.7±0.6	1.7	4.8±0.2	1.6	NS[4]	NS[4]
B1	137	NS[4]	NS[4]	4.9±0.2	5.1	NS	NS
B2	137	4.3±0.5	5.8	4.7±0.2	5.3	NS	NS

1) Measured with bucket and stop watch, 1/14/97 to 2/14/97, n=9
2) Measured with flow meters, 4/29/97 to 5/20/97, n=35
3) Measured with flow meters, 8/20/97 to 9/16/97, n=19
4) NS = Not sampled.

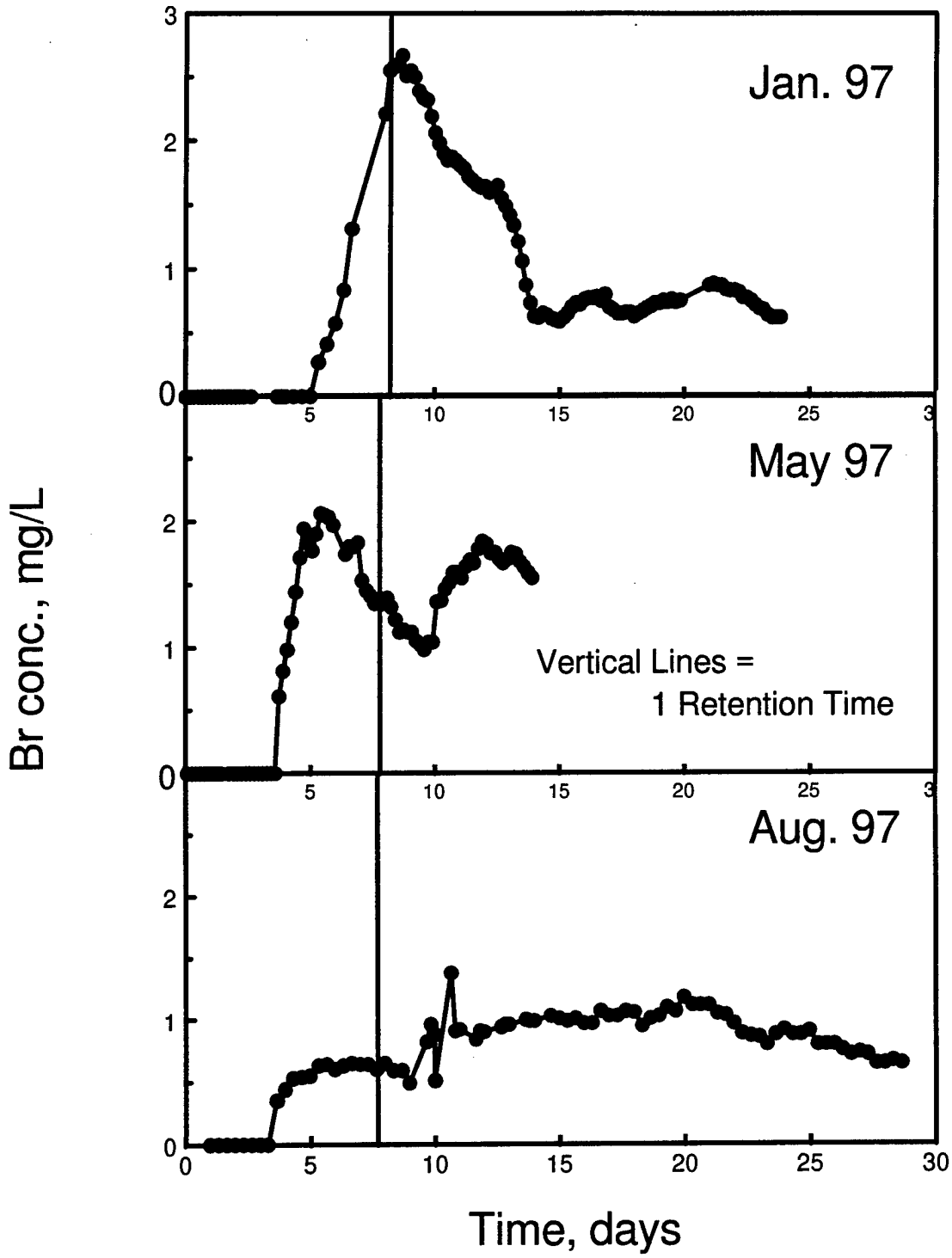


Figure 6-22

Tracer Study Results for Gravel-Based Cell A1

indicates there may have been some sorption of bromide onto the gravel which was slowly released. Bromide is supposed to be a nonconservative tracer–meaning the bromide does not interact with the media through which transport is being studied. It is unclear why the bromide was slowly released in this system and not released in other gravel-based wetland systems. The gravel-based wetland used in this demonstration was 4 feet deep and the system is deeper than most gravel-based wetlands. The greater gravel depth may have caused some physical retention of bromide, at deeper depths, which was slowly released with time.

The pattern of bromide movement through cell A1 was considerably different during the tests conducted in May and August 1997 (Figure 6-22). In May 1997, there were two bromide peaks which indicate some bromide was either physically or chemically being retained in the wetland. This result was similar to the slow release of bromide after 14 days during the January 1997 test, but, more pronounced with the formation of a second peak. The abrupt increase in bromide concentration leaving A1 observed in January and May 1997 was not observed in August 1997. Rather, the concentration increased to about 0.6 mg/liter then gradually increased to 1.1 mg/liter before declining. The August 1997 bromide data was still characteristic of a plug-flow and complete-mix combination occurring. The much broader bromide peak in August 1997 indicated much more mixing was occurring than in the January 1997 test. This may have been due to a greater accumulation of solids in the interstitial spaces of the gravel. The solids caused some short-circuiting by releasing bromide at a time period less than what occurred in January, but probably caused more mixing resulting in a much broader bromide peak during release. The broader August peak may also have been caused by greater convective diurnal mixing since more mixing would be expected during the summer months.

Although a portion of the bromide (water) moved through cell A1 quickly, the bulk of the bromide was retained within the cell for longer than one retention time (Figure 6-22). This provided the bulk of the contaminated groundwater with additional time to interact with the microbial populations in the gravel cell.

The bromide tracer tests for cell A2 were conducted in January and May of 1997. The pattern of bromide release from cell A2 was much different than that for cell A1 (Figure 6-23). In cell A2, the bromide concentration peaked much earlier than the retention time. Since A2 is an

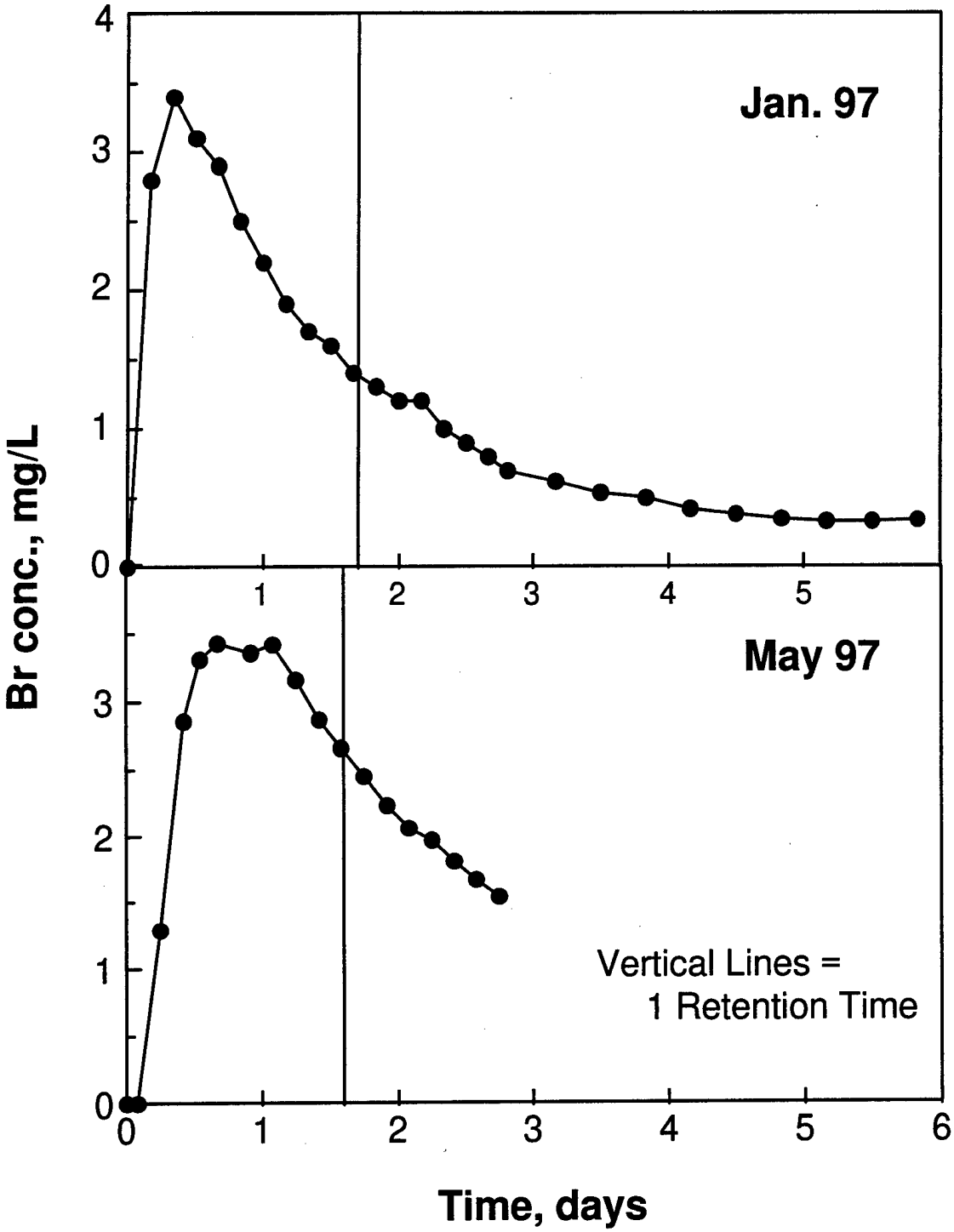


Figure 6-23

Tracer Study Results for Gravel-Based Cell A2

aerobic wetland, the water is well mixed and the hydraulic characteristic of this wetland approximates that of a complete-mix reactor.

Bromide tracer tests for cell B1 were conducted during May 1997 and for cell B2 during January and May 1997 (Figures 6-24 and 6-25). The retention times, shown as the vertical bars, were approximately 5.5 days for both cells. The shape of the lagoon's tracer curves are similar to those found in other lagoon-based systems[Ref.11] and the tracer curve's shape suggests the lagoons are well-mixed reactors that closely resemble complete-mix reactors. However, the bromide concentrations peaked much earlier than the retention time. In contrast, most 12-inch-deep lagoon-based wetlands have bromide peaks located closer to the retention time. This occurs because the water's movement through the lagoon is typically retarded by a dense thicket of emergent plant species.[Ref.11] During the demonstration, the lagoon's submergent plants did not thrive and, consequently, did not provide the required amount of resistance. Therefore, it can be concluded that a hydraulic disadvantage of a lagoon wetland is subject to a form of short-circuiting if the plants do not thrive. To minimize the potential for this kind of short-circuiting, and the possible release of untreated groundwater, it may be necessary to install several smaller lagoon cells in series as opposed to two larger ones.

Short-circuiting tests were conducted in cell A1 during May and August 1997. These tests were conducted to evaluate how evenly distributed the bromide, and thus water, was as it moved through the gravel-based wetlands. During the short-circuiting test, water was sampled in five interior wells placed along the width of the wetland close to the effluent header. Data taken from the five end wells in the May tracer test indicated a disparity in the movement of water; with bromide moving more quickly through the wetland section corresponding to well 38 (Figure 6-26). Figure 3-3 shows the location of these wells. The general order of bromide movement through the wetland was well 38 > well 39 = well 42 > well 40 = well 41. A curious aspect of these results was that bromide moved more quickly through the section with dense plant growth (38) and more slowly through the section with sparse growth (42). The majority of plant roots only grew to a depth of 6 inches in the gravel bed. With the wetland having a 4-foot depth, some other factor probably produced the disparate data. One possibility considered was that the bromide might have been unevenly distributed by the inlet header. This could have occurred, for example, if portions of the header were blocked with

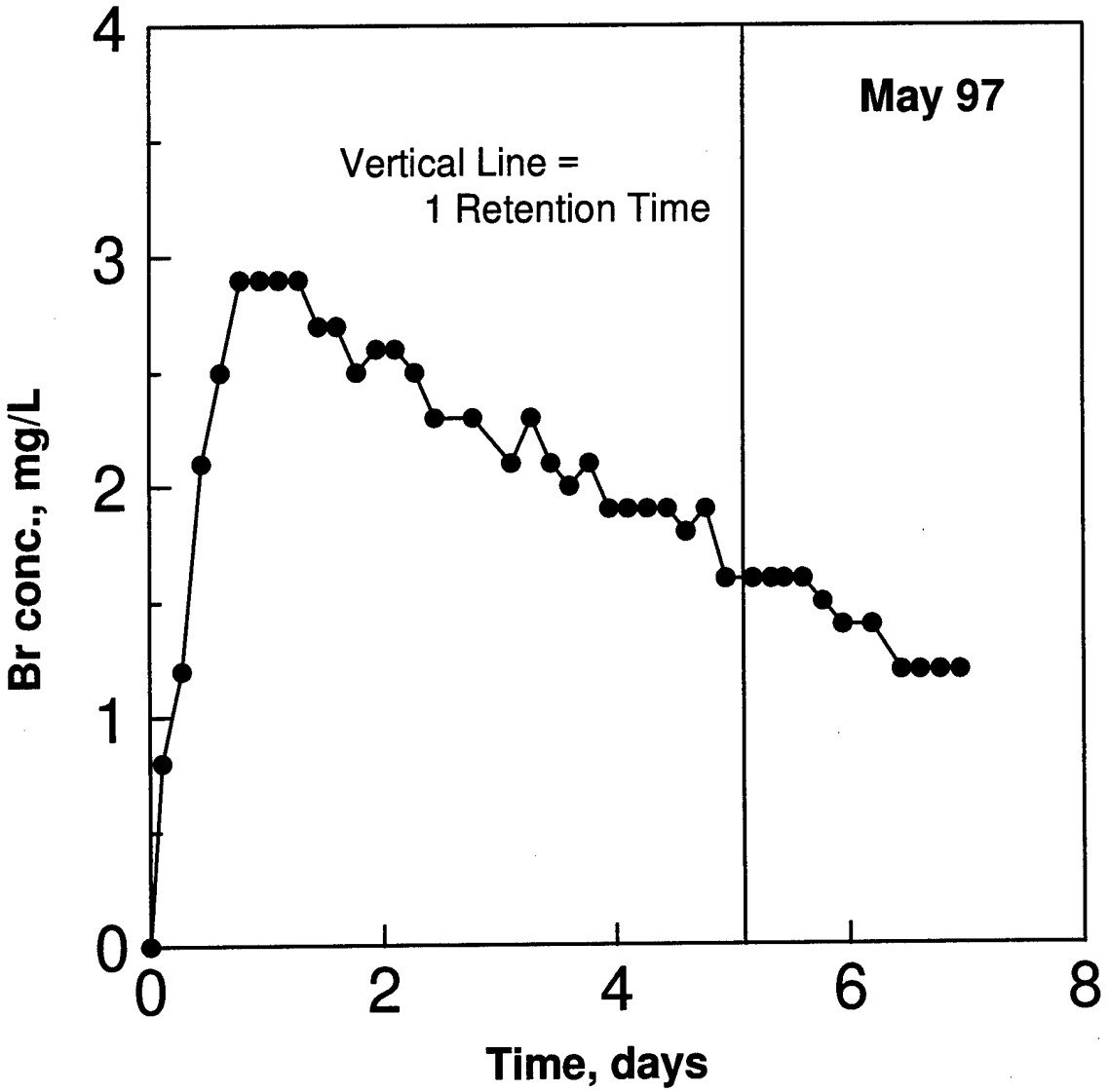


Figure 6-24

Tracer Study Results for Lagoon-Based Cell B1

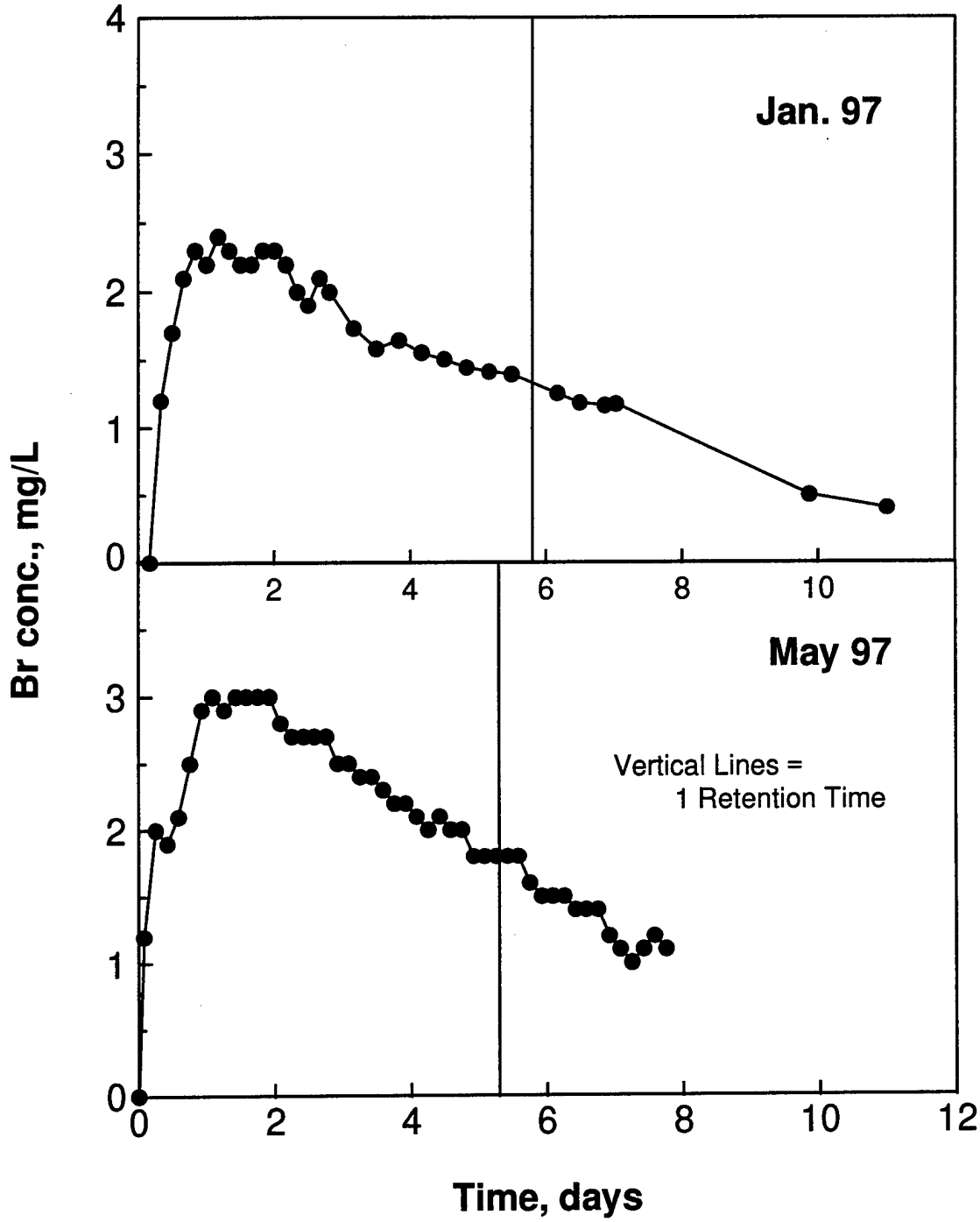


Figure 6-25

Tracer Study Results for Lagoon-Based Cell B2

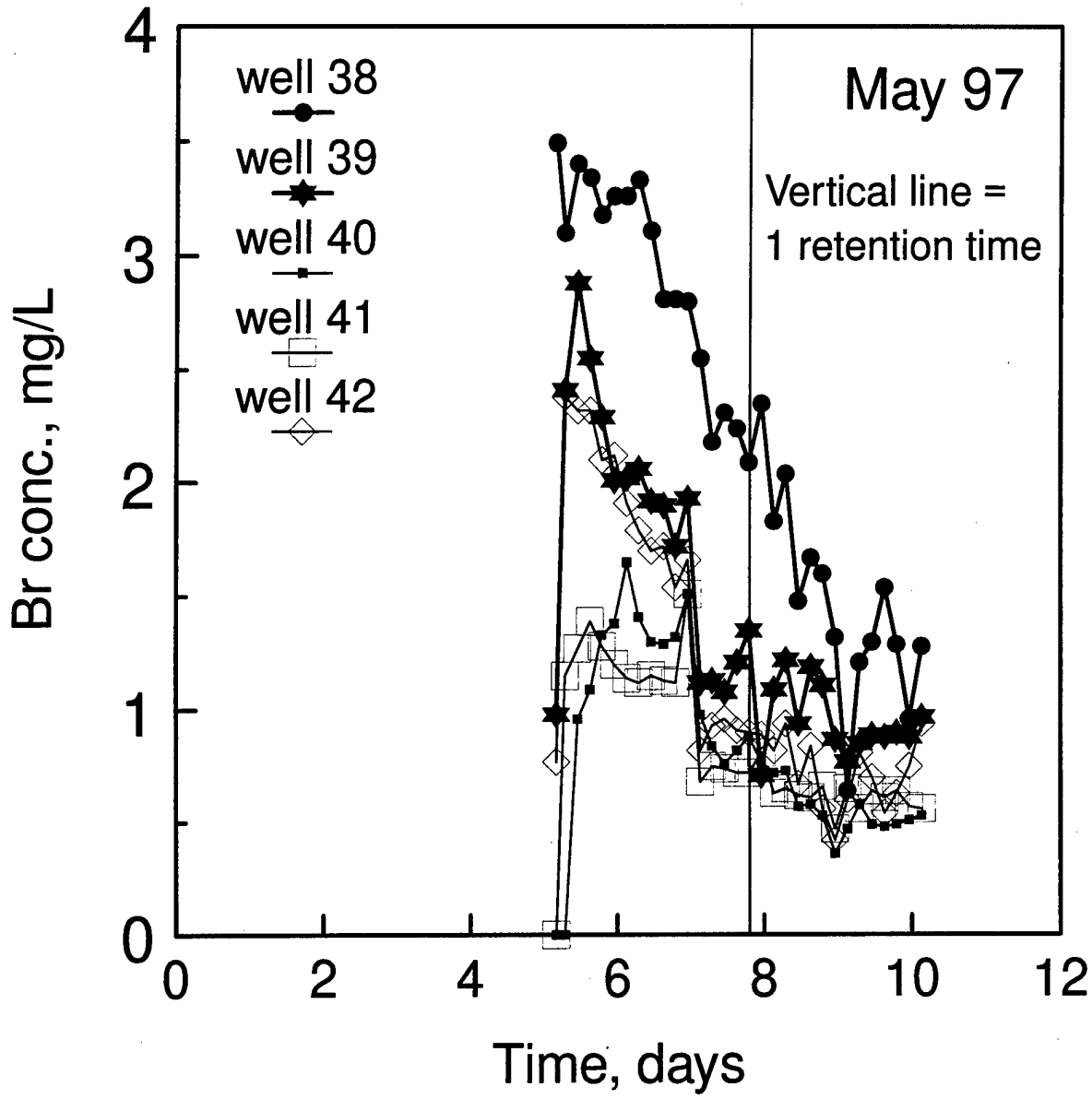


Figure 6-26

May 1997 Short-Circuit Test Results for the Gravel-Based Wetland (Cell A1)

roots. To eliminate this possibility, the old header was replaced with a new header prior to conducting the August 1997 short-circuiting test. The new header was of a different design and is described in Section 5.2.6. However, even after replacing the header, discrepancies were observed (Figure 6-27). During the August 1997 test, the bromide reached all of the wells at about the same time. However, bromide was continually released at higher concentrations in the sampling wells nearest the sides of the wetland (sampling wells 38 and 42).

During the August 1997 short-circuiting test, bromide movement through the cells was also monitored by sampling water from wells at sampling points 53-64 (Figure 3-4). This monitoring was conducted to better understand the gravel cell's mixing characteristics. Water samples were collected at three depths within each well. The data from these wells are presented in Figure 6-28, along with a vertical line showing the theoretical amount of time needed to reach the wells (i.e., the retention time). The most striking flow characteristics noted in Figure 6-28 were the high concentrations observed in the bottom of wells 53 to 55 and the slow movement of bromide through the middle and bottom of wells 58, 59, and 64. The slow water movement suggests that plant roots were not interfering with water movement. Consequently, the observed flow characteristics are most likely the result of local channeling within the heterogeneous gravel matrix. A less significant observation was that, after six days, the bromide concentrations in the wells nearest the discharge point (wells 62 to 64) were very close to one another. Similar results were obtained at sampling point 39, 40, and 41 during the May and August tests (Figures 6-26 and 6-27). This suggests the behavior observed at sampling points 53-64 corresponds with that for the center of cell A1, but may not explain the behavior observed at the outer edges of the wetland, as illustrated by the behavior of bromide at sampling points 38 and 42 (Figures 6-26 and 6-27).

Water was also sampled in end wells placed at the end of B2 during the May short-circuiting test. Bromide concentrations in water collected from these wells are presented in Figure 6-29. Unlike data collected in the end wells in A1 (Figure 6-26), the bromide concentrations were very similar in each well. This was due to lagoons having very limited plug-flow characteristics and strong complete-mix hydraulics (Figures 6-22 and 6-24) where the open body of water gets evenly mixed due to temperature differences by depth and wind velocity at the surface.

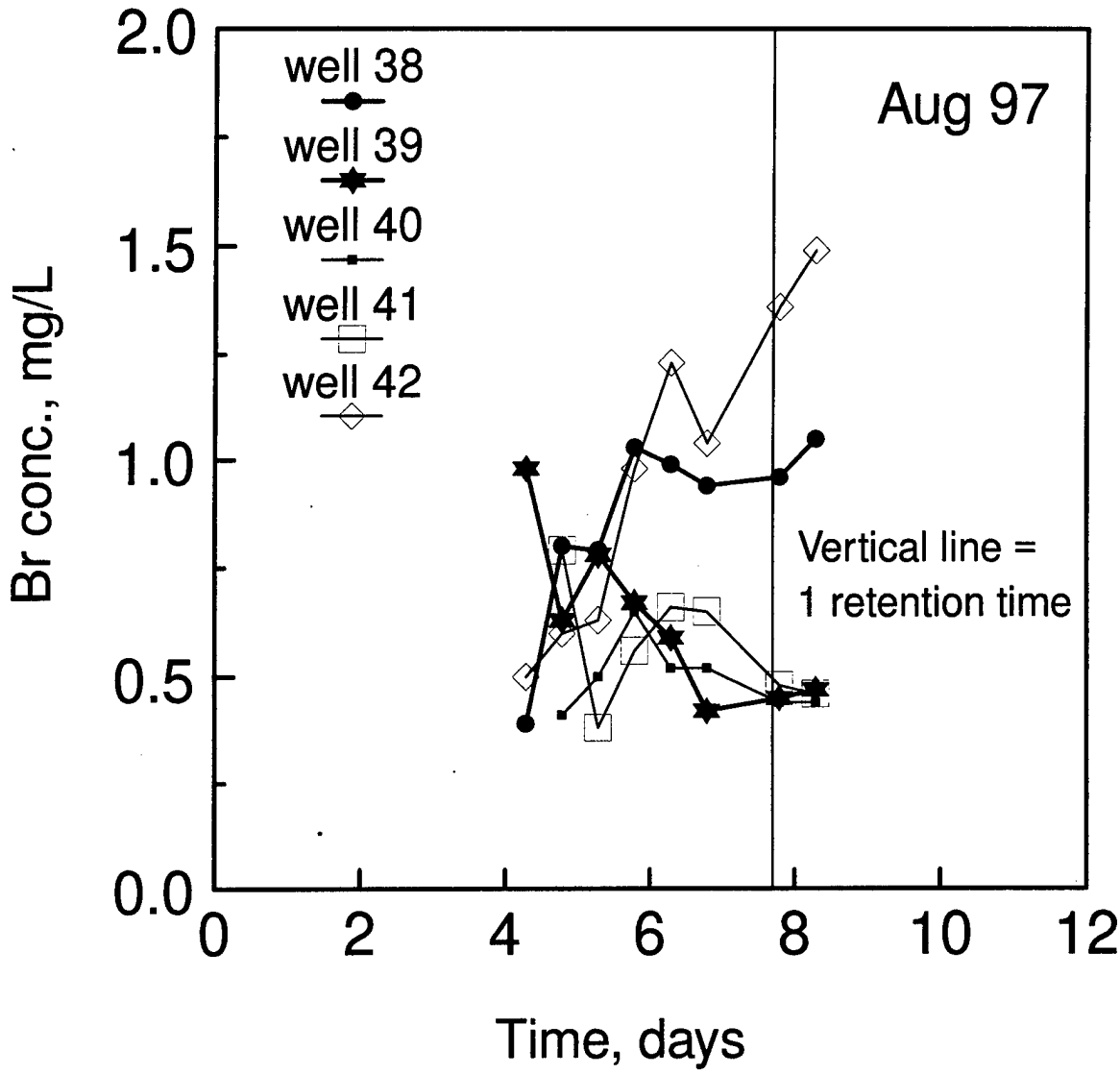
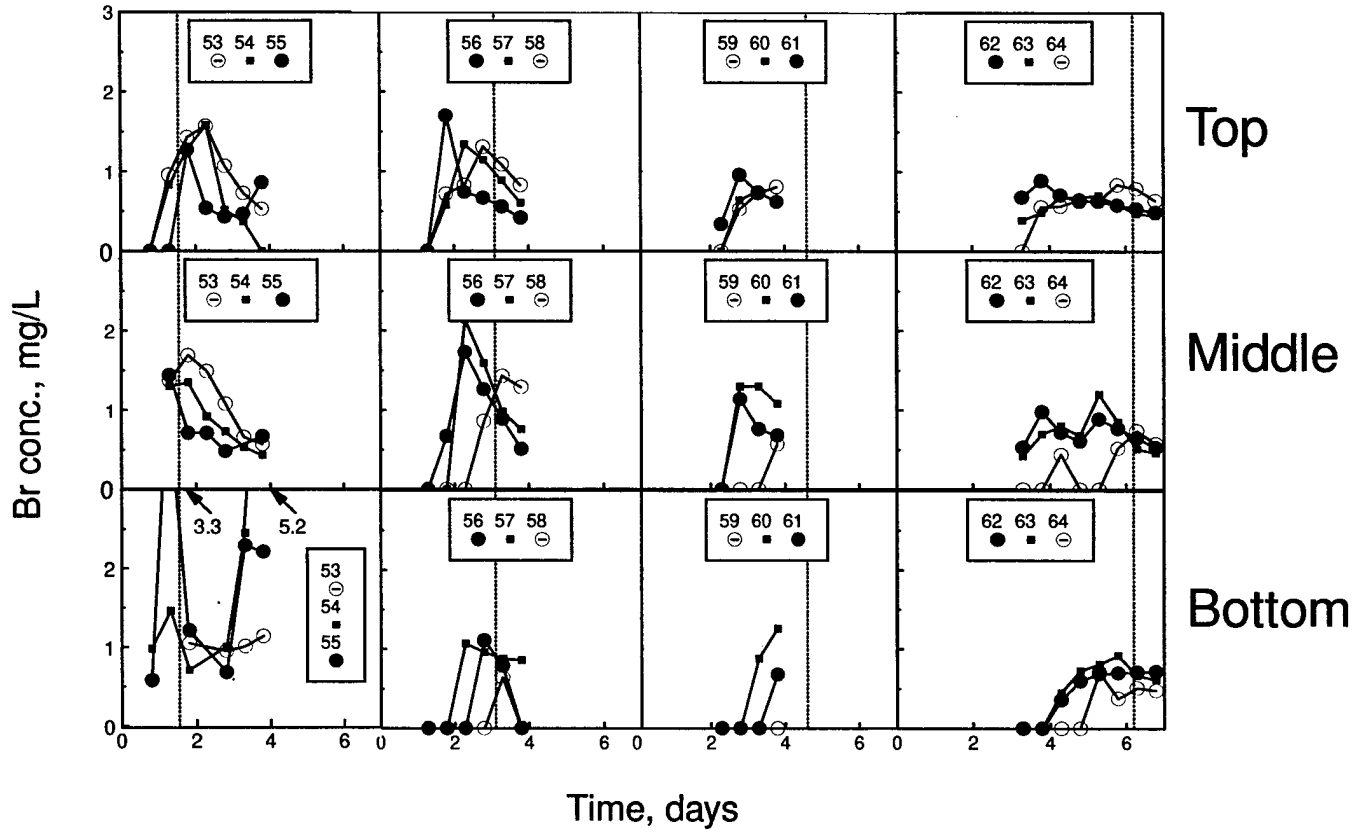


Figure 6-27

August 1997 Short-Circuit Test Results for the Gravel-Based Wetland (Cell A1)



Vertical dashed lines = retention time for water to reach wells

Sampling depths: Top = 8 inches from water surface
Middle = 24 inches from water surface
Bottom = 40 inches from water surface

Figure 6-28

Vertical Movement of Tracer Through Gravel-Based Wetland Cross-Sections in August 1997

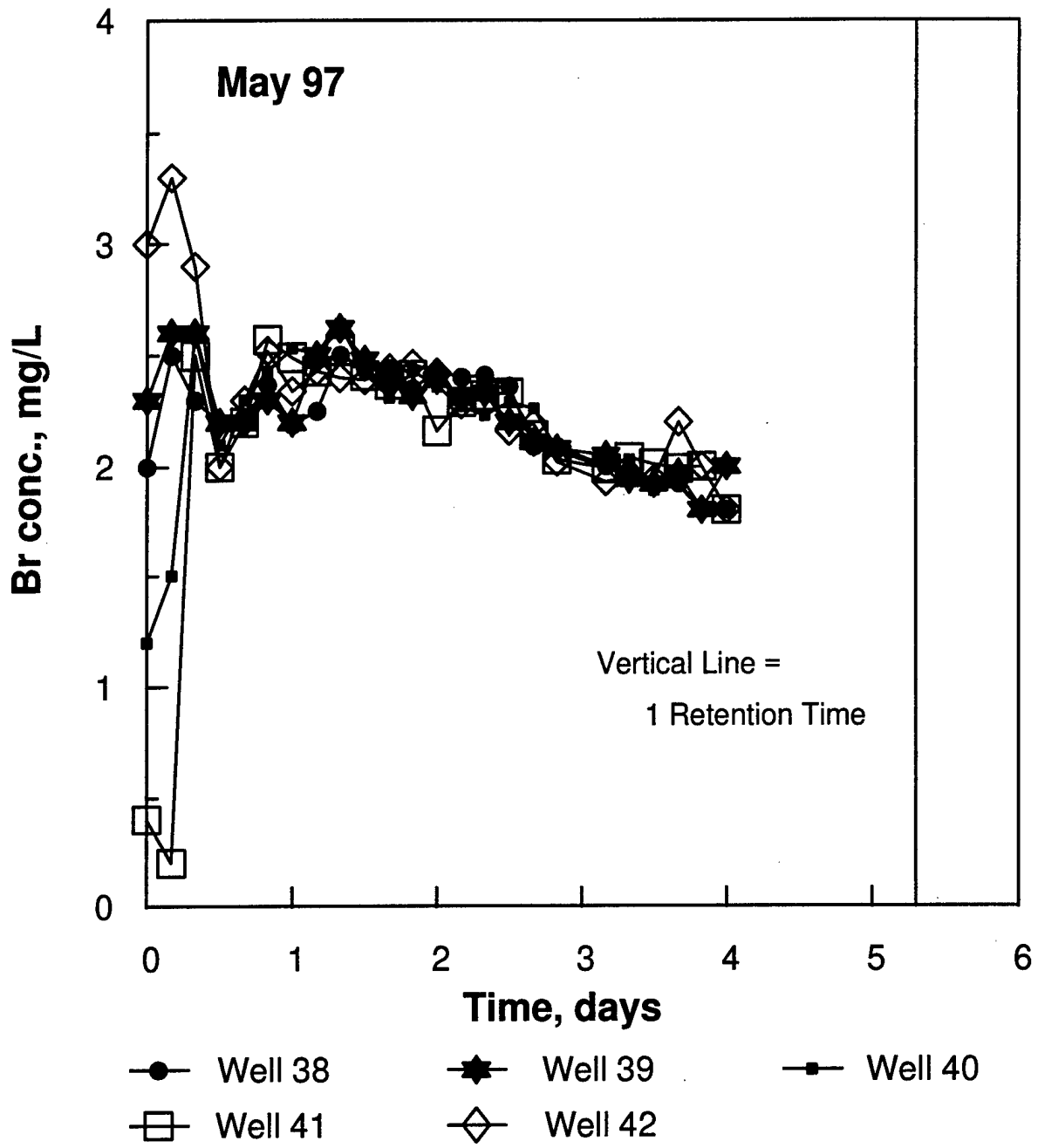


Figure 6-29

May 1997 Short-Circuit Test Results for Lagoon-Based Wetlands

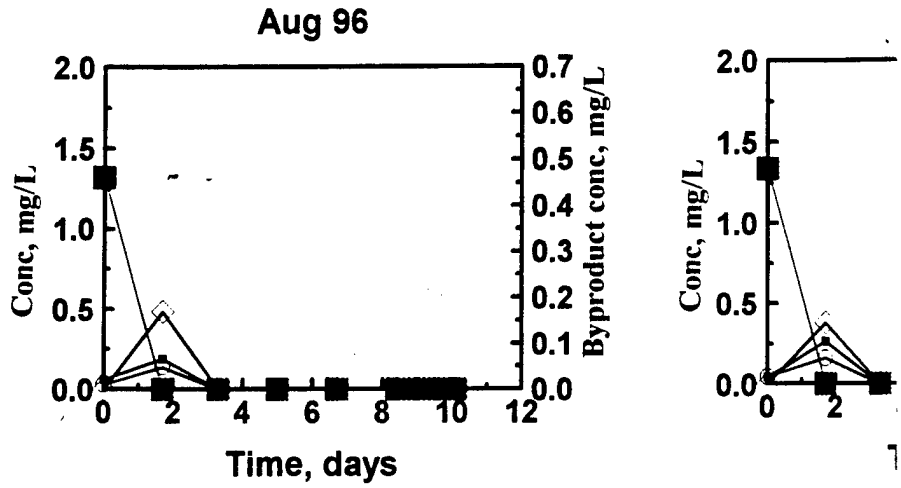
In summary, the anaerobic gravel-based wetland (A1) had the hydraulic characteristics of both plug-flow and complete-mix type reactors. These hydraulic characteristics are typical of wetlands of this type and control water movement through the cell. The aerobic gravel-based wetland (A2) is designed such that a complete-mix type of hydraulic movement predominates. Movement of water through the lagoon cells are not governed by plug-flow hydraulics and more closely resemble complete-mix reactors. Plug-flow hydraulics in a reactor are desired since there is less chance of contaminated groundwater leaving the reactor without being treated. For this reason, a single gravel-based wetland will have an advantage over a single lagoon-based wetland. However, if several lagoon-based cells were constructed in series, then the desired plug-flow hydraulics behavior might be obtained and this advantage might diminish.

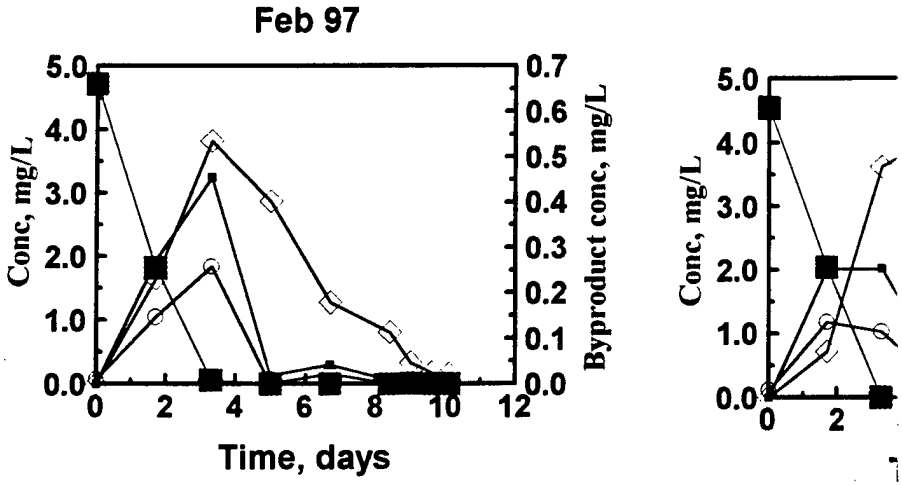
6.2.4 Wetlands Efficiency

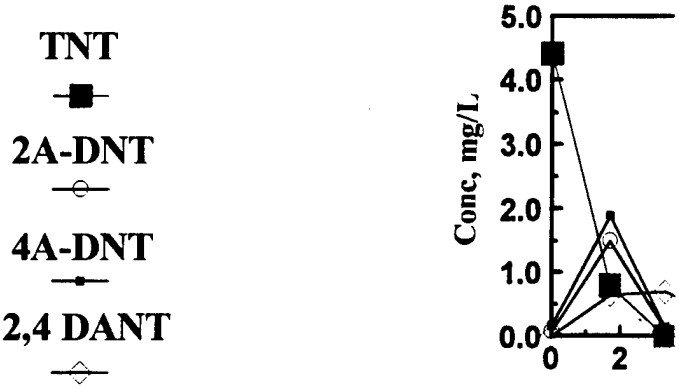
The routine data (collected every other week) were valuable in determining the relative effectiveness of the two wetland systems at removing explosives and explosive by-products. However, the routine data could not determine how quickly explosives were removed in the wetland. Information on how quickly the explosives were removed is vital to design systems to treat contaminated groundwater. To determine how quickly explosives were degraded in the wetland systems, water samples were taken from sampling wells located in the interior of the wetlands. These samples were taken every other month (bimonthly) as part of the intensive sampling program. An example of the data taken at these interior locations is shown for TNT removal in the gravel-based wetland (Figure 6-30).

Bimonthly sampling data in this section are presented as plot of concentration as a function of retention time. The amount of time theoretically needed for the water to reach the sampling wells appears on the x-axis. The explosive concentration appears on the y-axis.

The total retention time in the gravel- and lagoon-based wetlands was 10.1 and 11.4 days, respectively. For the gravel-based wetlands, the time period ranging from 0 to 8.4 days represents the hydraulic retention time within the first anaerobic wetland (A1). The time period from 8.4 to 10.1 days is the hydraulic retention time within the aerobic wetland (A2).







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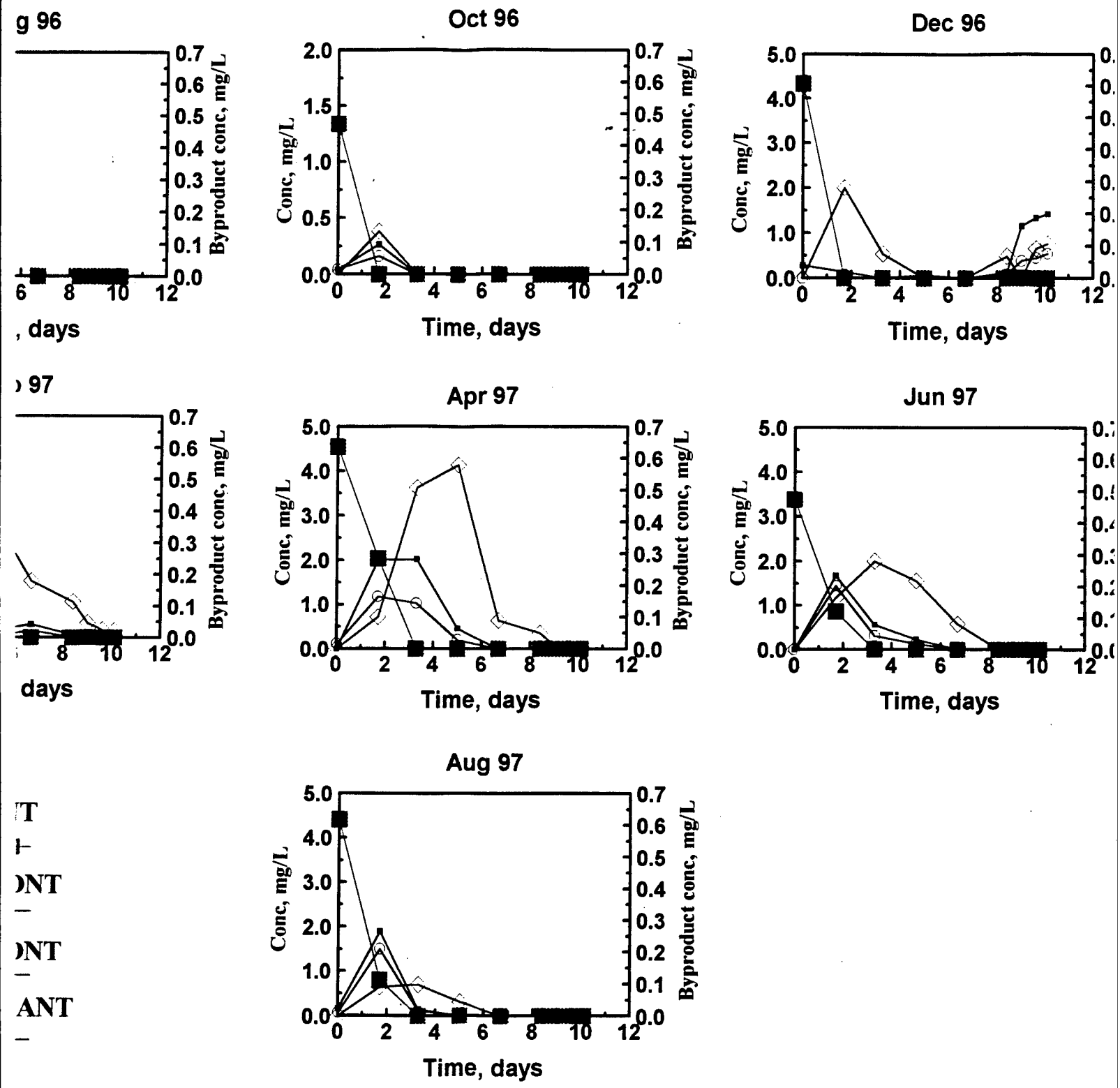

Figure 6-30
Time- and Season-Dependent Degradation of TNT in Gravel-Based Wetlands From August 1996 to August 1997

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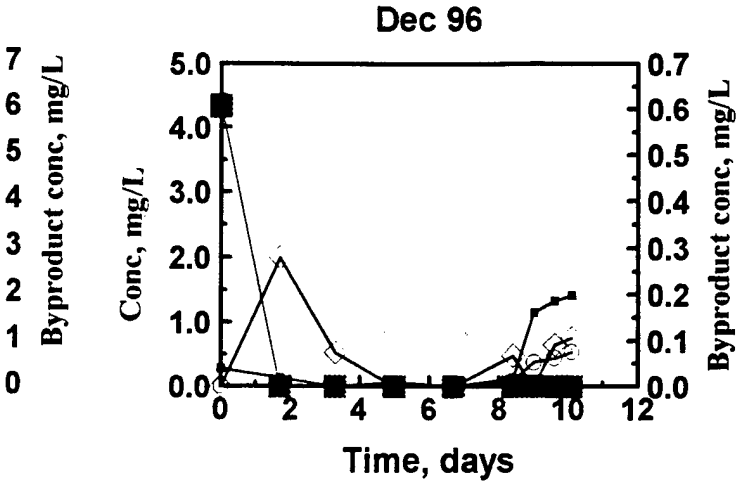

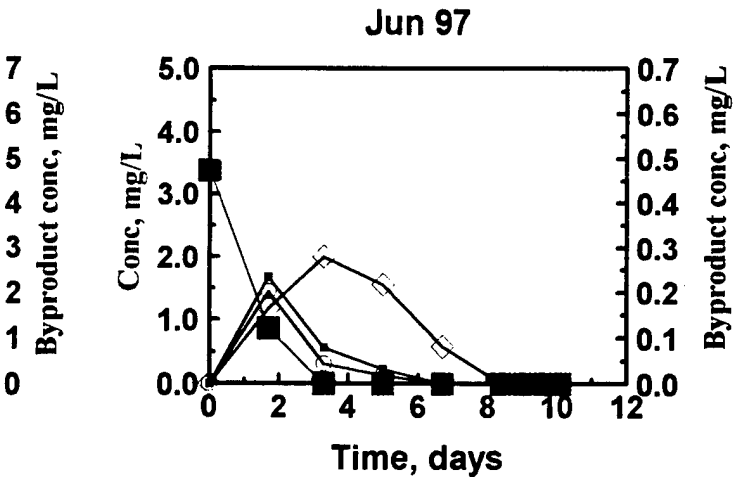

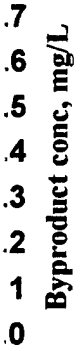

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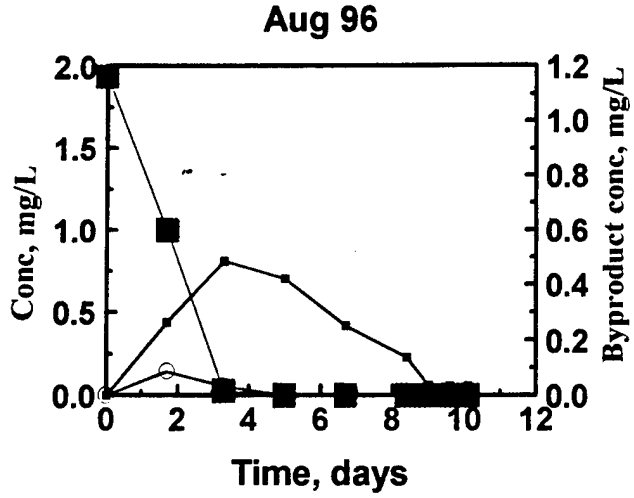
For the lagoon wetland, the time period ranging from 0 to 5.7 days represents hydraulic retention time within the first lagoon (B1). The time from 5.7 to 11.4 days represents the hydraulic retention time within the second lagoon (B2). All sampling times are identified by a month and year. Sampling occurred within the first 10 days of the month.

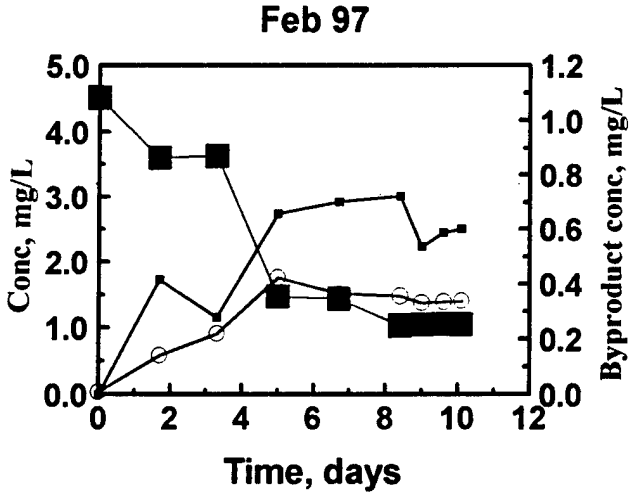
6.2.4.1 Efficiency of the Gravel-Based Wetlands

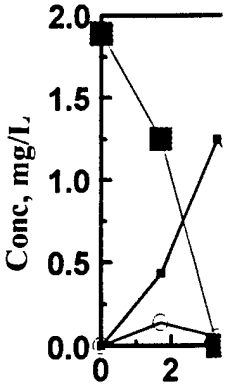
Removal of TNT and the formation and subsequent degradation of TNT by-products are shown in Figure 6-30 for the gravel-based wetlands. In August and October 1996, TNT was rapidly removed with concentrations reduced to the detection limit after 1.7 days. The amino by-products increased to low concentrations with the removal of TNT during this period. After moving to well MI-051, which had higher TNT concentrations, TNT removal was still quite rapid as indicated by the December 1996 data (Figure 6-30). The increase in TNT by-product concentrations observed by the last three data points represents water samples taken from the aerobic cells. As discussed earlier, the increase in TNT by-product concentrations in the aerobic wetland may have been due to a rainfall event that released higher than normal concentrations of the by-products from A1 into A2 before sampling.

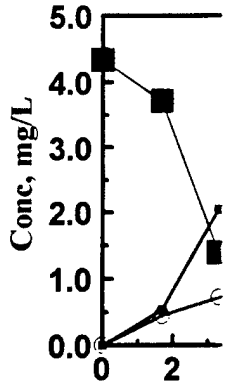
During February and April 1997, the rate of TNT removal began to decrease with complete removal not occurring until 3.3 days (Figure 6-30). By June 1997, the rate of TNT and TNT by-products removal increased as evidenced by lower TNT and TNT by-product concentrations after 1.7 days. By August 1997, the rate of TNT and 2,4-DANT removal was even faster. These results suggest a strong temperature-dependent relationship.

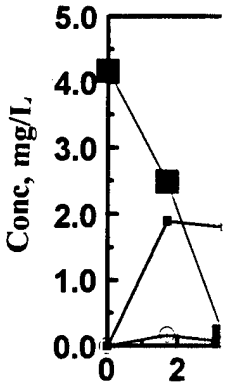
The degradation of RDX in the gravel-based wetlands was not as rapid as TNT removal (Figure 6-31). In August and October 1996, complete RDX removal occurred after 3.3 days as opposed to 1.7 days for complete TNT removal during this period. The concentration of the RDX by-products, m-RDX and t-RDX, increased as RDX concentrations decreased. The t-RDX was more prominent than m-RDX. In December 1996, RDX concentrations were observed to increase at the A1 outlet. This was also observed for the TNT by-products (Figure 6-30). The higher RDX concentration was probably due to a rainfall event causing











RDX

m-RDX

t-RDX

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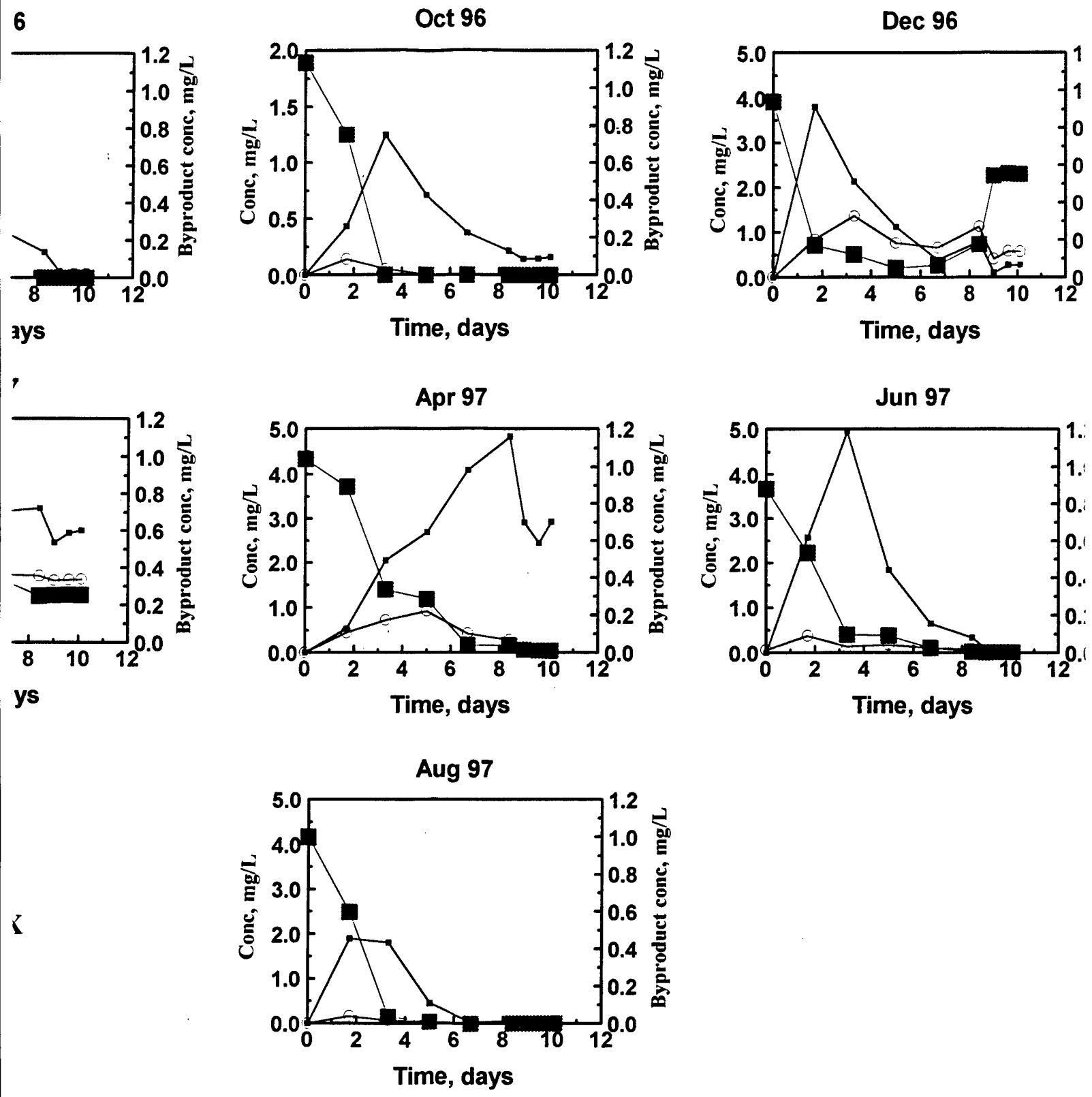

Figure 6-31
Time- and Season-Dependent Degradation of RDX in Gravel-Based Wetlands From August 1996 to August 1997

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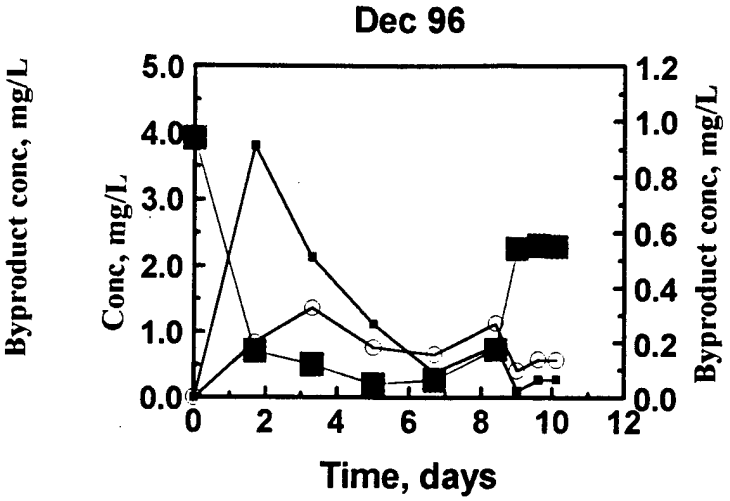
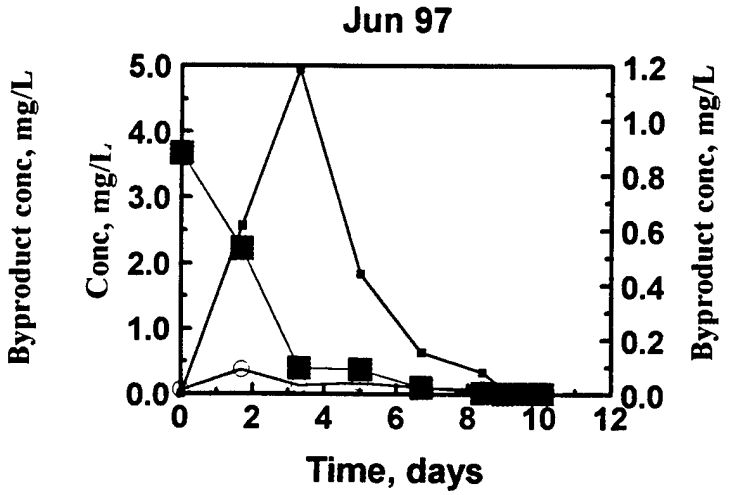




Byproduct conc, mg/L

water to rise above the gravel surface and resulted in influent groundwater short-circuiting across the top of the wetland.

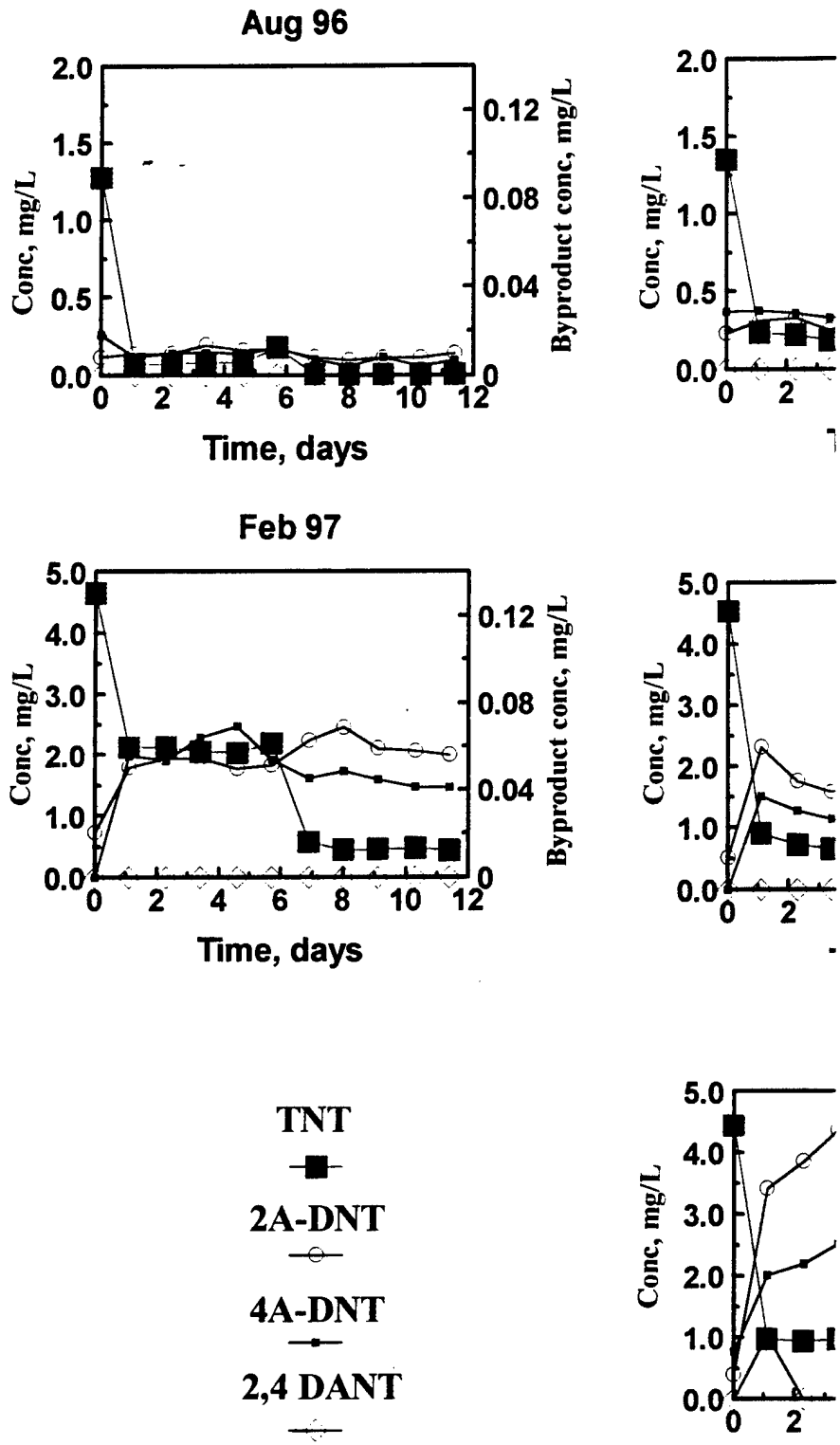
The removal rate of RDX declined in February and April 1997. With the decrease in the RDX removal rate, the formation of the RDX by-products also occurred at later time periods. Complete removal of RDX by-products was not achieved during these sampling periods. In April 1997, the approximate concentration of t-RDX released from A1 was 1,200 ppm. The aerobic wetland, with the retention time of 1.7 days, was effective in reducing this concentration by 50%. In June and August 1997, there were significant improvements in the rates of RDX removal and subsequent removal of t-RDX.

6.2.4.2 Efficiency of the Lagoon-Based Wetlands

The removal of TNT and subsequent formation of TNT by-products in the lagoon-based system are shown in Figure 6-32. TNT removal was rapid during 1996. The TNT removal rate declined in February 1997 and slowly improved as temperatures increased throughout the rest of the year.

Unlike the first order decline of TNT and RDX concentrations observed in the gravel-based system, the decline of TNT concentrations in the lagoon-based system was not first-order. Rather, the TNT concentrations declined rapidly in the first sampling wells (day 1.1 in cell B1 and day 6.9 in cell B2) and then remained relatively constant downstream of the first sampling wells. Since the bromide tracer data suggests the lagoons act more like complete-mix reactors (Figures 6-24 and 6-25), the nonconformity to first-order kinetics is thought to be due to mixing. Such mixing would be normal in open bodies of water like the lagoons.

Normally, during any given bimonthly sampling period, the initial decrease in TNT concentrations described above was accompanied by an increase in TNT by-product concentrations (see the data for 2A-DNT and 4A-DNT in Figure 6-32). However, after the by-product concentrations rose, they remained relatively constant throughout the lagoon-based system. One exception occurred in December 1996. During this sampling period, the 2A-DNT



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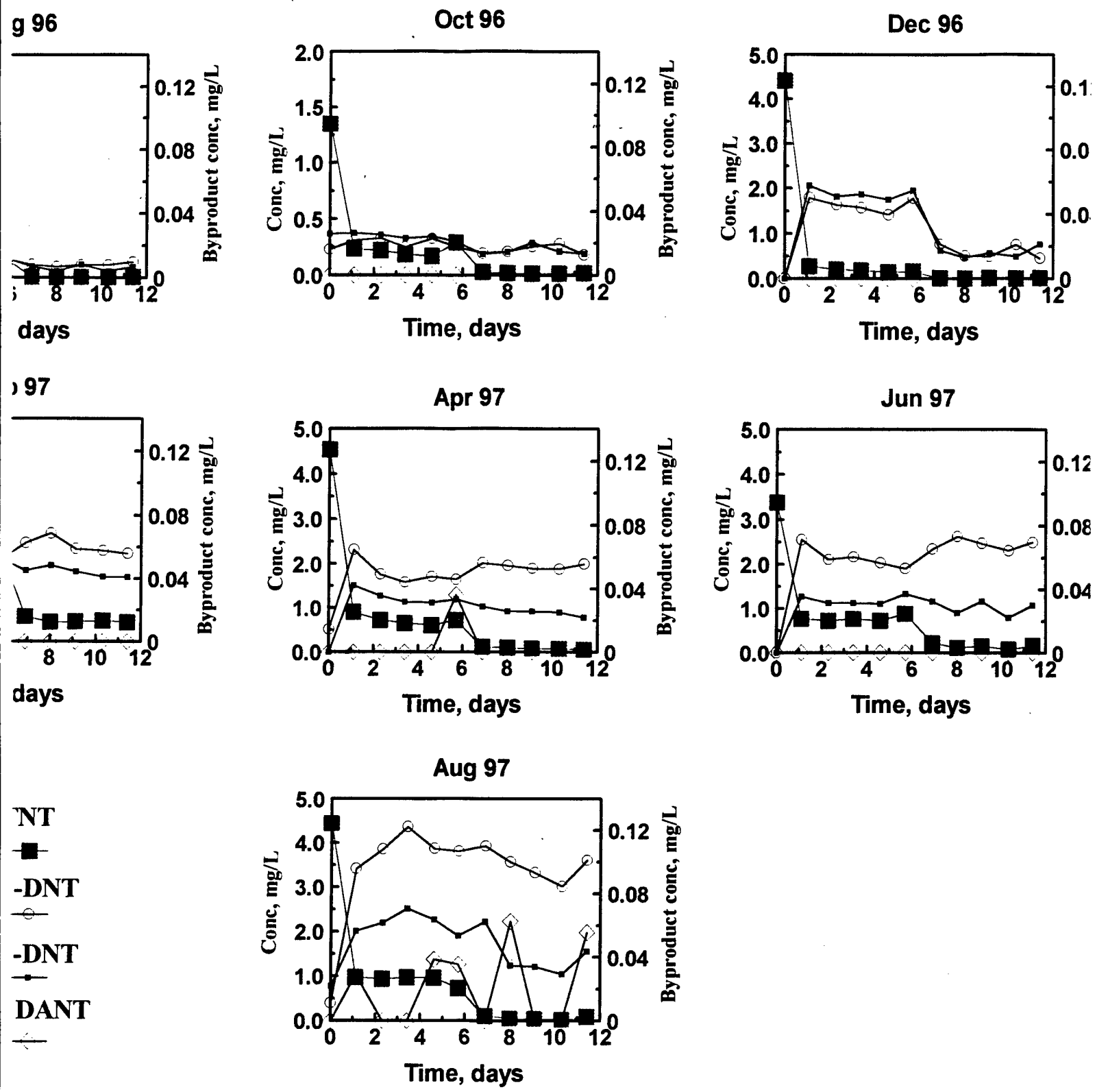

Figure 6-32
Time- and Season-Dependent Degradation of TNT in Lagoon-Based Wetlands From August 1996 to August 1997

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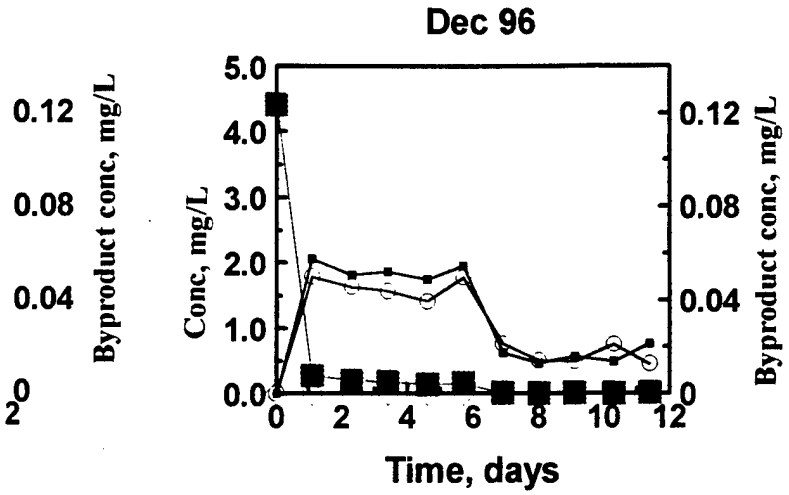

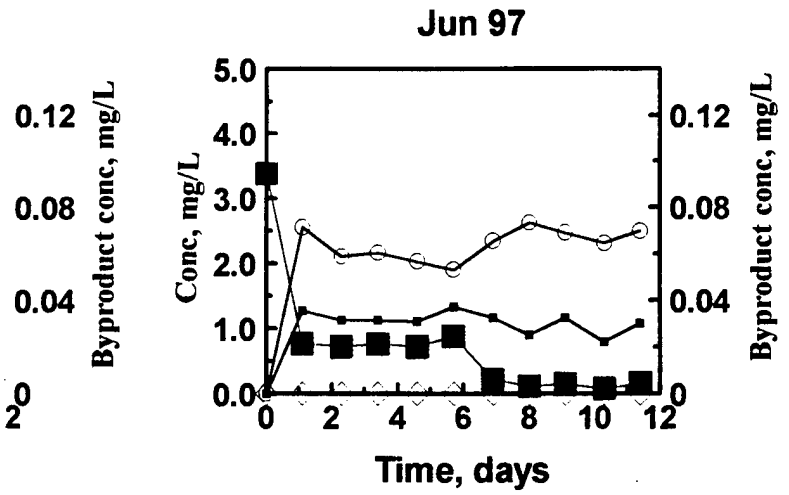

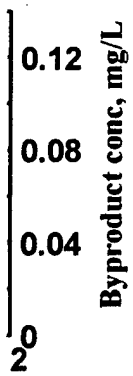

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and 4A-DNT concentrations actually declined as the groundwater moved from cell B1 to cell B2.

However, the 2A-DNT concentrations at all sampling locations increased throughout the demonstration (compare 2A-DNT data from August 1996 to August 1997 in Figure 6-32). A similar increase in TNT by-product concentration was also observed in effluent data (Figure 6-3). This data clearly indicates that the lagoon-based system's ability to degrade TNT by-products declined with time.

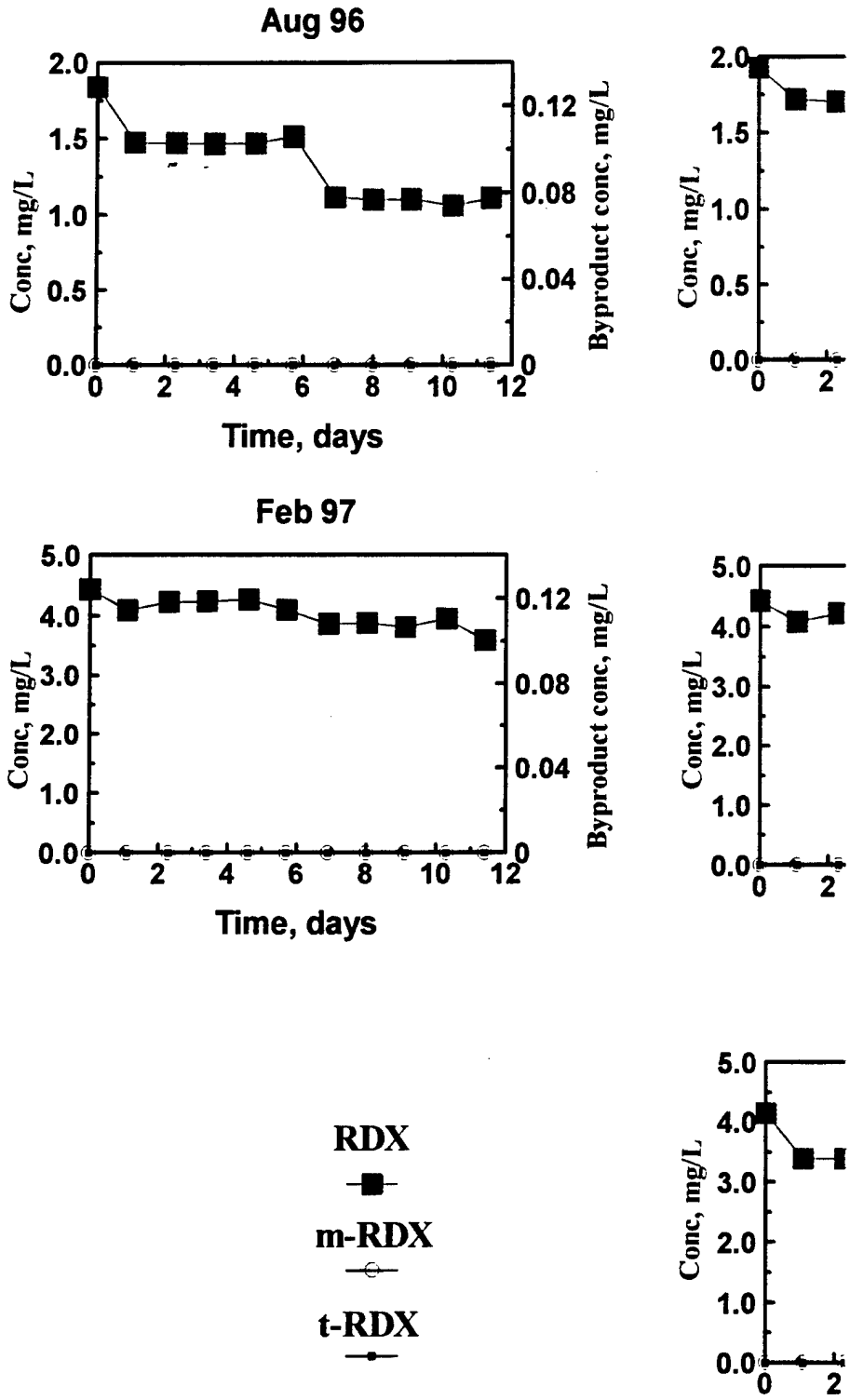
The lagoon-based system's ability to remove RDX was also poor (Figure 6-33). Like TNT, RDX concentrations plateaued in each of the lagoon cells (Figure 6-32). RDX removal was greatest in December 1996. The removal rates declined greatly in February 1997, then slowly increased throughout the rest of the demonstration.

The RDX by-products, m-RDX and t-RDX, were not observed except for a single sample in December 1996. Either the small amount of RDX that was removed in the lagoon-based system was removed via a pathway that did not involve m-RDX or t-RDX, the by-products were diluted to such an extent in the lagoon water that concentrations were below limits of detection, or, once formed, the by-products were rapidly sorbed onto the sediment.

6.2.4.3 Kinetic Rate Constants for TNT and RDX Removal

Rate constants for TNT and RDX removal in the anaerobic gravel-based wetland (cell A1) and both lagoon-based wetlands (cells B1 and B2) were determined as described in Section 3.6.1. Since water movement through A1 was similar to plug-flow (Figure 6-22), the use of a first-order kinetics model was appropriate to evaluate the rate of degradation. Since water movement through the lagoon-based wetlands (B1 and B2) resembled complete-mix reactors, only the data points entering and exiting the wetland cells were used to determine the first-order rate constants.

The explosive degradation rate constants for the anaerobic gravel-based cell were higher than those for the lagoon-based system by an approximate factor of 10 (Figure 6-34). In the anaerobic cell, there was a noticeable decrease in the RDX degradation rate in December 1996.



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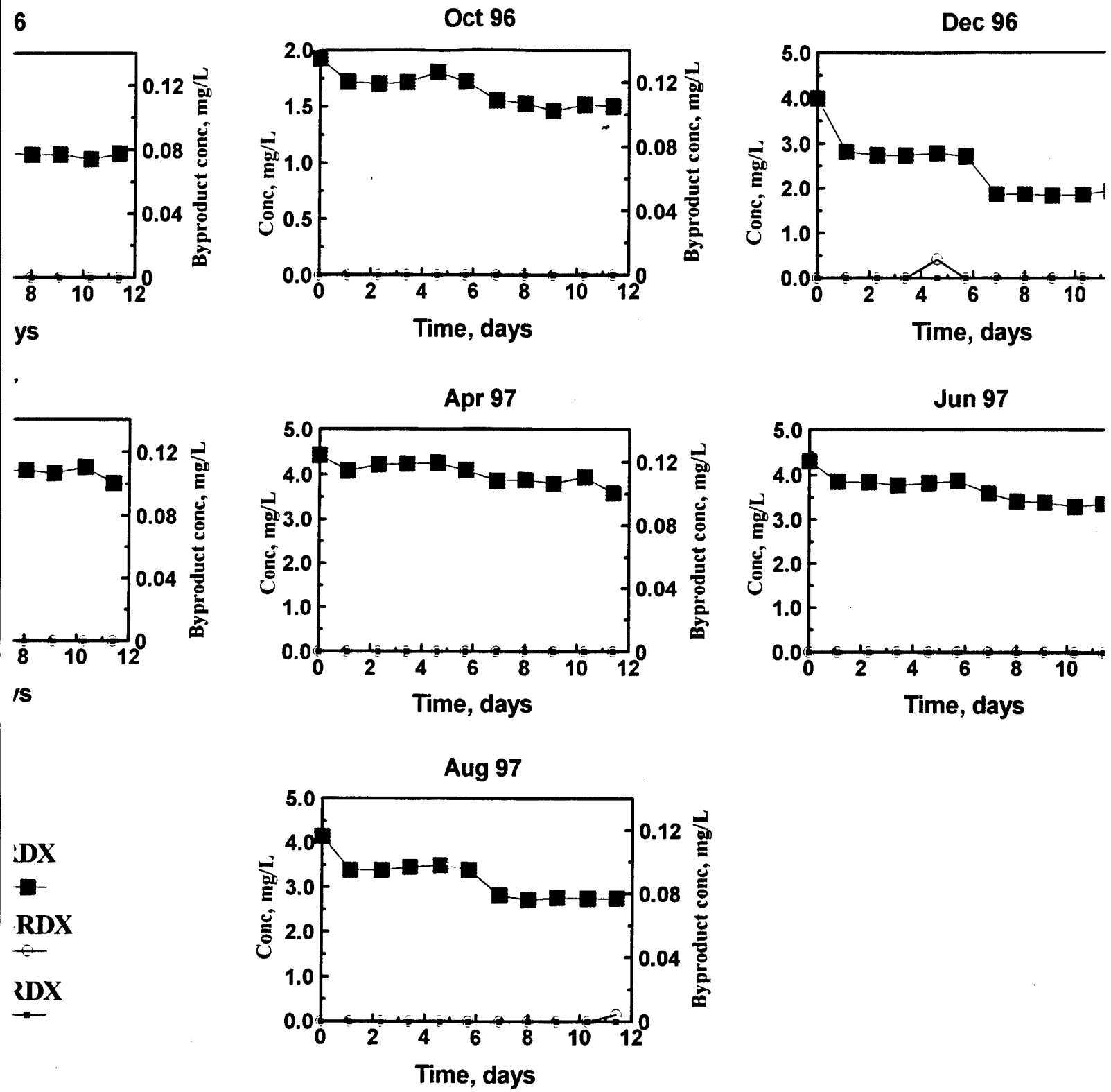

Figure 6-33
Time- and Season-Dependent Degradation of RDX in Lagoon-Based Wetlands
From August 1996 to August 1997

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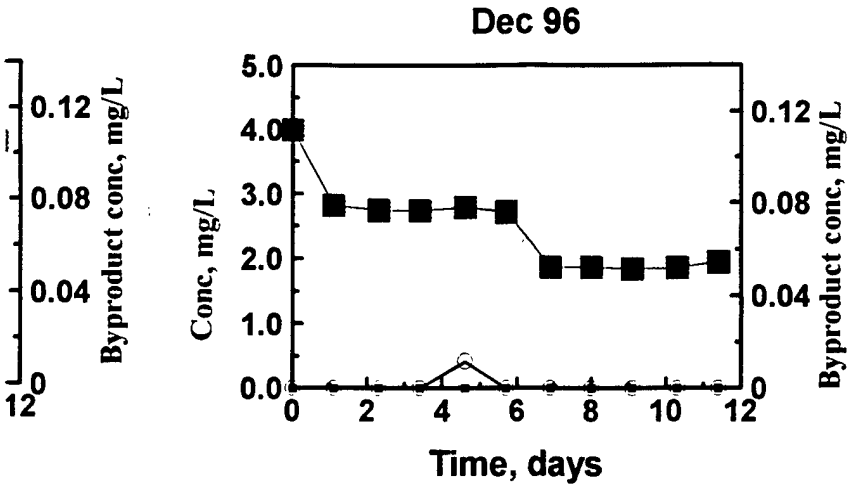
Dec 96
Conc, mg/L
Byproduct conc, mg/L
Time, days
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4.0
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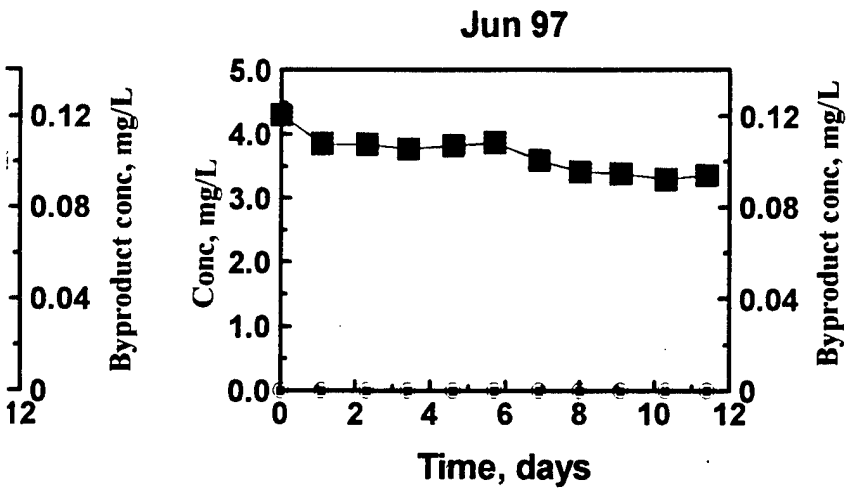
0
2
4
6
8
10
12


Jun 97
Conc, mg/L
Byproduct conc, mg/L
Time, days
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4.0
3.0
2.0
1.0
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0.08
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2
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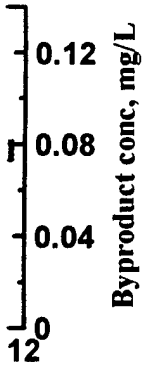
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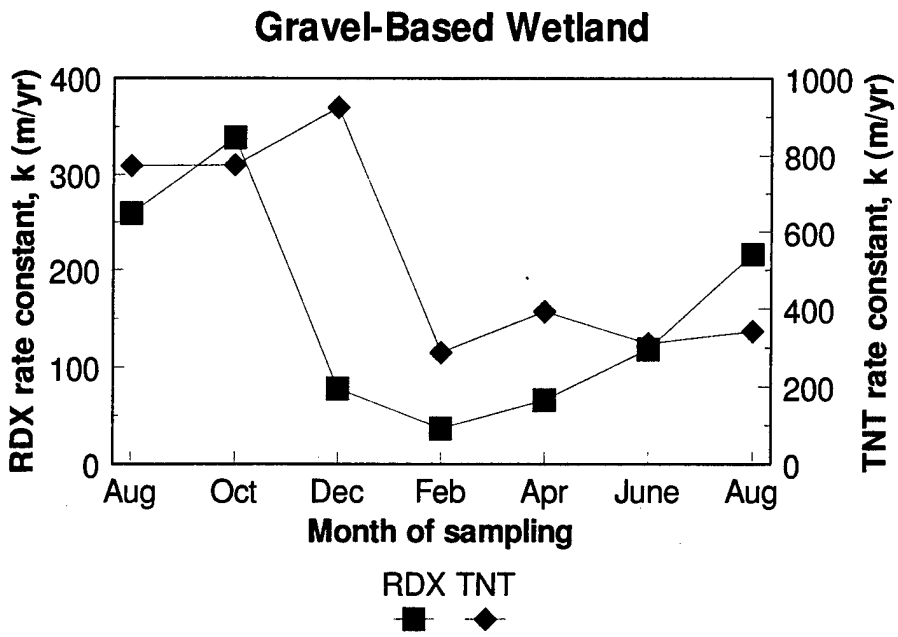


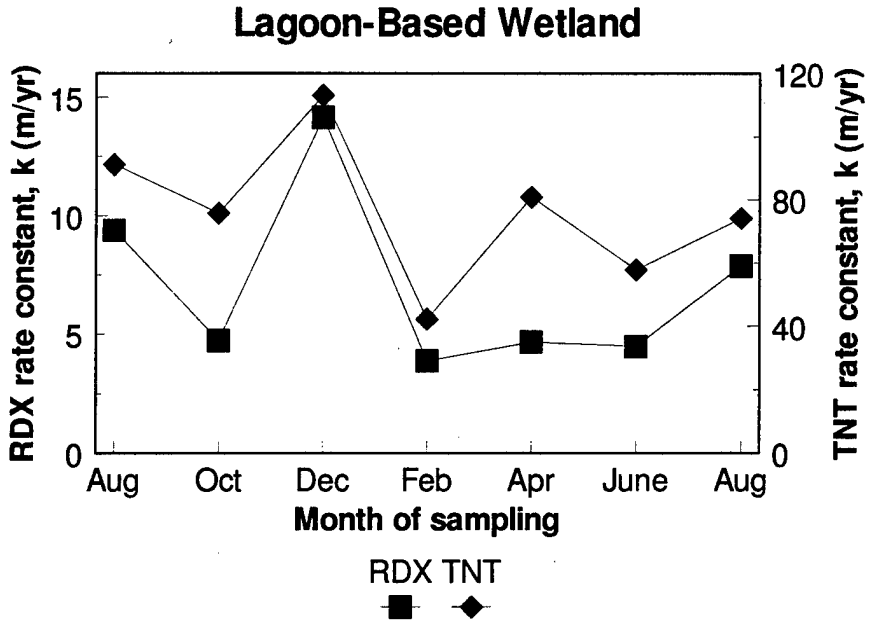


Figure 6-34

Seasonal Variation of Rate Constants for TNT and RDX Degradation in Gravel- and Lagoon-Based Wetlands From August 1996 to August 1997

The degradation rate for TNT in the anaerobic cell decreased in February 1997, then increased slightly throughout the rest of the demonstration period. The rate constants for TNT and RDX degradation in the lagoons decreased from December 1996 to February 1997 and increased slightly throughout the rest of the demonstration period. The decrease in TNT and RDX degradation rates in the anaerobic cell during the winter months could have been due to:

- The higher contaminant levels encountered when well MI-051 was put into service on November 21, 1996

- Colder temperatures (Figure 6-9)

- A decrease in redox potential due to the decreased use of carbon (MRS) during the winter of 1996/1997 (Table 6-1)

In gravel-based systems, TNT and RDX degradation is primarily the result of anaerobic microbial degradation. The increase in explosives concentrations which accompanied the change of wells in November 1996 may have temporarily decreased the degradation rates by adversely affecting the microbial population. However, the degradation rates should not be affected by different explosive concentrations in the long term, since degradation rates are independent of initial concentration. The colder temperatures experienced during the winter months may have had a larger impact by decreasing the microbial biomass which, in turn, would have decreased removal rates for TNT and RDX. However, the degradation rate changes could not be solely ascribed to temperature changes because carbon input into the system was limited in the winter months to avoid clogging of the effluent headers.

The anaerobic cell's RDX removal rates rebounded to higher values as time progressed from colder winter months to warmer spring and summer months (Figure 6-34). However, TNT removal rates in the gravel-based wetland increased only slightly from February 1997 to August 1997. This result suggests that TNT removal was initially rapid and then stabilized to a lower rate as the wetland matured. The very slight increase in the rate constants from winter 1996/1997 to summer 1997 suggests that TNT removal was not significantly affected by temperature differences. However, temperature increases did accelerate the removal of TNT by-products (Figure 6-30).

The lagoon-based system's explosive degradation constants were an order of magnitude smaller than those for the gravel-based anaerobic cell. However, the lagoon's rate constant followed a pattern similar to that for the gravel-based wetland. The rate constants decreased from December 1996 to February 1997 (Figure 6-34) and increased slightly during sampling periods following February 1997. The main mechanism responsible for degrading TNT and RDX in the lagoons is not known. The degradation may be due to nitroreductase enzymes released from submergent plants, microbial digestion, or photo-degradation. The decrease in TNT and RDX degradation rates, which occurred in February 1997, corresponds with a winter temperature drop, lower microbial activity, and lower light intensity. All of these factors may have contributed to the decreasing degradation rates. The TNT and RDX removal rate constants increased slightly after February 1997, along with the increased water temperatures.

Graphical presentations of the degradation of TNT and RDX in the anaerobic gravel-based wetland (A1) are shown in Figures 6-35 and 6-36. These graphs were developed using bimonthly data, the first-order model (Equation 1), and the rate constants in Figure 6-34. For the sampling periods from August 1996 to December 1996, the first-order rate model predicts the TNT concentrations will be reduced to non-detectable concentrations in two days or less. For sampling periods from February 1997 to September 16, 1997, non-detectable concentrations were attained in four days or less. The rate of RDX reduction in the anaerobic cell is shown to be clearly affected by the seasonal effects as shown in Figure 6-36. Nearly 100% RDX removal is predicted with the first-order models for August 1996, October 1996, June 1997, and August 1997. From 77% to 95% RDX removal is predicted from December 1996 to April 1997.

The removal of TNT and RDX in the lagoon-based system, as predicted by the first-order model with rate constants from Figure 6-34, are graphically presented in Figures 6-37 and 6-38. As would be expected from the lower rate constants in the lagoon-based system as compared to the gravel-based anaerobic cell, TNT and RDX removal in the lagoons occur at a much less rapid pace. The curves for TNT removal in the lagoon-based system (Figure 6-37) are similar to RDX removal in the gravel-based anaerobic cell (Figure 6-36). The removal of RDX in the lagoons is very slow with 50% or less removed after 11.4 days (Figure 6-38).

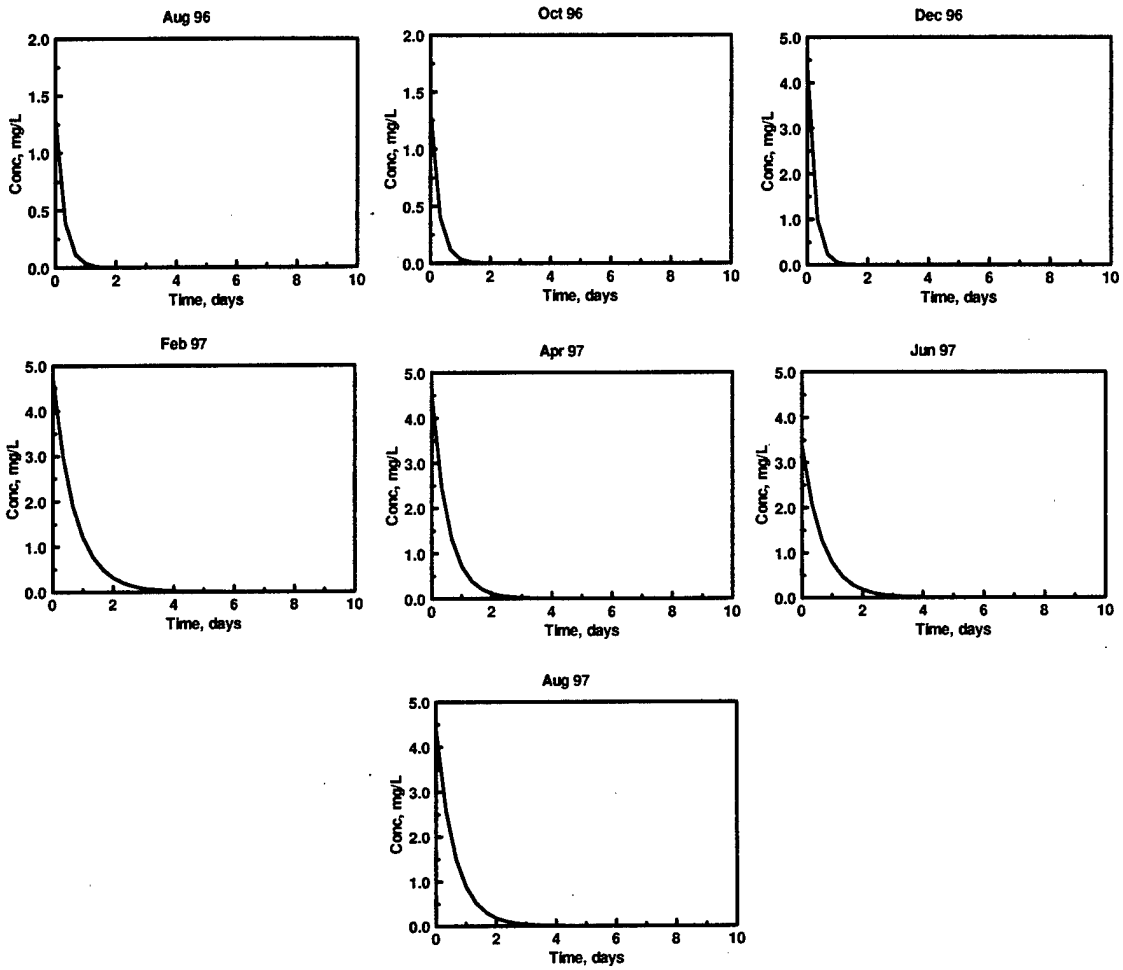


Figure 6-35

TNT Degradation in First Gravel-Based Wetland Bed (Cell A1)
From August 1996 to August 1997

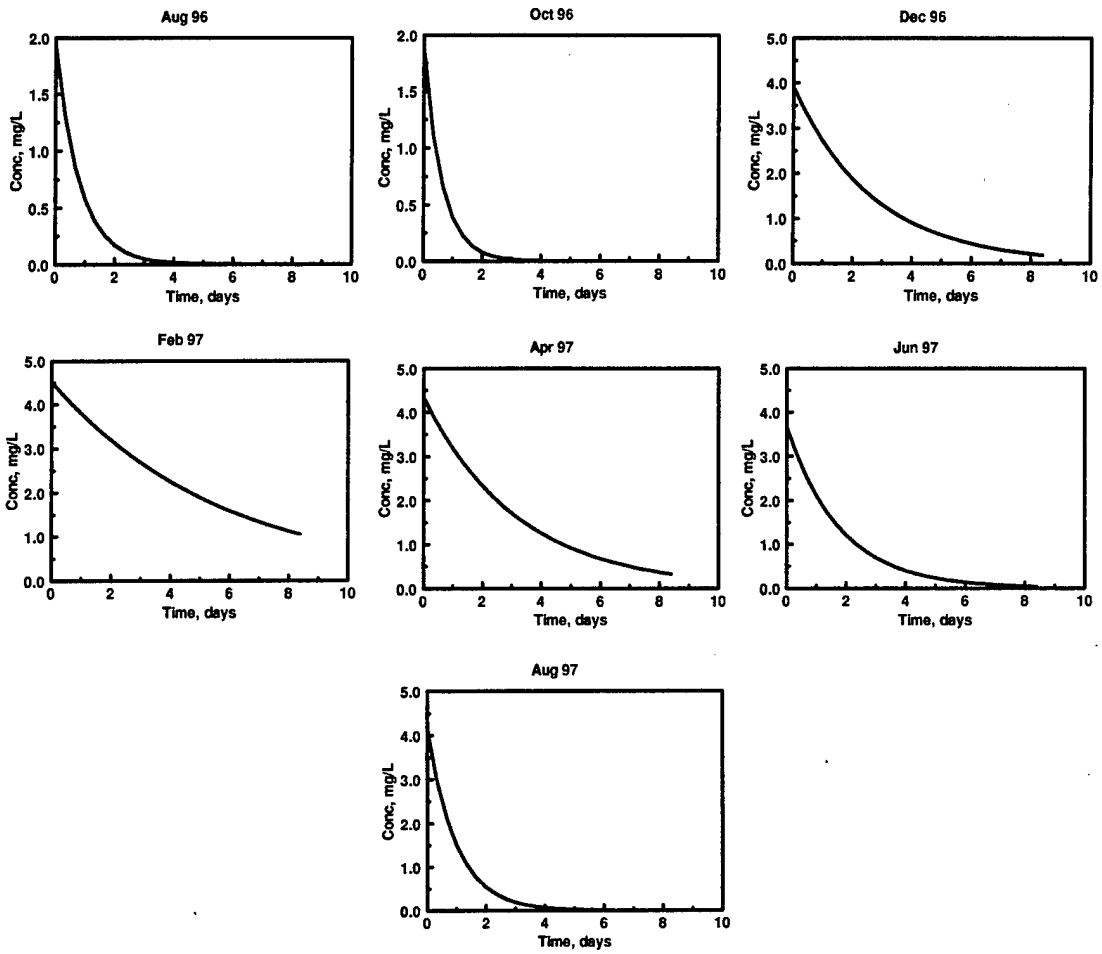


Figure 6-36

RDX Degradation in First Gravel-Based Wetland Bed (Cell A1)
From August 1996 to August 1997

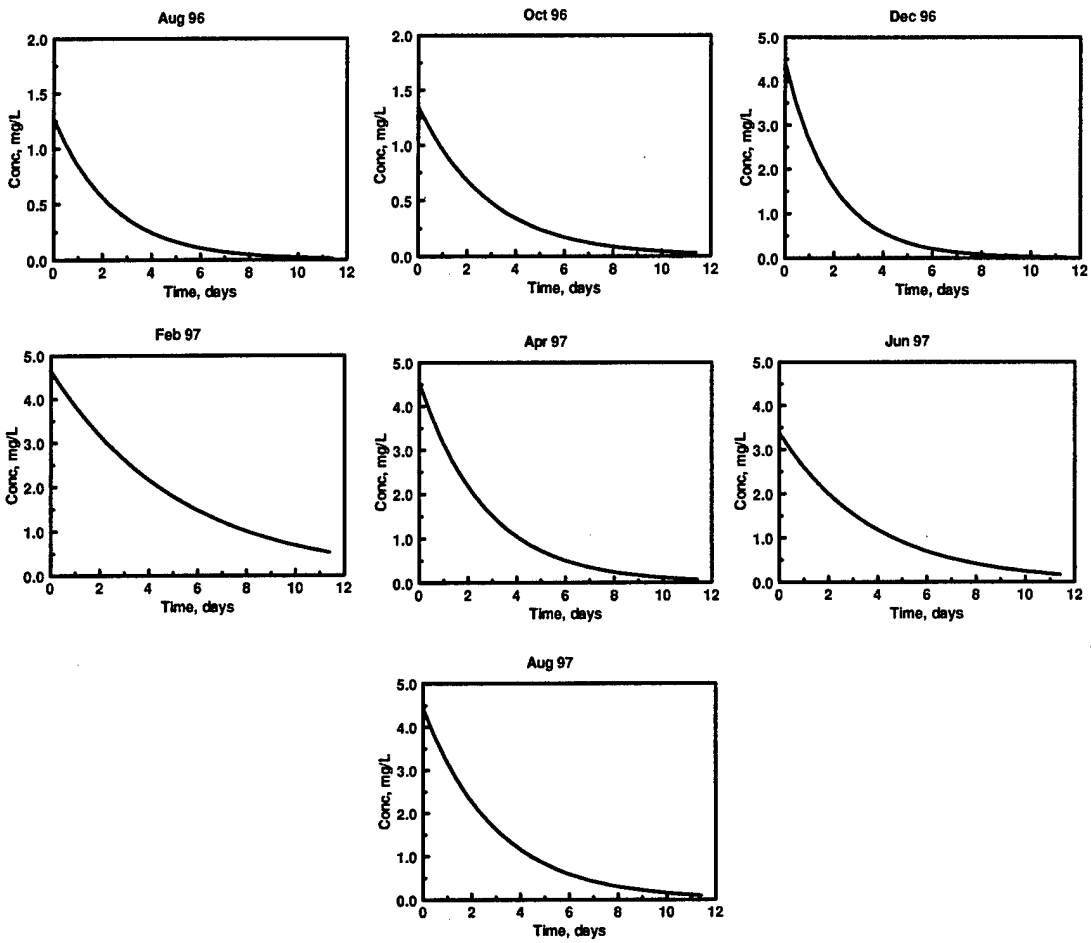


Figure 6-37

TNT Degradation in Lagoon-Based Wetlands From August 1996 to August 1997

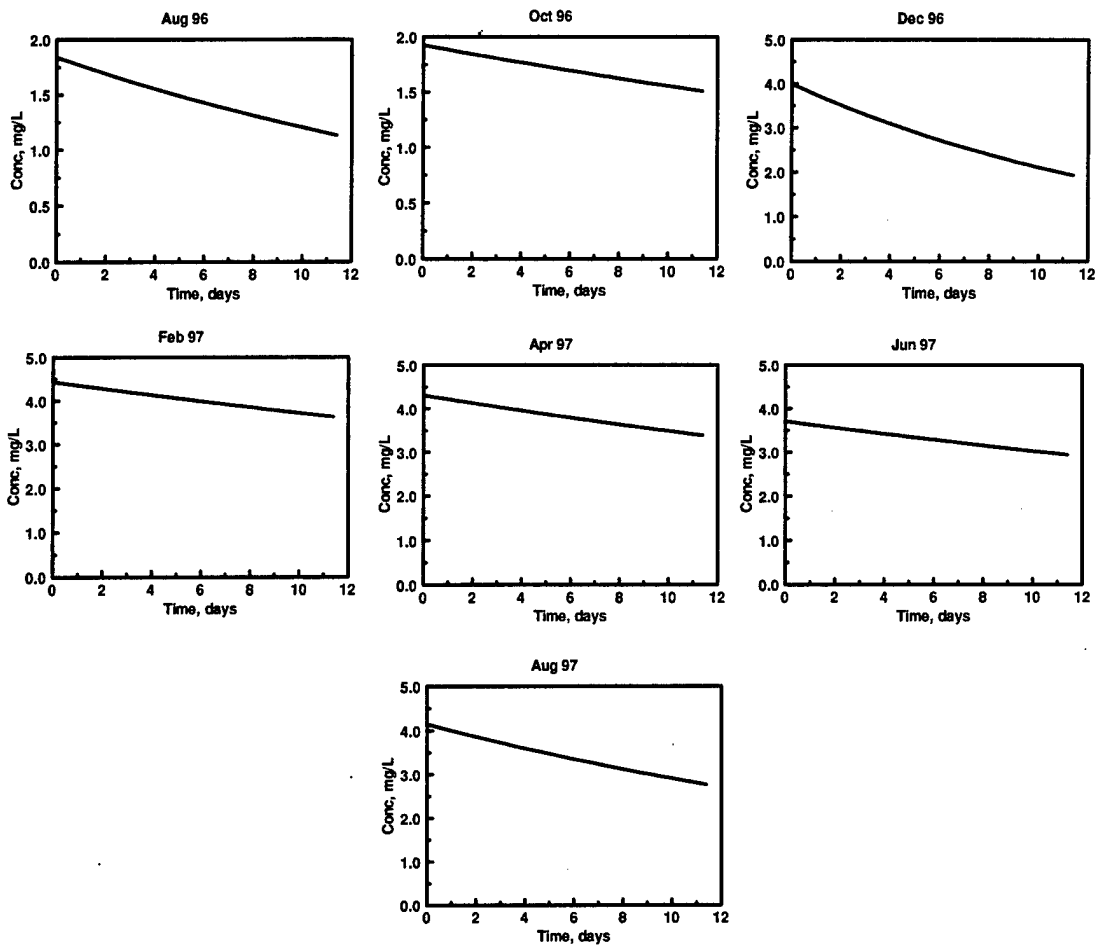


Figure 6-38

RDX Degradation in Lagoon-Based Wetlands From August 1996 to August 1997

Use of the k values obtained from the demonstration suggest that a larger lagoon-based system would have been needed to meet the demonstration goals (see Section 2.2). The size of a wetland can be determined from the equation:

$$y = \ln (Ci/C)*q/k \qquad \text{[Equation 2]}$$

Where:

y is the fractional distance between the cell's inlet to outlet (ranging from 0 to 1)

C is the pollutant concentration at y

Ci is the influent concentration of the pollutant

k is a first-order rate constant (with units in meter/year)

q is the hydraulic loading rate (in meters/year)

Equation 2 is a modification of equation 1 (described in Section 3.6.1). Assuming TNT must be reduced from 4,000 ppb to 2 ppb at a flow rate of 4.5 gpm and using the k value from June 1997 (Figure 6-34), equation 2 suggests that either a 2.56-acre lagoon-based system or a 0.06-acre anaerobic cell would have reduced TNT to the desired level. In comparison, the original lagoon-based system was 0.11 acre and the anaerobic cell was 0.09 acre. If a similar analysis is made, assuming the need to reduce RDX from 4,000 ppb to 50 ppb at a flow rate of 4.5 gpm and again using the k value from June 1997, then either a 2.0-acre lagoon-based system or a 0.08-acre anaerobic would have been needed to reduced RDX to the desired level.

6.2.5 Plant Uptake

6.2.5.1 Introduction

All of the plant species used in the demonstration were analyzed to determine the type and the amount of explosives and explosive breakdown products present due to plant uptake and metabolism of the explosive species. Based on the project's scope of work, this analysis was not designed to provide a comprehensive understanding of how the explosives were taken up, nor their location within the plant.

The WES studies indicated that the plants rapidly metabolize parent compounds in the plant, mainly in the growth areas of the plant (Appendix F). The concentration of breakdown products also appears to be relatively low in the plant tissues. The full reports are provided in Appendices E and F. The plant analysis for this part of the demonstration was limited to determining if explosives or by-products were present in the demonstration plants. Isotope studies for the demonstration were conducted by WES and were designed to evaluate the rate of uptake and migration of the explosives in the plant tissue and to quantitatively determine the amount of uptake occurring.

6.2.5.2 Analytical Methods

When the demonstration was started, there were no adequate methods available for the analysis of all the analytes under consideration. Over the course of the demonstration, TVA RM developed a new plant analysis procedure based on work conducted by TVA RM, the Cold Regions Research and Engineering Laboratory (CRREL), and WES. The new method is described in Appendix A-1.

6.2.5.3 Plant Sampling

Plant samples were taken at two points from each of the gravel- and lagoon-based cells. Bimonthly sampling of the gravel-based system was conducted as planned. It was assumed that the two points inside a particular cell would be equivalent and, thus, either sample could be used for analysis. As will be discussed later, the data indicates that this assumption was valid. However, sampling of the lagoon-based elodea and sago pond weed was discontinued after the February 1997 sampling due to poor plant growth within the lagoons. After the February 1997 sampling, only water star grass remained within the lagoon-based cells. After the April 1997 sampling, none of the lagoon-based plants were healthy enough to obtain a sufficient sample. Therefore, data analysis for the lagoon-based system ended in April 1997.

For this project, no attempt was made to identify where the explosives accumulated within the plants. Leaf and stem portions of a particular species were ground together to produce a single sample that was analyzed to obtain a value for the total amount of explosives in a particular species.

6.2.5.4 Procedure Development

The analytical procedure for the plant analyses is given in Appendix A-1. The analytical procedure was developed using radish leaves with multiple spike and replicate samples being analyzed. In general, the radish leaves were ground with liquid nitrogen, homogenized, then spiked and freeze-dried. The freeze-dried sample was then sonicated with acetonitrile for 18 hours. The acetonitrile was removed and analyzed using HPLC. The residue was sonicated a second time with acetonitrile. The remaining residue was digested with sulfuric acid. The acid hydrolysate was also analyzed. The three extracts were analyzed separately. The results were then added together to get the total amount of explosives and decomposition products in the plants. Data from the radishes and quality control spikes from the wetlands' plants showed good recoveries for most of the analytes. Two notable exceptions were the 2,4-DANT and 2,6-DANT.

6.2.5.5 Lagoon-Based Plants

General Information

After reviewing the data for the lagoon-based system's plants, it was determined that there was little difference in the plants' ability to uptake and metabolize explosives from cells B1 and B2. And since there was relatively poor growth in the plants in the lagoon-based system, samples were taken and compared from both cells. There seems to be a general buildup of explosive metabolites until the plants die. Because of the poor health of the plants, it was often not possible to obtain samplings needed for analysis. Thus, samplings for each plant in the lagoon may not contain the same number of samples nor be taken on the same date.

Sago Pond Weed (*Potamogeton pectinatus*)

Sago pond weed is a perennial, submersed plant with slender branched stems and creeping rhizomes. Sago pond weed leaves are long and narrow, 30 cm long and 1.5 mm broad, without teeth. The plant can be found in ponds and streams in fresh, saline, and brackish waters. The species is found in most parts of the world.

Figure 6-39 shows two data points for the analysis of the sago pond weed from the lagoon-based wetlands. It appears that the explosives TNT, RDX, and HMX are being taken up into the plants over time. It also appears that several breakdown products were either being accumulated or produced by the plants over a period of time. Since these plants were immersed in the lagoon's water, it is quite likely that there was a combination of accumulation and metabolic breakdown occurring.

By February 1997, the amount of metabolites had increased to high levels within the sago pond weed. The lagoon's red water color, which developed due to photodegradation, prevented light from reaching the plant, thereby, reducing photosynthesis. This factor may also have contributed to buildup of explosive metabolites within the plant tissues since reduced photosynthesis would have impaired the plant's ability to produce nitroreductase needed for metabolism of explosives. In turn, it is possible that the explosives and explosive by-product accumulation contributed to the poor health and eventual demise of the sago pond weed.

Elodea (*Elodea canadensis*)

Elodea is a slender, submersed, bottom-rooted, dioecious aquatic perennial. Its leaves are bright green, thin, and flimsy with inconspicuous rough edges. The leaves generally occur in a spiral of three leaves on the upper and middle portions of the stems. Elodea leaves are 8 to 13 mm long and 1 to 5 mm wide. The flowers have 3 sepals and 3 petals, are white, about 3 to 5 mm across, and grow on slender thread-like peduncles. The species is native to North America and is found in lakes, ponds, and slow-moving streams in most of the United States.

Figure 6-40 shows three data points for the analysis of elodea from the lagoon-based system. It appears that 4A-DNT is being significantly accumulated into the plants over time. It also appears that several other breakdown products are either being accumulated or produced by the plant over a period of time. Since these plants were immersed in the lagoon's water, it is quite likely that there was a combination of accumulation and metabolic breakdown.

It is possible, since the amount of 4A-DNT had increased to such high levels by February 1997, that this accumulation contributed to the poor health and eventual demise of the elodea.

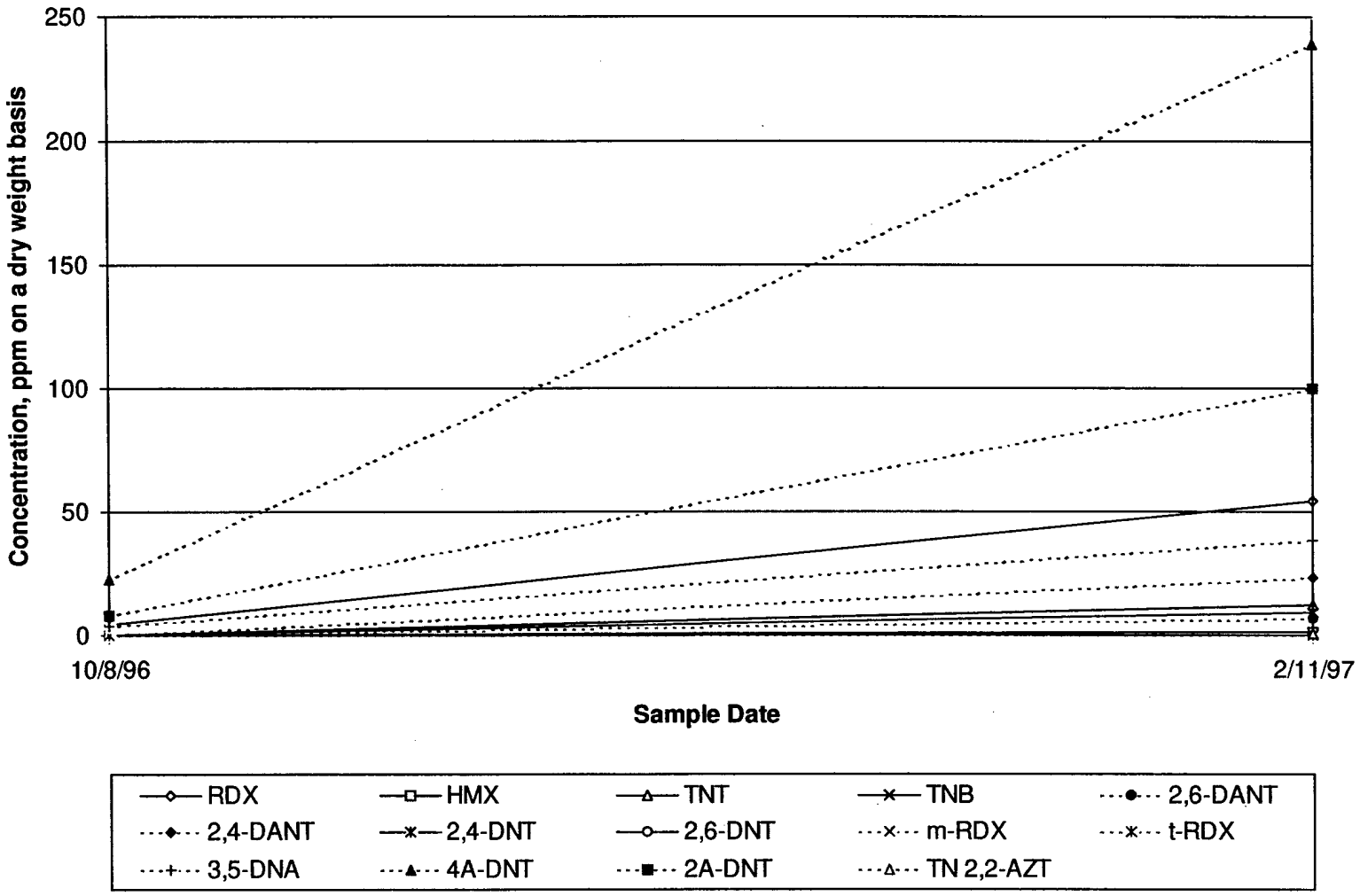


Figure 6-39

Accumulation of Explosives and Metabolites in Sago Pond Weed in Lagoons as a Function of Time

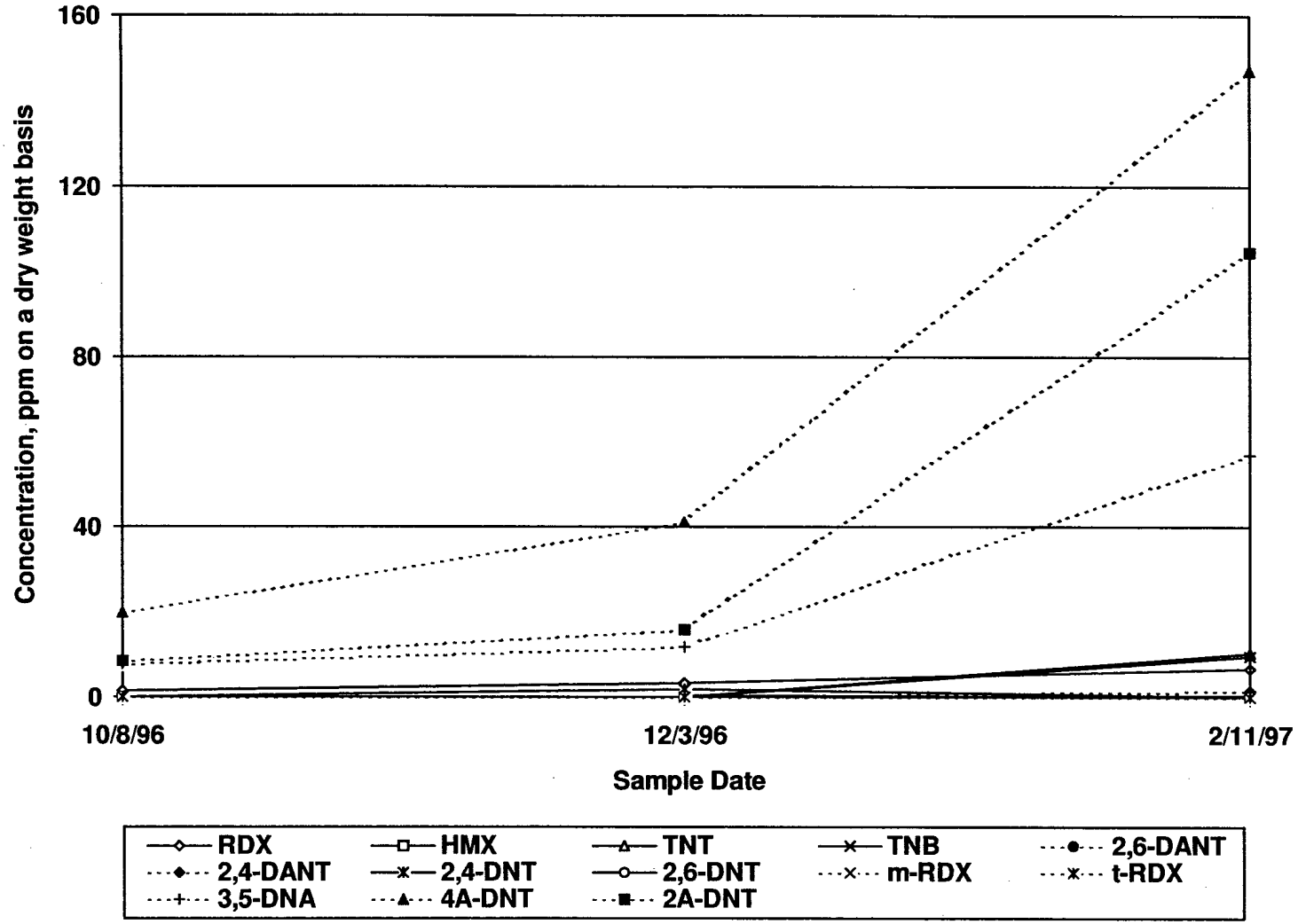


Figure 6-40

Accumulation of Explosives and Metabolites in Elodea in Lagoons as a Function of Time

As pointed out earlier, the lagoons became highly colored due to photo-degradation of the explosives in the water and, as a result, the plants could not effectively photosynthesize. Poor photosynthesis may have led to reduced nitroreductase production, limiting the plant's ability to fully metabolize the explosives which, in turn, contributed to the plant's death.

Water Star Grass (*Heteranthera dubia*)

Water star grass is a submersed aquatic perennial which roots firmly in bottom sediment. It has long, slender, branched stems and alternate linear leaves up to 15 cm long, from 2 to 6 mm wide, with no discernible central vein. A sheath-like structure with a pair of pointed lobes occurs at the base of each leaf. Its star-shaped, six-parted yellow flowers rise to the surface on stalks from enclosing, leaf-like spathes in the upper leaf axils. Viable seeds over-winter in bottom sediments and germinate the following spring. Water star grass also reproduces asexually, producing new plants from broken stems. The species is native and widespread in the Eastern and Midwestern United States.

Figure 6-41 shows two data points for the analysis of the water star grass from the lagoon-based system. It appears that 2A-DNT, 4A-DNT, and 3,5-DNA increase significantly over time. It should be noted that although this plant survived long enough to take a sample during the April 1997 sampling period, the levels of accumulated explosives, particularly the metabolites, continued to rise. Since these plants were immersed in contaminated water, it is likely that they experienced both accumulation and metabolic breakdown. The metabolites accumulated significantly in the plant tissue which, in the end, probably contributed to the death of the water star grass.

6.2.5.6 Gravel-Based Plants

General Information

After reviewing the data for the gravel-based system's plants, it was determined that the behavior of the plants in cell A1 and cell A2 were different. Thus, data for cells A1 and A2 will be presented separately. As mentioned above, the results of the plant sampling were not

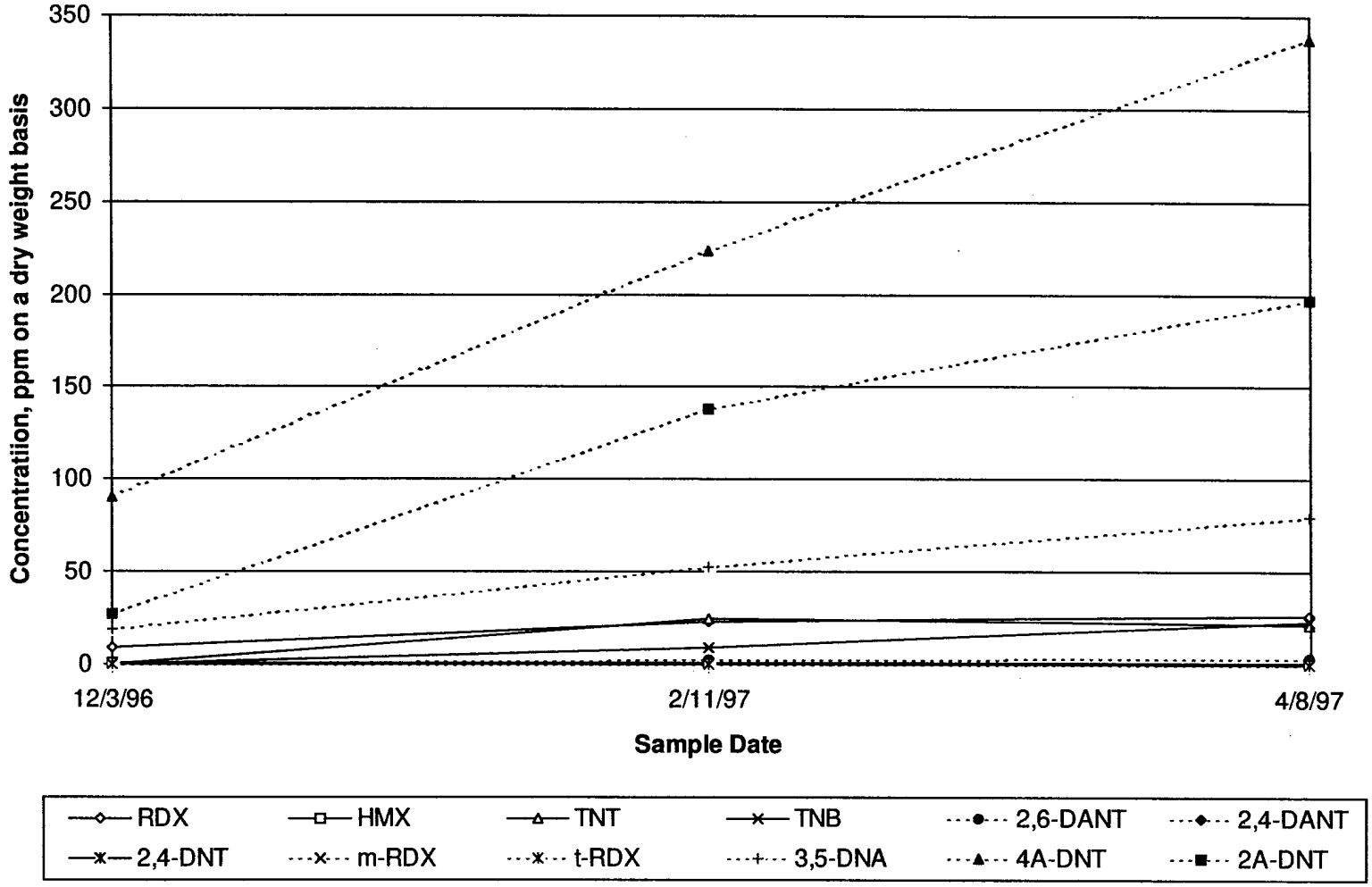


Figure 6-41

Accumulation of Explosives and Metabolites in Water Star Grass in Lagoons as a Function of Time

meant to be exhaustive, but to give a general idea on the behavior of the explosives as they were taken up into the plant systems. In general, however, there appears to be a buildup of RDX and some of the amino breakdown products during the winter months. With the onset of the growth season, the explosives and breakdown products in the plant decrease significantly. This may have been due to a rapid increase in biomass which effectively diluted the concentration of the explosives and metabolites, or it may have been due to increased physiological metabolism in the plants.

Canary Grass (*Phalaris arundinacea*)

Canary grass is an emergent rhizomatous aquatic perennial. The plant has an erect smooth stem with flat leaf blades. The plant stems lie on the ground near the base with rooting occurring at nodes along the base. The plant stands 0.6 to 1.5 meters tall. Leaf blades are 5 to 12 mm wide. The plant ranges from Alaska southward to North Carolina, Kentucky, Missouri, New Mexico, Arizona, Tennessee, and California.

Figure 6-42 shows five data points for the analysis of explosives and breakdown products for canary grass in cell A1 over the course of the demonstration. As the figure shows, the RDX, 4A-DNT, and 2A-DNT concentrations increased during the winter months and then decreased as the growth season began. The metabolites appear to begin to be metabolized as early as February 1997. However, RDX does not begin to metabolize until plant growth begins in late March 1997. A decrease in the explosives and in the metabolites occurs as the system moves from winter to summer for the canary grass in cell A2, as indicated in Figure 6-43. In both cases, the concentration in the canary grass had dropped below the detection limit by the summer of 1997.

Sweetflag (*Acorus calamus*)

Sweetflag is a perennial herb with a thick rhizome and sword-shaped leaves. The leaves are 3 to 15 cm long, 0.7 to 2.5 cm wide, and are sessile (i.e., lie on the main stem). The flowers are bisexual 3-parted and greenish. The fruit is a gelatinous, few-seeded berry. Sweetflag can be found in shallow waters near meadows, marshes, and swamps. In the United States, the plant can be found south of the Canadian border from Georgia to northeast Texas.

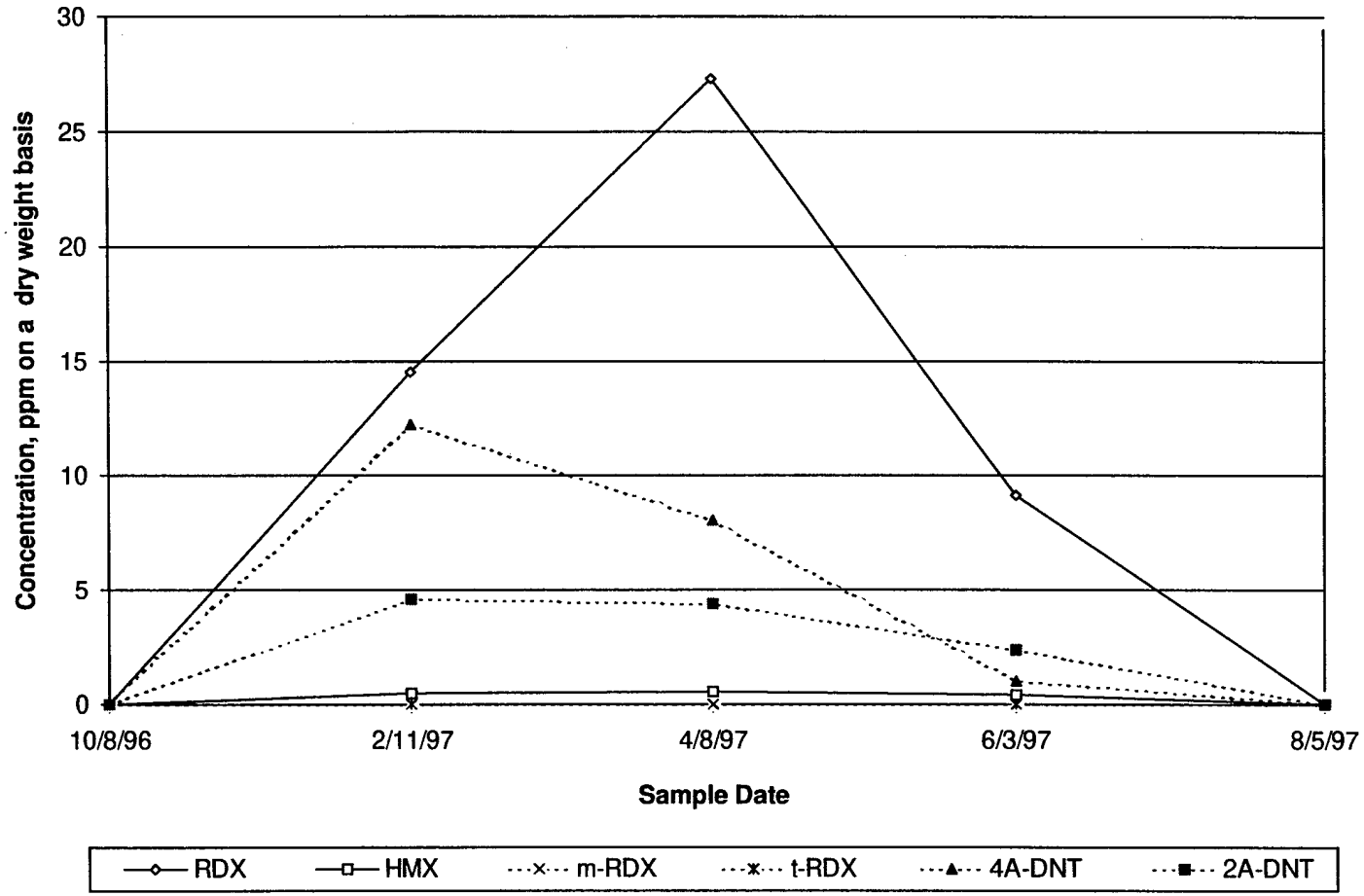


Figure 6-42

The Concentration of Explosives and Metabolites in Canary Grass in the Anaerobic Gravel-Based Cell (Cell A1) as a Function of Time

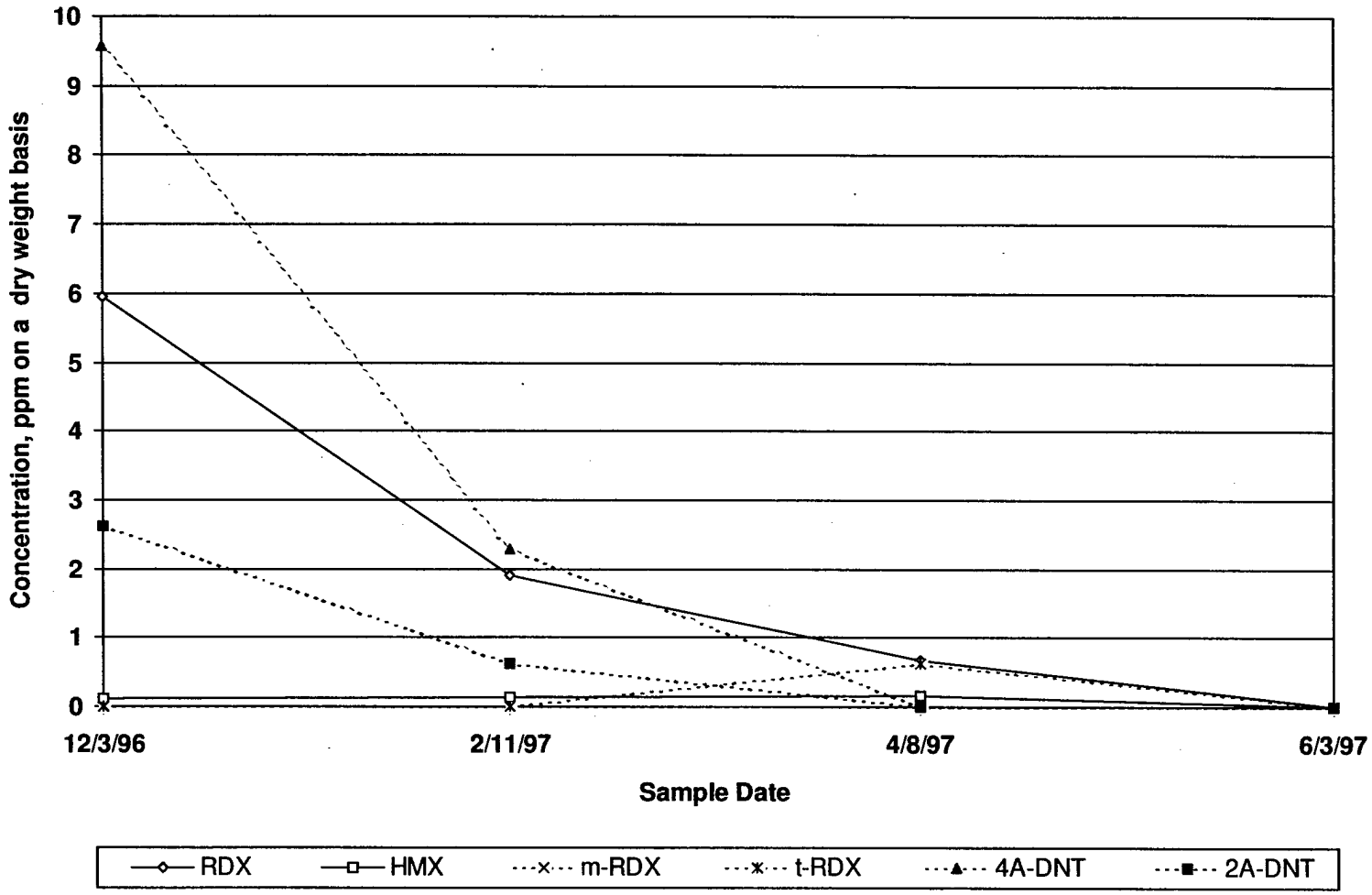


Figure 6-43

The Concentration of Explosives and Metabolites in Canary Grass in the Aerobic Gravel-Based Cell (Cell A2) as a Function of Time

Figure 6-44 shows the concentration of explosives and metabolites for sweetflag in cell A1. For this cell, there does appear to be some buildup of some of the explosives and by-products during the winter months. However, the general trend indicates a decrease in all of the analytes over the period of the demonstration. This might suggest that, as the biomass increases and the sweetflag becomes established, it can more easily metabolize the explosives and the metabolites it absorbs. Figure 6-45 shows the concentration of explosives and metabolites for sweetflag for cell A2. Again, this shows the general decrease in explosive and metabolite concentration over the period of the demonstration.

Wool Grass (*Scirpus cyperinus*)

Wool grass is a perennial from short, tough fibrous rhizomes. Stems are 3- to 6-mm thick, obscurely triangular above, with four to nine leaves. Leaf blades and sheaths are nearly smooth, sometimes with short cross-partitions or thickenings. Wool grass is found in wet meadows, marshes, and ditches. In the United States, the plant can be south of the Canadian border to Georgia and west to Texas and Nebraska.

Figure 6-46 shows the concentration of explosives and metabolites for wool grass over the course of the demonstration. It is interesting that the concentration for RDX continued to increase until June 1997 when it began to decline.

Figure 6-47 shows six data points for the analysis of explosives and metabolites for Wool Grass in cell A2. In this cell, the concentration of RDX drops off early in the year and does not increase. This behavior is quite different than that found in A1. It should also be noted that the other breakdown products observed (m-RDX, t-RDX, 4A-DNT, and 2A-DNT) do not drop below the detection limit as has been observed in other cases.

Parrotfeather (*Myriophyllum aquaticum*)

Parrotfeather is a submersed/emergent aquatic perennial milfoil. It roots to the bottom and has relatively stout stems up to 2.0 meters long. Parrotfeather is unusual among the milfoils because most of its leaves emerge above the surface (generally about 25 cm) rather than being

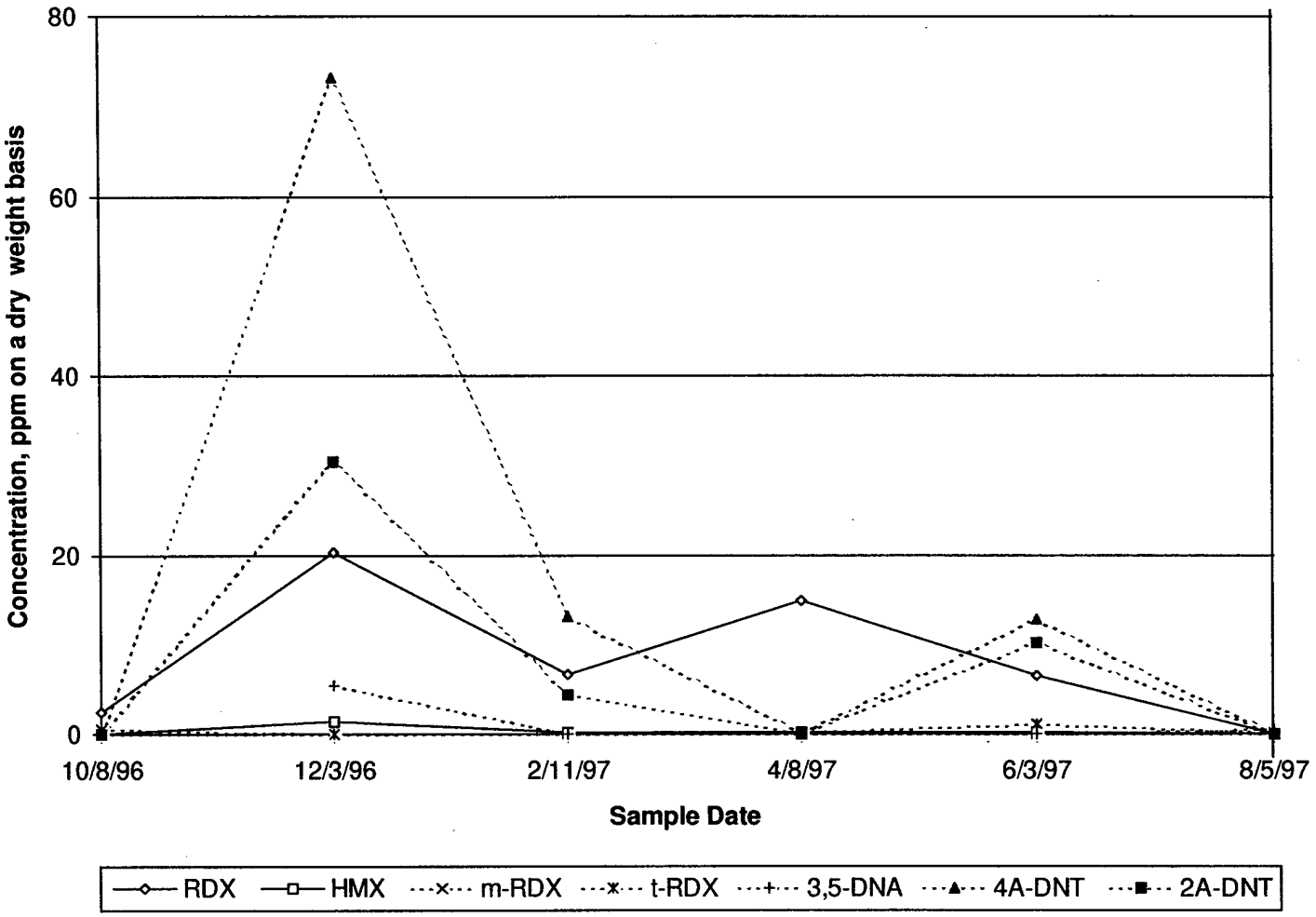


Figure 6-44

The Concentration of Explosives and Metabolites in Sweetflag in the Anaerobic Gravel-Based Cell (Cell A1) as a Function of Time

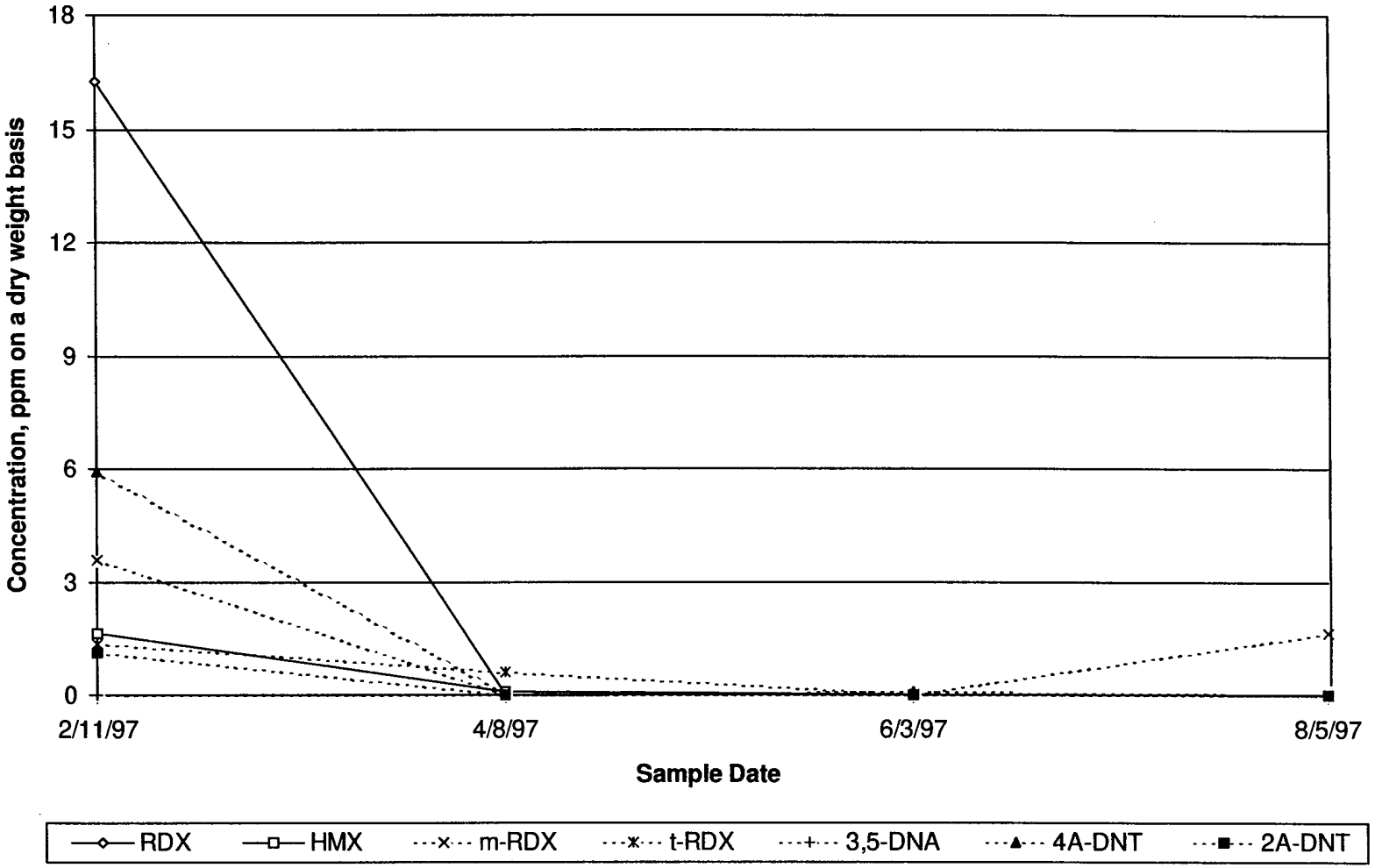


Figure 6-45

The Concentration of Explosives and Metabolites in Sweetflag in the Aerobic Gravel-Based Cell (Cell A2) as a Function of Time

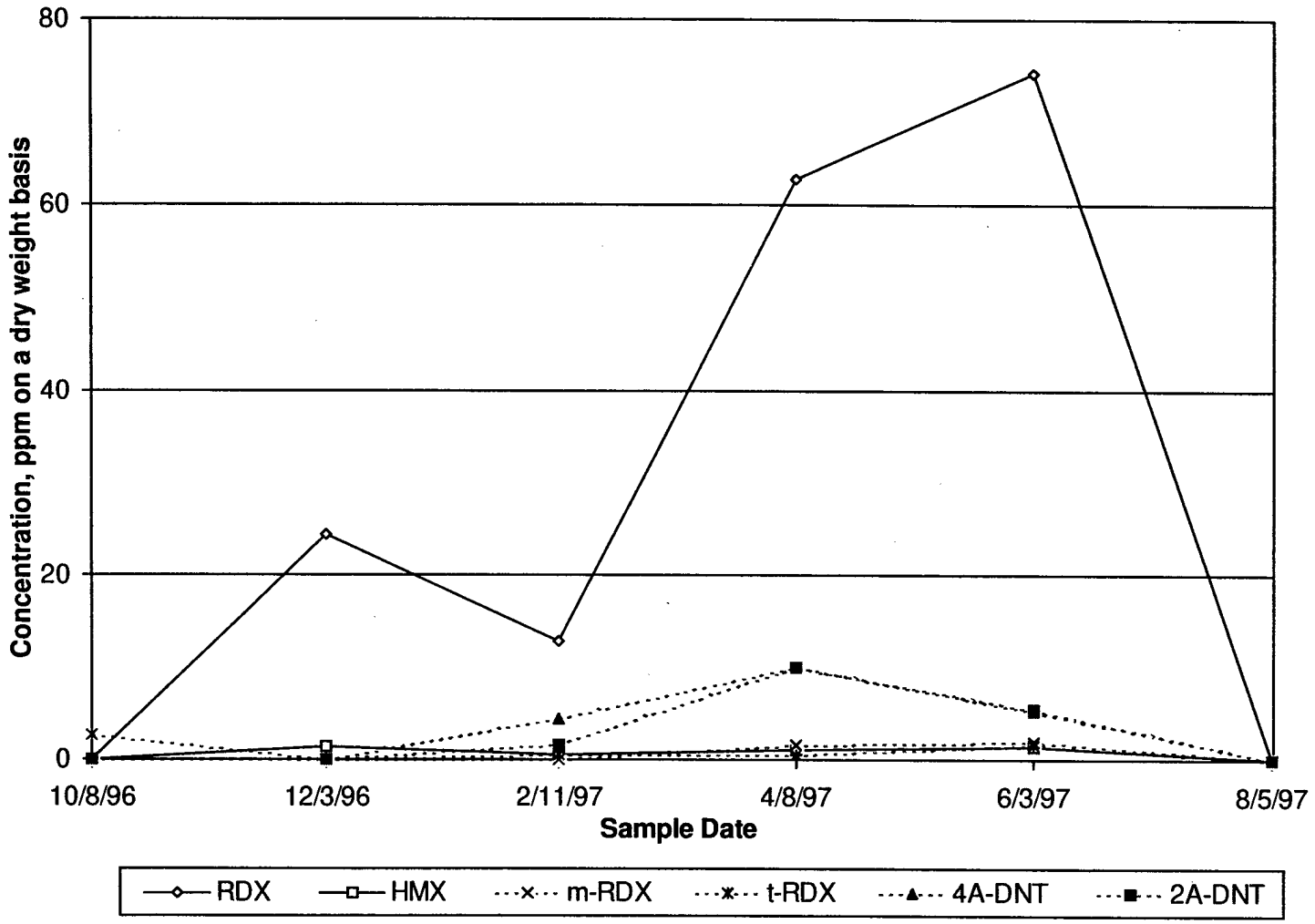


Figure 6-46

The Concentration of Explosives and Metabolites in Wool Grass in the Anaerobic Gravel-Based Cell (Cell A1) as a Function of Time

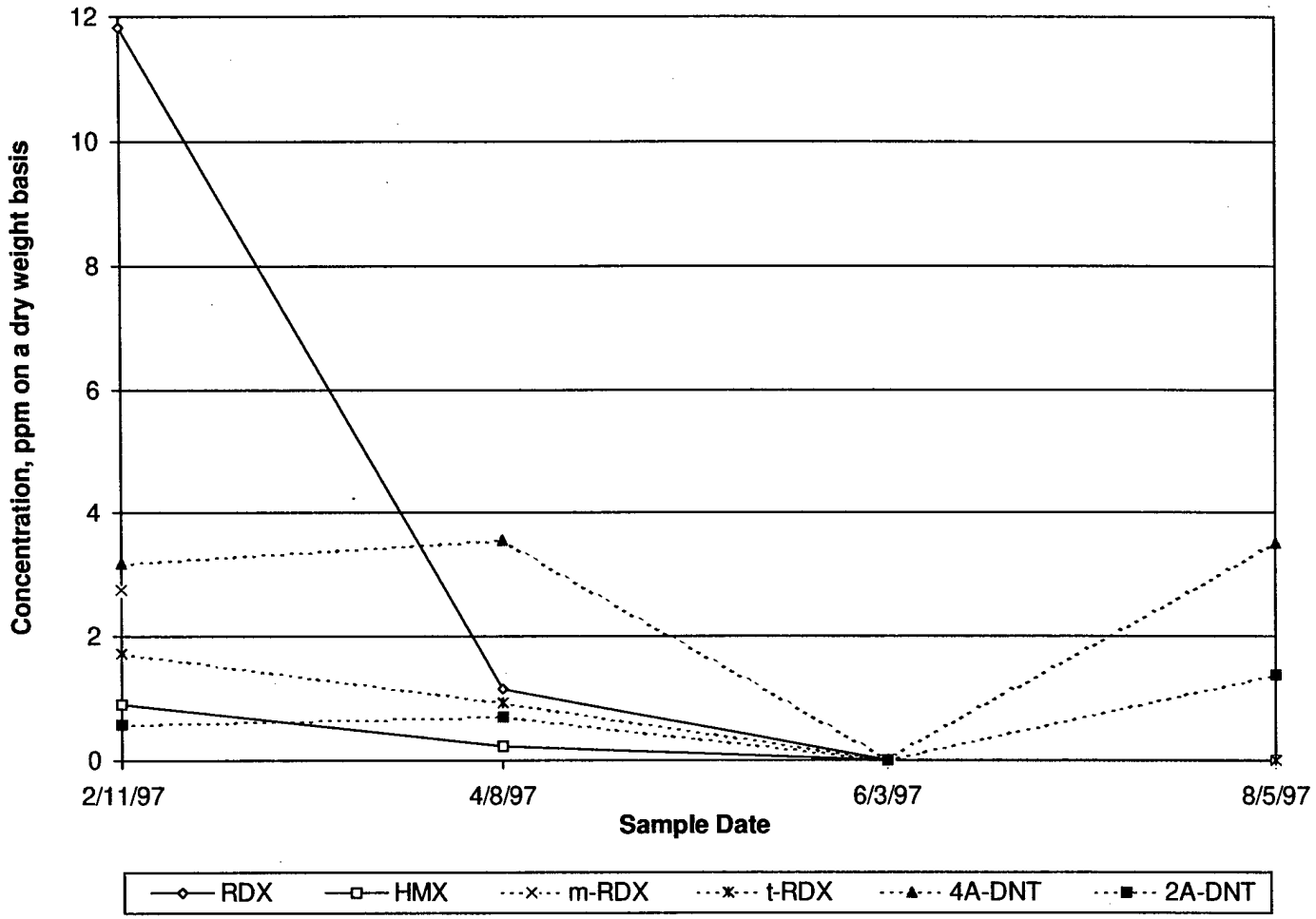


Figure 6-47

The Concentration of Explosives and Metabolites in Wool Grass in the Aerobic Gravel-Based Cell (Cell A2) as a Function of Time

submersed. It has green-gray leaves that resemble feathers and are 2- to 5-cm long with 6 to 18 pairs of thread-like segments. Leaves are arranged in whorls of 3 to 6 around the stems. The flowers are small, unisexual, and located in the leaf axils. The plant seldom flowers and only plants with female flowers are known to occur in the United States. Thus, propagation is solely through fragmentation. The species is native to South America. It grows in cooler lakes, ponds, springs, and canals in scattered areas of the southeastern United States. In the Tennessee Valley, the plant is commonly found in springs and small spring-fed streams.

The parrotfeather in the gravel-based system did not grow as well as the other plant species. The wetland's gravel surface experienced significant temperature increases from solar radiation and it is believed that the parrotfeather, which lay on the gravel surface, could not tolerate the increased temperature. Analysis of the parrotfeather also showed it contained a much wider variety of metabolites than other species. Parrotfeather even contained un-metabolized TNT in the plant material which was unique in the emergent plant species. The concentration of the metabolites also tended to be higher than in other species. Figure 6-48 shows the concentration of explosives and the metabolites for parrotfeather in cell A1. Figure 6-49 shows the concentration of explosives for parrotfeather in Cell A2. In both cases, there are several metabolites that did not appear in any of the other plants in the gravel-based system. In addition to those found in the other plants, 1,3,5-TNB, 2,6-DANT, 2,4-DANT, 2,4-DNT, and 3,5-DNA were also found in the parrotfeather. However, the overall trend for accumulation is similar for those analytes found in other emergent species. It is also interesting to note here that in the study conducted by WES, they found that 81% of the observed radioactivity was in the leaves which was far higher than other plant species. This might suggest that parrotfeather is much more efficient in metabolizing the explosives and incorporating it into new growth than other species tested.

6.2.5.7 Plant Uptake Conclusions

It appears that the plants involved in the wetlands demonstration, in either the lagoon- or gravel-based system, take up and metabolize explosives to some degree. This is consistent with the experiments conducted by WES where they showed that the explosives were taken into the growing portions of the plants and then metabolized (Appendices E and F). The plants

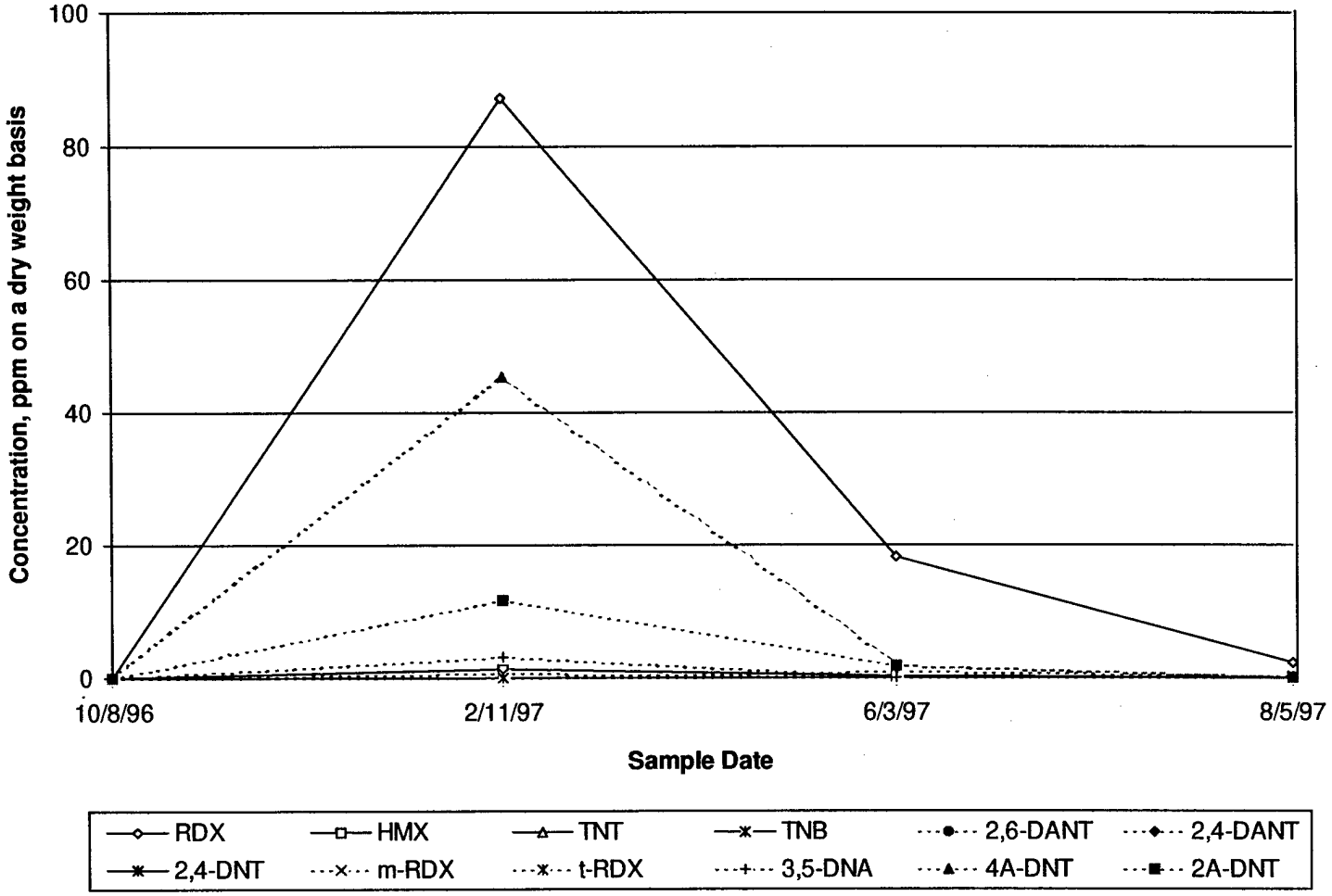


Figure 6-48

The Concentration of Explosives and Metabolites in Parrotfeather in the Anaerobic Gravel-Based Cell (Cell A1) as a Function of Time

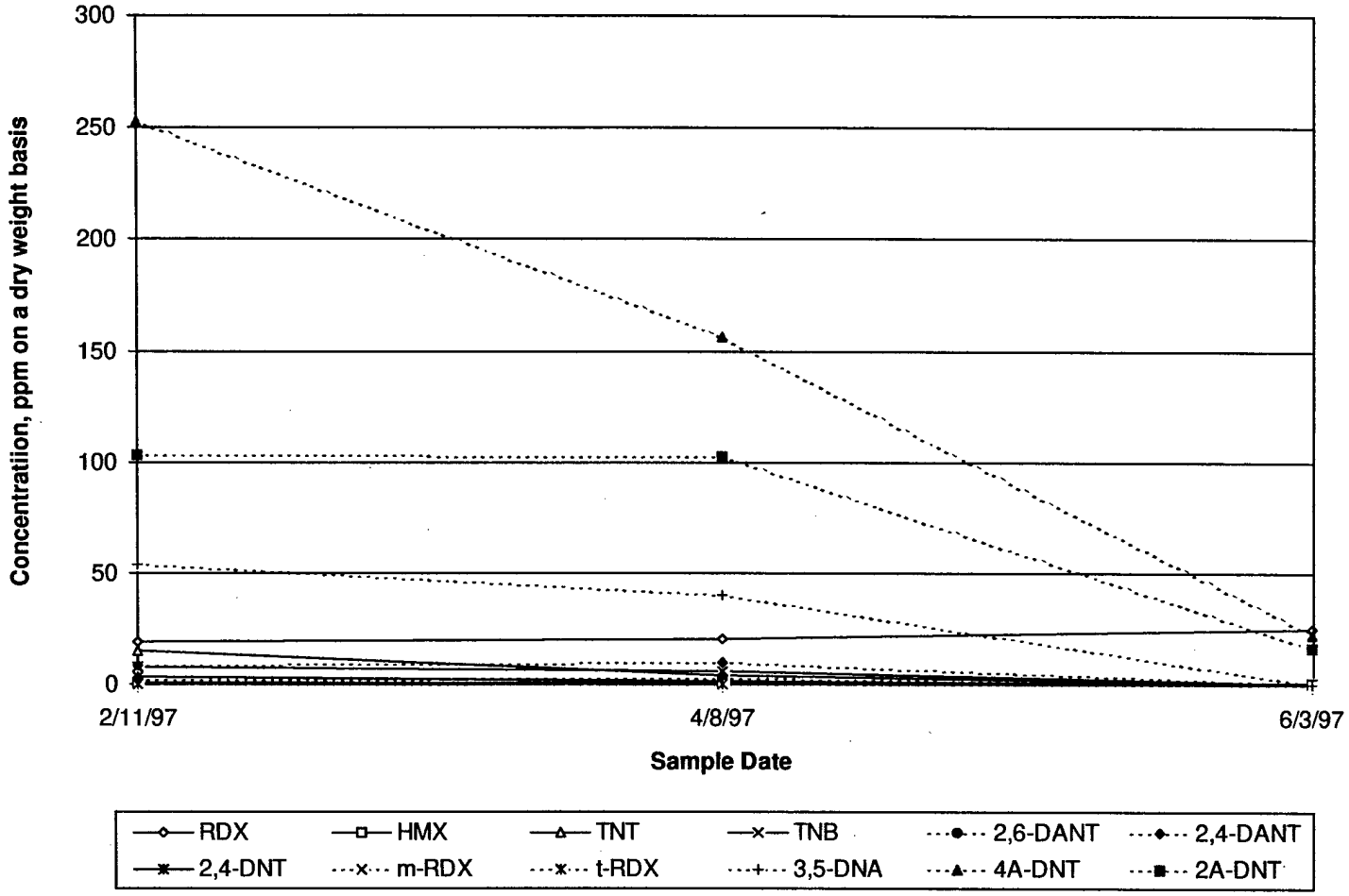


Figure 6-49

The Concentration of Explosives and Metabolites in Parrotfeather in the Aerobic Gravel-Based Cell (Cell A2) as a Function of Time

in the lagoon did not fare well due to several contributing factors. First, problems occurred with the natural introduction of tadpoles that ate the plants, as described in Section 4.2.2. Second, the water developed a deep red color due to photodegradation that reduced the light reaching the plants, limiting their ability to photosynthesize. It is beyond the scope of this demonstration to determine which of these factors caused the failure in the lagoon-based plant's ability to thrive.

In the gravel-based system, the plants seemed to do an increasingly better job at metabolizing the explosives they adsorbed over the course of the demonstration. This could have been due to several factors. First, the biomass of the plants increased very rapidly during the growth period at the beginning of the summer of 1997. This quick increase in biomass may have effectively diluted the concentration of explosives and by-products in the plant tissue making it appear as if the concentration had decreased. Second, as the plants began growing in the spring of 1997, their metabolism increased. This would have increased the metabolism of the explosives in the tissue. Third, it may have taken the plants a year to fully acclimate to utilizing explosives as a nutrient source. Thus, as the demonstration progressed, the plants in the gravel-based system more effectively metabolized the explosives and their metabolites. It would require another year of sampling plant tissue during the different seasons to determine which of these effects is the most significant. However, in terms of overall system operation, there does not appear to be any large buildup of explosives in the plant tissue.

Because of the nature of this demonstration, it was difficult to conduct a mass balance for uptake of explosives into the plants. However, the work that WES conducted with the radio-labeled material attempted to address this question. Utilizing plants from the demonstration site, they conducted radiolabel tracer studies to determine the rate of uptake and metabolism of the explosives. They showed that for submersed plants, the highest rate for TNT uptake came from elodea (0.05 mg TNT g FW^{-1} d^{-1}) and for emergent plants, parrotfeather, sweetflag, and reed canary grass (0.006 mg TNT g $FW^{-1}d^{-1}$) had the fastest uptake. They showed that the rate of RDX uptake was significantly lower, but uptake did occur. They also found in their studies that TNT was rapidly metabolized in the plants resulting in no accumulation and that RDX was also metabolized, but at a lower rate. This is consistent with the information found in the field demonstration. They determined that most of the explosives and metabolites in the plant tissue were broken down or were accumulated in

the active growth areas of the plants. They also saw very little CO_2 generation, indicating that the degraded compounds stayed within the plant biomass. The field demonstration indicates that there is a strong seasonal variation in the effectiveness of the plants to metabolize the explosives. Seasonal variations were not included in the scope of work conducted by WES. To understand how the plants sequester and metabolize the explosive materials during seasonal variations, an isotope study would have to be conducted that included seasonal variation.

Since the plants are metabolizing the explosives over time and the plant biomass changes seasonally, it is not possible to determine the total amount of explosives that are taken up by the plants in the field demonstration. However, based on one year's worth of limited samples, the plants do not appear to be sequestering the explosives to any high concentration. This is also consistent with the data collected by WES in the radiolabel studies. Furthermore, even though the plants in the lagoon died, it was not possible from this data to determine if they died as a result of toxicity or due to poor growing conditions.

Based on the limited data from the demonstration and WES's report, it appears that plants can be effective in metabolizing and effectively reducing the concentration of explosives in groundwater.

SECTION 7.0

INFORMATION NEEDED TO DETERMINE PROJECT-SPECIFIC ECONOMIC AND TECHNICAL FEASIBILITY

Although generally competitive with other remediation methods, a wetland's economic and technical feasibility is dependent upon site-specific factors. These factors include: regional temperature variations, rainfall patterns, groundwater flow characteristics, explosive type, explosive concentration, the presence of other contaminants, regulatory restrictions on the use of non-native plant species, and other regulatory requirements. These factors can affect a wetland's configuration, size, performance, and cost. As a general rule, wetlands perform better in warmer climates with moderate levels of rainfall. Operational performance in colder climates is reduced. However, cost-competitive operation in less attractive climates is not out of the question. The nature of the explosive can also affect the system cost. For example, sites contaminated with TNT may be remediated with a low-cost, lagoon-based system while sites contaminated with RDX and HMX would require the use of a gravel-based system. A comparison of the advantages and disadvantages of these systems is provided in Table 7-1.

Because of the complexity of these questions, it is generally advisable to consult with wetlands experts when attempting to determine economic and technical feasibility. The TVA RM or AEC can provide assistance in this regard by providing access to the required expertise. A certain amount of information will be needed to perform a CERCLA feasibility study. This information includes:

- A description of local groundwater conditions including:
  - A description of the location of contaminated groundwater
  - AN understanding of groundwater movement (rate and direction of movement)
  - The maximum pumping rate that can be sustained by local wells
  - The minimum pumping rate required to ensure groundwater capture
  - The necessary treatment flow rate for the entire system
  - A listing of explosive and explosive by-product contaminant concentrations, including average concentrations and maximum known concentrations

Table 7-1

Comparison of Advantages and Disadvantages of Gravel- and Lagoon-Based Wetlands

Characteristic Compared	Gravel-Based System	Lagoon-Based System
Public perception	Favorable	Less Favorable
Total Cost	Low	Lower
Ability to degrade explosives	Various explosives degradable	Generally limited to TNT
Mixing characteristics	Plug-flow (desirable)	Complete Mix (less desirable)
Capable of removing metals from groundwater	Yes	No
Absolute need to use:		
Local plant species	Optional[1]	Required
Plant species as carbon source	Optional[1]	Not Applicable
Nirtoreductive plant species	Not Required	Required
Locally exotic plants	Not Required	May be Required
Exposure of Wildlife to:		
Open water	Minimal[2]	High
Exposed plant life	High to None[1]	High

1) Assumes plant use is optional in the gravel-based systems.

2) Open water is present in the gravel-based system only when excess water is present after periods of high rainfall.

- A listing of the average and maximum concentrations of any other known contaminants in the groundwater (metals, hydrocarbons, etc.)

- A listing of local regulatory requirements including:
  - Whether surface or groundwater discharge is preferred
  - The discharge limits for explosives, metals, and other chemical contaminants
  - Any other discharge criteria (pH, BOD-5, COD, total suspended solids, etc.)

- A description of local weather conditions including:
  - Maximum and minimum temperature ranges
  - Rainfall data, including the maximum known 15-minute, 1-hour, and 24-hour accumulations; and both the average and maximum historical annual rainfall accumulations
  - Solar radiation, prevailing winds, and relative humidity

- A description of local site conditions including:
  - Area maps
  - Identification of a preferred location for the facility
  - Identification of discharge points
  - A description of soils likely to be encountered during construction
  - A list of local gravel suppliers and distance from potential construction site

Although a general recommendation can be made based on the information above, it may be necessary to conduct treatability studies to determine the feasibility of using constructed wetlands at a particular site. Such tests are conducted:

- To determine which plant species can be used
- To account for regional temperature extremes
- To verify a wetland's ability to remove specific explosives at the site concentration
- To verify sizing assumptions at high explosive concentrations
- To verify a wetland's ability to remove other local contaminants

SECTION 8.0
COMMERCIAL-SCALE DESIGNS

8.1 General Background

This section provides a description of a commercial-scale, gravel-based wetland. A commercial-scale, lagoon-based wetland could be constructed in a manner similar to the demonstration design (except for substituting earthen berms for prefabricated side panels). Therefore, the demonstration system's original description is adequate to describe commercial-scale, lagoon-based systems and they will not be discussed further.

The gravel-based, commercial-scale system described in this section is based on a conceptual design developed to remediate 200 gpm of groundwater at MAAP. The commercial-scale wetland was designed to remove both explosive and metal contaminants from groundwater beneath B-line. In contrast, the demonstration system, described previously in Section 2.3, was designed to treat 5 gpm of contaminated groundwater. The overall design of the commercial-scale system is similar to that developed for the demonstration system; however, some of the subsystems were altered to account for site differences and lessons learned during the MAAP demonstration. The conceptual design of the commercial-scale system also provides the basis for the cost estimate in Section 9.

The commercial-scale design was developed in October 1997 after MAAP requested that an evaluation of a gravel-based wetland be included in a feasibility study being developed by the U.S. Army Corps of Engineers (USACE), Mobile District. The goal of the USACE feasibility study is to determine the technical and economic feasibility of using commercial-scale systems for the treatment of explosives-contaminated groundwater near B-line. The study is being written by the U.S. Army Corps of Engineer's remediation contractor, ICF Kaiser. To facilitate technology transfer, TVA RM provided ICF Kaiser with design and cost data. ICF Kaiser will examine this and other available information and provide the Corps of Engineers with recommendations at a later date.

At ICF Kaiser's request, TVA RM analyzed two options. One was for treating groundwater to surface water discharge standards and the second was for treating groundwater to groundwater reinjection standards.

8.2 Groundwater Contaminant Levels at MAAP B-Line

The B-line groundwater contains both explosive and metal contaminants. The primary explosive contaminants include: RDX (807 ppb), HMX (91 ppb), and TNT (52 ppb). Other explosive-related contaminants are present such that the sum of regulated explosive and explosive by-products is at a maximum of 953 ppb (Table 8-1). Of the explosive contaminants, RDX will be the most difficult to degrade because of its relative concentration and recalcitrance. Metal contaminants present include: arsenic, barium, cadmium, copper, lead, and zinc (Table 8-2). Of these, zinc provides the greatest challenge.

8.3 Technical Performance Criteria

The commercial-scale system's technical performance criteria are based on MAAP's current needs and differ from those proposed for the demonstration (personal communication with ICF Kaiser). The new technical performance criteria are as follows:

For surface water discharge

A discharge limit of 100 ppb for all "regulated explosive and explosive by-products." Where the term "regulated explosive and explosive by-products" is defined to mean the sum of the following chemicals: 1,3-Dinitrotoluene; 2,4-Dinitrotoluene; 2,6-Dinitrotoluene; HMX; Nitrobenzene; RDX; Tetryl; Trinitrobenzene; 2,4,6-Trinitrotoluene (TNT); Mononitroso RDX; Dinitroso RDX; Trinitroso RDX; 2-Amino-4,6-dinitrotoluene; 4-Amino-2,6-Dinitrotoluene; 2,6-Diamino-4-nitrotoluene; and 2,4-Diamino-6-nitrotoluene.

Table 8-1

Expected Explosive and Explosive By-Product Discharges From Milan Wetland

Chemical	Maximum Concentration Encountered (ppb)	Expected Surface Water Discharge[1] (ppb)	Surface Discharge Limit (ppb)	Expected Groundwater Discharge[1] (ppb)	Groundwater Discharge Limit (ppb)
Overall Regulatory Standards					
The Sum of all Regulated Explosives and By-Products[2]	953	66	100	15	-
The Sum of RDX and RDX By-Products		59	-	13	26
Explosives					
2,4,6-Trinitrotoluene (TNT)	51.7	<1	-	<1	10
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	807	42	-	9.6	-
Tetryl	<1.56	<1.56	-	<1.56	20
Nitrobenzene	1.48	No Data Available	-	No Data Available	-
Trinitrobenzene (TNB)	2.34	<1	-	<1	
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	90.9	11	-	2.6	2,000
1,3-Dinitrotoluene	<0.611	No Data Available	-	No Data Available	No detect
2,4-Dinitrotoluene (2,4-DNT)	1.34	<1	-	<1	0.5
2,6-Dinitrotoluene (2,6-DNT)	<0.074	<1	-	<1	No detect

1) Expected discharge at the highest concentration to occur during winter operations.

2) Regulated explosive and by-products for surface discharge include: 1,3-Dinitrotoluene; 2,4-Dinitrotoluene; 2,6-Dinitrotoluene; HMX; Nitrobenzene; RDX; Tetryl; Trinitrobenzene; 2,4,6-Trinitrotoluene (TNT); Mononitroso RDX; Dinitroso RDX; Trinitroso RDX.; 2-Amino-4,6-dinitrotoluene; 4-Amino-2,6-dinitrotoluene; 2,6-Diamino-4-nitrotoluene; and 2,4-Diamino-6-nitrotoluene.

Table 8-1 (Continued)

Expected Explosive and Explosive By-Product Discharges From Milan Wetland

Chemical	Maximum Concentration Encountered (ppb)[1]	Expected Surface Water Discharge[1] (ppb)	Surface Discharge Limit (ppb)	Expected Groundwater Discharge[1] (ppb)	Groundwater Discharge Limit (ppb)
TNT By-Products					
2-Amino-4,6-dinitrotoluene (2A-DNT)	Not Analyzed	<1	-	<1	-
4-Amino-2,6-dinitrotoluene (4A-DNT)	Not Analyzed	<1	-	<1	-
2,6-Diamino-4-nitrotoluene (2,6-DANT)	Not Analyzed	<1	-	<1	-
2,4-Diamino-6-nitrotoluene (2,4-DANT)	Not Analyzed	<1	-	<1	-
RDX By-Products					
Mononitroso RDX (m-RDX)	Not Analyzed	6.9	-	1.6	-
Dinitroso RDX (d-RDX)	Not Analyzed	No Data Available	-	No Data Available	-
Trinitroso RDX (t-RDX)	Not Analyzed	29	-	6.5	-
Water Quality Parameters					
Biochemical Oxygen Demand (BOD-5)	Not Analyzed	1,500	Unknown	1,500	Unknown
Total Suspended Solids	Not Analyzed	8,000	Unknown	8,000	Unknown
pH	Not Analyzed	7.0	Unknown	7.0	Unknown

1) Expected discharge at the highest concentration to occur during winter operations.

Table 8-2

Expected Metals Discharge From the Milan Wetland Using Average Incoming Metals Concentration as a Design Basis

Chemical	Expected Initial Metals Concentration (ppb)	Expected Discharge[1] (ppb)	Surface Discharge Limit (ppb)	Groundwater Discharge Limit (ppb)
Metals				
Arsenic	1.4	No Data Available	1.4	50
Barium	23.6	<23.6	No Requirement	2,000
Cadmium	0.127	0.025	4.48	5
Chromium	<6.02	<6.02	100	100
Copper	4.18	0.50	34	1,300
Lead	1.4	0.23	17.3	15
Mercury	<0.2	<0.2	0.01	2
Nickel	<34.3	<34.3	363	100
Selenium	<1.0	<1.0	5	50
Silver	<0.10	<0.01	4.06	No Requirement
Zinc	461	115	368	No Requirement

1) Expected discharge based on percent removal as reported in Kadlec and Knight.

For groundwater discharge

A limit of:

- 26 ppb for the sum of RDX and RDX by-products (i.e., RDX, Mononitroso RDX; Dinitroso RDX; and Trinitroso RDX)
- 10 ppb TNT
- 20 ppb Tetryl
- 2,000 ppb HMX
- 0.5 ppb 2,4-Dinitrotoluene (2,4-DNT)
- Non-detectable for 1,3-Dinitrotoluene and 2,6-Dinitrotoluene (2,6-DNT)

Both treatment systems were also required to meet the metals discharge limits outlined in Table 8-2.

The standards listed above are stricter than that set for the demonstration system in that:

- The performance standards established here involve the remediation of more explosive by-product components than envisioned under the original standard of less than 50 ppb total nitrobody and TNT of less than 2 ppb TNT (see Section 2.2).

- The groundwater discharge performance standards are stricter for RDX and its by-products.

- The metal concentrations coming from B-line are higher than those coming from the demonstration wells at K-line.

Consequently, the commercial system was designed with a substantially longer retention time than the demonstration system (see discussion in Section 8.4).

It should be noted that the use of gravel-based wetlands provides a means for negotiating higher metal discharge limits. This is possible because metal discharge limits are often set as a function of water hardness. Generally, higher metal discharges are permitted with increased water hardness. Since the groundwater flows through a gravel bed, the treated water's hardness increases with time. Therefore, gravel-based wetlands are often able to discharge water with higher metal concentrations than might otherwise be the case. The wetland's ability to both remove metals and increase water hardness gives it a distinct advantage over other technologies being reviewed.

8.4 Technical Feasibility

TVA's evaluation of the B-line data indicated that the explosive concentrations at B-line can be reduced to the required discharge limits without post-treatment (Table 8-1). The evaluation also indicated that a 10.5-acre, gravel-based system would be required to meet the surface discharge limit. This system would have a hydraulic retention time of 14.5 days. The system designed for groundwater reinjection would have to be slightly larger--about 12.8 acres and a retention time of 18.5 days. The larger retention time was required to reduce RDX and RDX by-products to the desired level.

TVA RM also concluded that the wetland could meet the metals discharge limits (Table 8-2). Given the influent metals concentrations at B-line, combined with the increased hardness of the wetland effluent, it appears that none of the incoming metals will have to be removed from the influent if the groundwater is treated by a wetland and discharged by groundwater reinjection. However, if the effluent is to be discharged to surface waters, then the wetland will have to remove zinc from the influent. The gravel-based wetland is expected to remove sufficient zinc to meet the discharge limit.[Ref. 9]

8.5 System Design and Scale-Up Methods

8.5.1 System Scale-Up

The size of the proposed gravel-based wetland was calculated from data obtained at the wetland demonstration while treating contaminated water at a rate of 5 gpm from June 1996 to September 1997. The disappearance rate of TNT and RDX was modeled using first-order kinetics. Assuming plug-flow hydraulics, the first-order equation for the reduction of a pollutant in a wetland is:

$$\ln (C/Ci) = -y (k/q) \qquad \text{[Equation 1]}$$

Where k is the first-order rate constant with units of m/yr, q is the hydraulic loading rate at 28 m/yr, y is the fractional distance from inlet to outlet (ranging from 0 to 1), Ci is the influent concentration of the pollutant, and C is the concentration at y. The k value for removal of TNT and RDX in the gravel-based wetland was determined via linear regression of ln (C/Ci) versus -y/q where the intercept was maintained at zero. The slope from the regression was the rate constant, k.

Since RDX was the most recalcitrant explosive, sizing of the wetland was based on the removal rate for RDX. Based on first-order kinetics and the initial RDX concentration to be experienced at B-line, the retention time of 7.5 days in the anaerobic wetland at the Milan demonstration was not adequate to reduce total explosive and explosive by-product concentrations below 100 ppb for surface water discharge or 26 ppb for RDX and RDX by-products for groundwater reinjection.

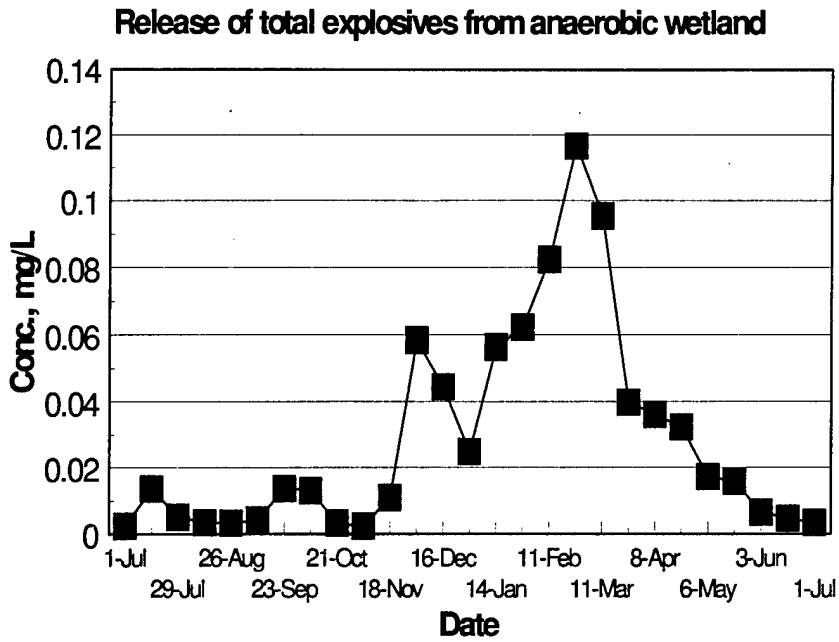
Equation 1 was used to determine the additional wetland area and retention time required to remove RDX and RDX by-products to desired levels.

To determine the effluent concentration from a proposed system with an increase in retention time over the demonstration at Milan, the concentration released from the anaerobic gravel-based cell was used as Ci. The removal of RDX by-products was assumed to occur at a similar rate as the parent RDX compound. The same rate

constant was assumed to apply to TNT degradation. Since TNT degradation is much faster than RDX degradation, the use of the RDX constant for TNT removal was a conservative estimate. The rate constant used for the calculation was the constant for RDX degradation in April 1997 (Figure 6-32). This was the next to the lowest rate constant observed. The lowest rate constant was not used since it occurred when the demonstration system experienced severe operational upsets that negatively affected the system's performance.

A first-order kinetics model, as just described, was used to determine effluent concentrations with increased retention time for the gravel-based wetland's anaerobic cell. The effluent concentrations for the aerobic cell were assumed to experience the same percent reduction observed in the Milan demonstration. A 2.5-day retention time was assumed.

Figures 8-1 and 8-2 show the calculated seasonal variations of the effluent "RDX and RDX by-products" and "regulated explosive and explosive by-products" concentrations. Figure 8-1 shows the expected concentrations from the anaerobic and aerobic wetland, respectively, for a total retention time of 14.5 days in the wetland. The 12 days in the anaerobic wetland and 2.5 days in the aerobic wetland ensures effluent concentration of regulated explosive compounds will remain less than 100 ppb year-round, as dictated for surface water discharge. Figure 8-2 shows the expected concentrations from the anaerobic and aerobic wetlands, respectively, for a total retention time of 18.5 days in the wetland. The 16 days in the anaerobic wetland and 2.5 days in the aerobic wetland ensures concentration of RDX and RDX by-products will remain less than 26 ppb year-round, as dictated for groundwater reinjection. The retention time recommended for the commercial-scale system is higher than that for the demonstration-scale system due to a variety of factors including: differing RDX concentrations, differing regulatory requirements, and the development of a stricter standard of wintertime emissions control.



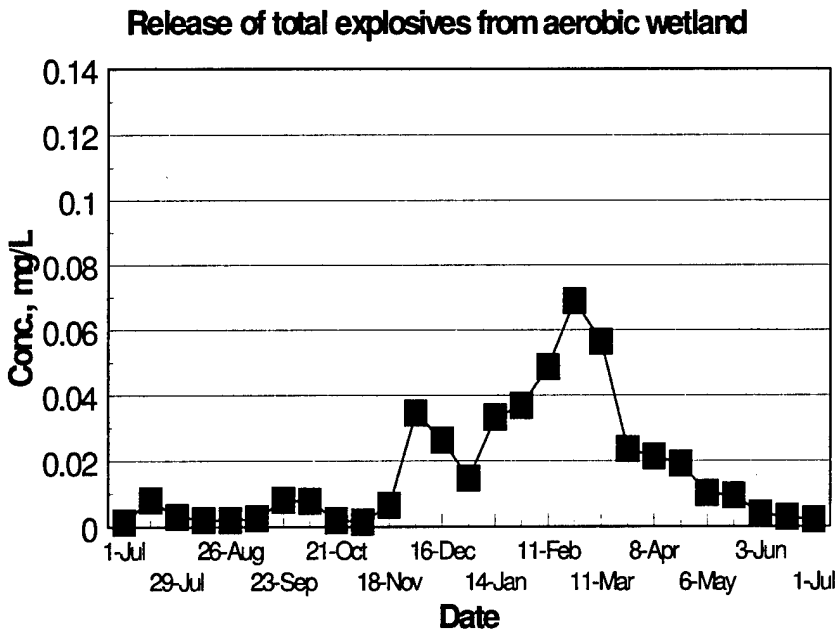
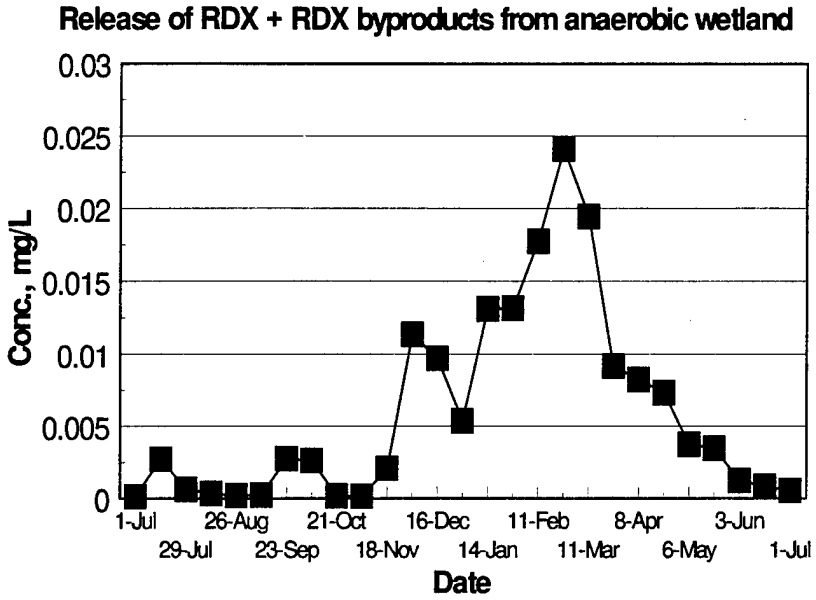


Figure 8-1

Expected Seasonal Variation of Regulated Explosive and Explosive By-Products From a Commercial-Scale Gravel-Based Wetland



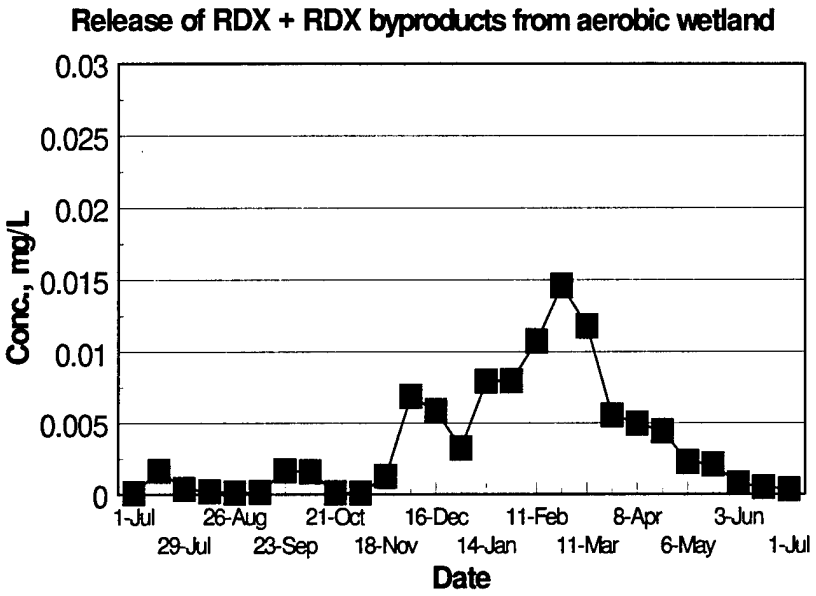


Figure 8-2

Expected Seasonal Variation of RDX and RDX By-Products Concentrations From a Commercial-Scale Gravel-Based Wetland

8.5.2 Considerations for Metals Removal

Allowable metal discharge limits vary with the calcium concentration in the effluent. Because wetlands increase calcium concentrations in the water, higher metal discharges are typically allowed. Therefore, it was important to determine the expected calcium concentration in the effluent water prior to determining how much metal must be removed.

During the wetland demonstration, the incoming water had an average calcium concentration of 23 mg/liter (after November 20, 1996). In comparison, the average calcium concentration leaving the gravel-based wetland was 67 mg/liter. This corresponds to an increase of 44 mg/liter calcium contributed by the wetland. The amount of calcium added via MRS, used as a carbon addition, can be calculated to contribute 3 mg/liter to the wetland water.

Therefore, the gravel from the wetland contributed 41 mg/liter calcium to the water. Converting the increased calcium concentration to calcium carbonate equivalence (CCE) results in 102 mg/liter CCE. This increase in the hardness of the water from wetland treatment results in reduced toxicity from metals in the effluent. The discharge limits for metals in effluent waters with a hardness of 100 mg/liter are shown in Table 8-2 for groundwater reinjection and surface water discharge.

8.6 Process Description

The approximate location of the proposed commercial-scale wetland is shown in Figure 8-3. The system is similar to the demonstration system in that it consists of two gravel-based wetland trains (Figure 8-4). Each train consists of an anaerobic cell and an aerobic cell. The cells are connected in series with the anaerobic cell being the first cell. To operate the wetland, 100 gpm of contaminated water is pumped into each anaerobic cell. The contaminated water is retained in the anaerobic cells for 12 to 14 days, where the combined action of microbial activity and plant enzymes break down the explosive-related contaminants. The metals are removed by the combined actions

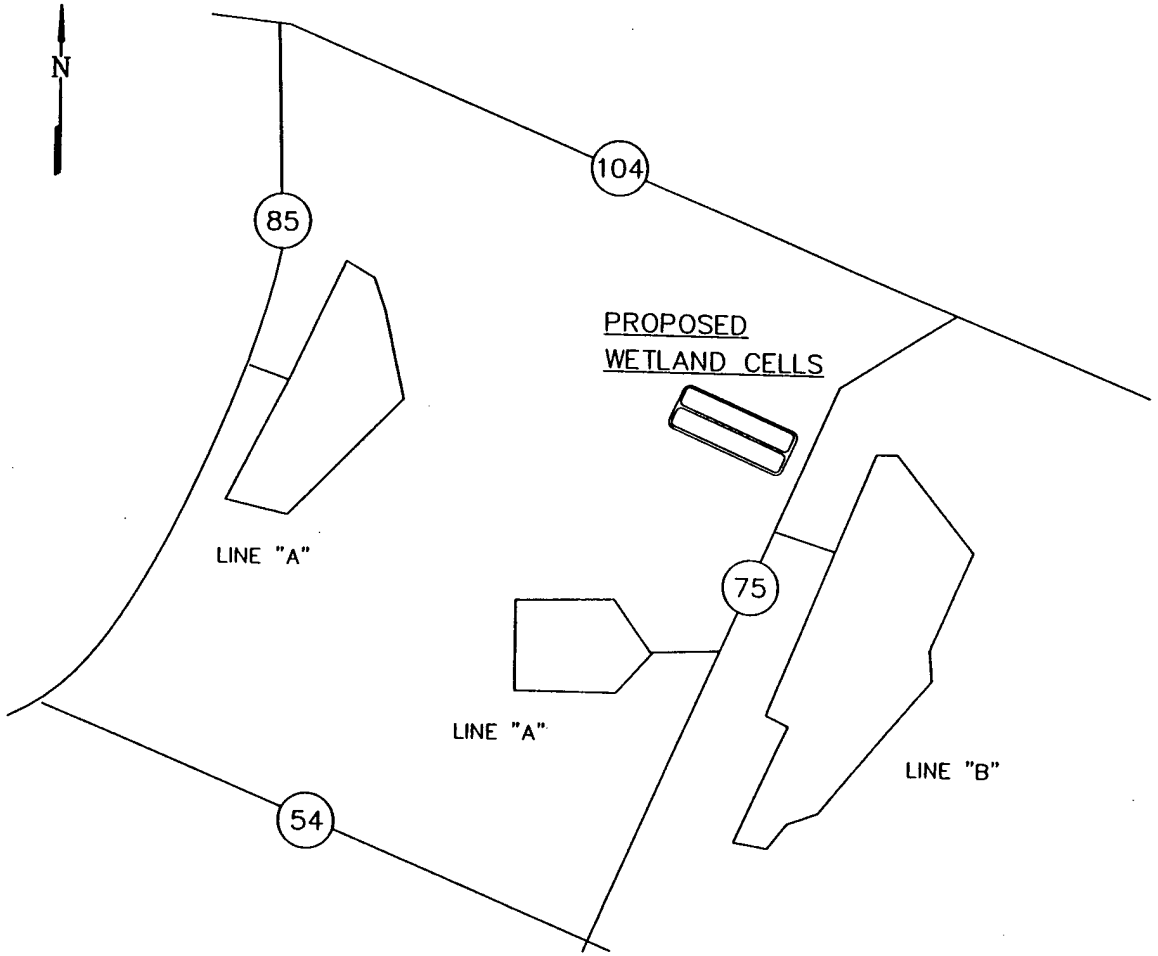


Figure 8-3

Approximate Location of Proposed Milan Wetland

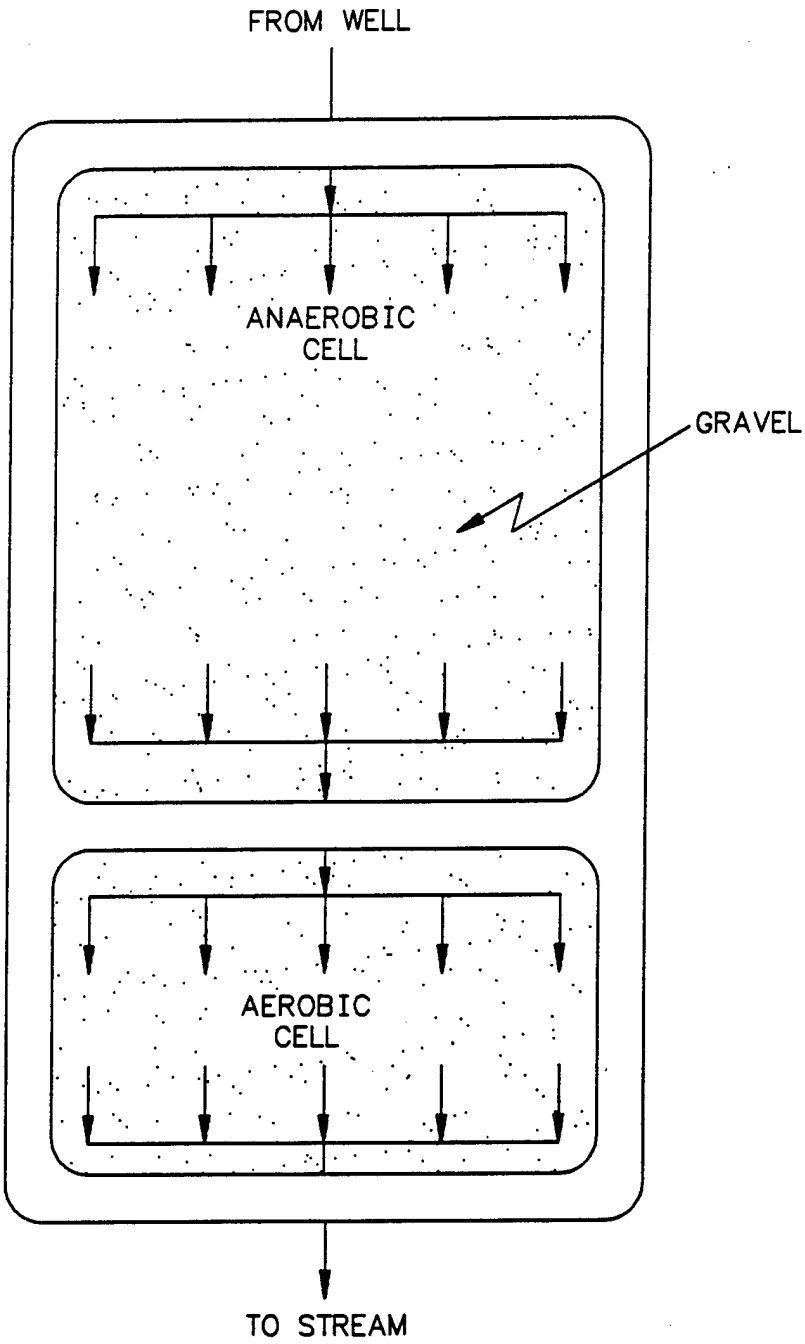


Figure 8-4

Flow Diagram for Typical Wetland Train

of precipitation and sorption in the gravel beds. The water is then discharged to an aerobic cell through a water collection system located at the end of each anaerobic cell.

To promote anaerobic conditions, liquid sucrose (a carbon source) is added to the anaerobic cell on a daily basis. This differs from the demonstration system where the carbon source was MRS. Use of sucrose was evaluated as part of the Alternate Carbon Source and Higher Flowrate Study (see Section 11.3 "Recommendations for Future Work"). A small amount of liquid ammonium phosphate fertilizer (with a N-P-K content of 10-34-0) will also be added.

A system for automatically injecting the carbon and nutrient sources into the wetlands is included in the project design. The design includes: a 7,500-gallon sucrose storage tank; a 100-gallon liquid fertilizer storage tank; 16 dissolved oxygen meters (to be installed in the anaerobic cells); a pumping system; piping; headers; a control system; a control board; and a building to house the tanks, pumps, and control system.

The aerobic cells were designed to further treat the remaining explosive by-products, BOD-5, nutrients, and total suspended solids. The pH is maintained near neutral by direct contact of the water with the calcareous gravel. The aerobic cell is expected to remove 30% to 50% of the explosives and explosive by-products entering the aerobic cell and, therefore, provides additional insurance against the possible release of explosive-related contaminants. The aerobic cell is a proprietary TVA design (patent number 5,863,433). The aerobic cell has been successfully used to treat municipal wastewater at Benton, Tennessee, and was used during the Milan demonstration. Water leaving the aerobic cell does not require any additional treatment and may then be discharged to a local stream by gravity flow. Alternately, it may be re-injected into underground strata.

Physically, each wetland train consists of two gravel-filled basins surrounded by earthen berms. Each basin will be lined with two layers of 30-mil PVC liner to prevent seepage of contaminated water to the underlying soil. This grade of liner is rated for environmental applications and is commonly used at municipal landfills. The first liner holds the basin contents. The second liner provides secondary containment and is also part of a leak detection system. Four inches of gravel separate the first and second liners. The gravel serves as a catch basin for the leak detection system. The bottom of the basins are located two feet below

ground level. The earthen berms rise three feet above ground level. Approximately one foot of freeboard exists between the top of the gravel and the top of the berms. This freeboard space is used to retain rainwater entering the system. The proposed freeboard provides sufficient volume to retain Milan's worst case 100-year, 24-hour rainfall event.

The anaerobic cell's inlet and outlet subsystems were substantially modified to ensure that all rainwater entering the wetland is treated over the specified treatment period, to minimize the possibility of short-circuiting, and to minimize the header blockage problems experienced during the demonstration.

In the new design, the pipe-based inlet and outlet headers were replaced with a distribution channel-based inlet system and dam-based outlet system. In addition, a second distribution channel was placed in the middle of the anaerobic cell to minimize possible short-circuiting. A flood wall was installed near the end of the wetland to encourage the movement of rainwater to the bottom of the gravel bed.

Each of the wetland trains contains two distribution channels. The first channel is located along the width of the anaerobic cell, approximately 15 feet downstream from the top to the exterior berm at the inlet end (starting where the base of the berm and the floor of the basin meet). The second channel is located across the width of the anaerobic cell, approximately midway between the first distribution channel and the discharge end of the anaerobic cell.

Each distribution channel consists of a 5-foot-wide, 5-foot-high concrete trough surrounded by gravel beds. For cost purposes, the walls are assumed to be constructed of 12-inch-wide concrete. A large wall width was specified to ensure that the wetland remained operationally intact in case of an earthquake (MAAP is in a level three earthquake zone). The distance between the exterior of each wall will be 5 feet, providing a 3-foot-wide channel between the walls. Water flows through the upstream wall via twenty 12-inch slotted PVC pipes located at the bottom of the channel. Flow through the downstream wall is through twenty 12-inch slotted pipes located near the surface of the gravel bed. A 5-foot-wide steel walkway straddles the top of each distribution channel. After construction, the basins on either side of each distribution wall will be filled with gravel. Finally, a nutrient/carbon source header will be placed at the bottom of the channels next to the bottom of the upstream wall.

As part of the distribution channel system, a flood wall will be installed about 15 feet upstream of the discharge end of each anaerobic cell. The flood wall will consist of a single 12-inch-wide concrete wall with twenty 12-inch slotted PVC pipes located at the bottom of the wall.

Three dams will be constructed in the berm at the discharge end of each anaerobic cell. The dams will be equally spaced along the width of berm. Each dam provides a 3-foot-wide, gravel-filled channel for incoming water flow. Provisions have been made to allow for flow control through the dam system should this be deemed necessary. Water entering each dam flows over each dam into a sump and then through piping to another sump located on the aerobic side of the dam. Water leaving each dam flows out of the aerobic side sump into a 3-foot-wide, gravel-filled channel leading to the aerobic cell. No headers are used in the dam system, minimizing the possibility of blockage.

Fluid flow through the anaerobic cell is as follows. Contaminated water enters the first distribution channel through three PVC lines which empty into the distribution system's upstream wall. Along the bottom of the channel's upstream wall, a small amount of water will be allowed to flow to the small volume of gravel located behind the first distribution channel. This will relieve any hydraulic pressure which might otherwise affect the upstream wall. The bulk of the fluid flows into the first channel, up to the discharge point (at the top of the downstream wall), and into the gravel bed. The water then flows to the second distribution channel where it enters from the bottom and is discharged at the top. The water leaving the second distribution channel flows through the gravel bed until it encounters the flood wall. The water is forced to the bottom of the flood wall where it empties into a narrow (15-foot-wide) gravel-filled basin between flood wall and the dams at the discharge end. The dam system defines the end of the anaerobic cell. Water from the narrow basin flows to one of three dams located within each anaerobic basin and is discharged to the aerobic cell.

During rainstorms, the horizontal movement of rainwater (surface flow) entering the anaerobic cell is restricted by the walls of the second distribution channel and the flood wall. These walls force the rainwater to flow to the bottom of the anaerobic cell's gravel bed. The flow rate of the water leaving the anaerobic cells is also regulated during rainstorms. When rain

falls, a sensor located in a sump in front of the dams detects the rising water levels. This sensor closes the groundwater inlet line. When the water level recedes, the sensor reopens the groundwater inlet line.

The distribution channel/flood wall system was designed to achieve several objectives:

- Assure an even distribution of water across the width of the anaerobic cell
- Relieve, or assure, even hydraulic pressure across the width of the cells
- Assure good mixing of water and the nutrient/carbon source feeds
- Prevent the development of channels through the gravel beds
- Restrict the horizontal movement of rainwater and force vertical movement to assure treatment of any rainwater entering the cells
- Improve access to the piping for cleaning or backwashing purposes

Both the anaerobic and aerobic cells will be planted with a mix of emergent plant species. Emergent species proposed for the anaerobic cells are canary grass (*Phalaris arundinacea*) and wool grass (*Scirpus cyperinus*). In the aerobic cells, both canary grass (*Phalaris arundinacea*) and sweetflag (*Acorus calamus*) are proposed. Plant selection was based on the use of plants native to western Tennessee and was influenced by the plant's relative ability to thrive in the Milan AAP wetlands demonstration facility and supply carbon to the anaerobic cell. The ability to supply organic carbon is expected to decrease long-term facility operating cost. The plant species selected are perennial and will not require replanting.

The anaerobic cells will initially be inoculated with commercially available forms of anaerobic bacteria. The microbial population is expected to increase rapidly due to the available nutrient supply from fertilization with the carbon and nutrient fertilizer sources. Rapid establishment of the microbial population is more important than early establishment of plant population because the microbes are the primary contributor to the remediation of explosive materials.

SECTION 9.0

ESTIMATED CONSTRUCTION COST OF COMMERCIAL FACILITIES

9.1 General Background

This section provides cost information for the commercial-scale, gravel-based wetland described in Section 8. Cost data for lagoon-based wetlands are not presented because the lagoon-based system did not remove RDX effectively. Since most sites contaminated with TNT also contained significant quantities of RDX, it does not appear that lagoon-based systems are likely to be constructed.

9.2 Capital Cost for the Surface Discharge Option - Gravel-Based-Type Wetlands Only

The estimated battery limits cost of constructing the a 10-acre, gravel-based wetland for treating 200 gpm of groundwater is approximately $3,466,000 (Table 9-1). A total of nine months is allowed for design and construction of the wetland. The battery limits cost provided include all costs associated with constructing the wetland and should be considered a "turnkey" estimate. These costs include:

- Construction of the anaerobic and aerobic cells
- Planting of initial emergent macrophytes and seeding of microbes
- Installation of a carbon/nutrient feeding system
- All instrumentation needed to operate the facility
- An operating manual
- Electrical utility lines to 100 feet from the base of the wetland at the influent end
- 100 feet of 4-inch PVC line from the base of the wetland at the influent end (inlet for the contaminated water)
- 100 feet of 3.5-foot I.D. (minimum) culvert from the base of the discharge end of the wetland (discharge outlet for wetland)

Table 9-1

Estimated Battery Limits Cost for a Gravel-Based Wetland with Surface Water Discharge

	Battery Limits Cost, $
Direct Cost	
Excavation and Fill	$82,180 [1]
Gravel Fill	$840,238 [1]
Liner	$754,500 [1]
Pumps	$12,115 [1]
Tanks	$8,754 [1]
Instruments	$28,079 [1,2]
Insulation	$16,351 [1]
Piping	$151,673 [1]
Walls and Structures	$157,033 [1]
Foundations	$52,886 [1]
Electrical	$35,929 [1]
Cleanup and Painting	$1,188 [1]
Planting	$34,399 [1]
Misc. (survey, soil tests, overheads, etc.)	$252,026 [1]
Total Direct Cost	$2,427,349
Indirect Cost	
Additional System Cost	
Health and Safety	$12,474 [3]
Bid Contingency, 15% of Direct Cost	$364,102 [4]
Scope Contingency, 15% of Direct Cost	$364,102 [4]
Subtotal	$740,679
Construction Subtotal (system cost + direct costs)	$3,168,027
Implementation Cost	
Engineering Services During Construction	$150,328 [3]
Engineering & Design	$147,332 [3]
Total Battery Limits Investment	**$3,465,687**

1) Based on TVA assessment of a conceptual design of a commercial-scale facility.

2) Includes the cost of sixteen oxygen meters for monitoring the anaerobic cell's performance as well as other instrumentation.

3) Based on TVA's assessment of actual needs for site construction.

4) Used the same method outlined in previous U.S. Army Corps of Engineers' Focused Feasibility Studies.

The battery limits cost provided do not include:

- Groundwater extraction wells
- Utilities other than electricity (none expected)
- Post-construction sanitation facilities (none expected)
- Equipment for collecting and monitoring effluent
- Roads or parking lots
- Operator training

Estimated operation and maintenance costs are provided in Table 9-2. A description of related operator duties is outlined in Section 9-4. Assuming a 95% system availability and 30-year life, the total cost (operation and maintenance cost plus capital cost) for treating groundwater with this gravel-based system is estimated at $1.78 per thousand gallons of groundwater.

Since any present worth analysis of project-specific costs will require the insertion of other project-related costs, a breakdown in the format of a typical feasibility study is provided in Table 9-3. Table 9-3 was developed using the data from a June 1996 evaluation of Milan's 600 gpm GAC/GMF system. The example is intended to show how TVA's estimates are likely to fit in a typical cost analysis and provides perspective of the total cost a facility might encounter. Table 9-3 is presented for informational purposes only and does not reflect actual costs allocated for any facility including MAAP. Present worth was calculated on the basis of a 20-year life with a 5% discount rate. A 30-year life figure is included for informational purposes.

9.3 Capital Cost for the Groundwater Reinjection Option - Gravel-Based-Type Wetlands Only

The estimated battery limits cost of constructing a 12.8-acre, gravel-based wetland for treating 200 gpm of groundwater to groundwater reinjection standards is approximately $4,125,000 (Table 9-4). A total of eleven months is allowed for design and construction of the wetland. The battery limits cost provided include all costs associated with constructing the wetland and should be considered a "turnkey" estimate. These costs include:

Table 9-2
Operation and Maintenance Cost for a Gravel-Based Wetlands With Surface Water Discharge

Item	Annual Cost, $/year	Basis
Maintenance		
Berms	$4,000	$400 per acre * 10 acres[1]
Pumps	$485	4% of direct cost
Tanks	$350	4% of direct cost
Walls and Structures	$6,281	4% of direct cost
Pipes	$6,067	4% of direct cost
Electrical Equipment	$1,437	4% of direct cost
Instruments	$1,123	4% of direct cost
Total Maintenance	$19,743	
Raw Materials		
Carbon Source[2]	$14,334	357 lb/day * 365 day * $0.11/lb
Phosphate Source[2]	$1,200	$220/ton fertilizer * 5.45 ton/year
Electricity	$6,400	106,670 kWh per year * $0.06 per kWh[3]
Total Raw Materials	$21,934	
Subtotal Maintenance & Operations	**$41,677**	
Operator	$15,800	One $79,000/yr operator at 20%[3]
System Effluent Monitoring	$5,200	52 samples at $100 per sample[3,4]
Total O&M	**$62,677**	

1) Rough cost from "Treatment of Wetlands" by Robert H. Kadlec and Robert L. Knight, 1996, page 607.

2) Bioavailable carbon and nutrient sources provided to encourage anaerobic microbial activity.

3) Cost from "Milan Army Ammunition Plant: Northern Boundary Groundwater Focused Feasibility Study," June 1996.

4) Cost for obtaining one inlet and one outlet water sample and analyzing each sample for explosives each month. Other analytical cost associated with operating the system are included in the figures for capital cost, maintenance, and operating labor. This includes the cost of installing, monitoring, maintaining, and operating dissolved oxygen probes in the anaerobic cell.

Table 9-3

Present Worth Analysis on a 200-GPM Milan Wetland With Surface Water Discharge With Data From the Milan Army Ammunition Plant Northern Boundary Groundwater Focused Feasibility Study (June 1994)

!! NOTICE !!

THE DATA PRESENTED IN THIS TABLE IS GENERIC IN NATURE AND DOES NOT CONTAIN SITE-SPECIFIC DATA FROM MILAN'S ONGOING FEASIBILITY STUDY FOR B-LINE - MAAP'S FEASIBILITY STUDY COST MAY VARY FROM THAT PRESENTED HERE.

!! NOTICE !!

Item	Quantity	Capital Cost	Annual O&M	Present Worth of Annual Cost	
				20 year, %5	30 year, 5%
I. Administrative Actions					
1. Institutional Restrictions/Emergency Provisions (a)		$25,000	$0	$0	$0
2. Public Education Program (a)		$20,000	$0	$0	$0
3. Program Oversight (a)		$0	$75,000	$935,000	$1,153,000
Subtotal		$45,000	$75,000	$935,000	$1,153,000
II. General Actions/Site Preparation					
1. Parking/Staging Area/Access Roads (b)		$34,291	$0	$0	$0
2. Treatment System Buildings (c)		$0	$0	$0	$0
3. Contractor Mobilization /Demobilization (d)		$0	$0	$0	$0
Subtotal		$34,291	$0	$0	$0
III. Groundwater Treatment System					
1. Extraction Systems (e,f)		$56,805	$16,667	$208,000	$256,000
2. Wetlands Systems (g)		$2,427,349	$41,677	$519,000	$641,000
4. One Part-Time System Operators (h)	0.2 @ 2080 hrs/yr.	$4,301	$15,800	$197,000	$243,000
Subtotal		$2,488,456	$74,144	$924,000	$1,140,000
IV. Discharge Systems(i)					
1. Piping system to Rutherford Fork (e)		$95,678	$0	$0	$0
Subtotal		$95,678	$0	$0	$0
V. Long-Term Monitoring & Review					
1. Effluent Monitoring & Residuals Sampling (e,i)		$3,117	$5,200	$65,000	$80,000
2. Quarterly Groundwater Monitoring and Reporting (j)	20 wells * 200 gpm / 600 gpm	$0	$33,667	$420,000	$518,000
3. Quarterly Surface Water Monitoring & Reporting		$0	$0	$0	$0
4. Five-Year Review (15,000 ea.) (a)	6 reports	$0	$3,000	$37,000	$46,000
Subtotal		$3,117	$41,867	$522,000	$644,000
SUBTOTAL (I, II, III, IV, and V)		$2,666,542	$191,010	$2,381,000	$2,937,000
ADDITIONAL SYSTEM COST					
1. Health and Safety		$36,000	$0	$0	$0
2. Bid Contingency		$400,000	$0	$0	$0
3a. Scope Contingency		$400,000	$0	$0	$0
3b. Scope Contingency, 25% of Annual Subtotal		$0	$48,000	$598,000	$738,000
Subtotal		$836,000	$48,000	$598,000	$738,000
CONSTRUCTION SUBTOTAL (I, II, III, IV, V, and VI)		$3,502,542	$239,010	$2,979,000	$3,675,000
IMPLEMENTATION COST					
1. Engineering, Services During Construction		$201,000	NA	NA	NA
2. Engineering & Design		$182,000	NA	NA	NA
3. Permitting Coordination (a)		$0	NA	NA	NA
Subtotal		$383,000	NA	NA	NA
A. TOTAL CAPITAL COSTS		$3,885,542	NA	NA	NA
B. TOTAL ANNUAL COSTS		NA	$239,010	NA	NA
C. TOTAL PRESENT WORTH OF ANNUAL COSTS		NA	NA	$2,979,000	$3,675,000
TOTAL PRESENT WORTH OF CAPITAL AND ANNUAL COSTS				$6,864,542	$7,560,542

(a) Cost are the same as in the1994 estimate for GMF/GAC system. See Milan Army Ammunition Plant Northern Boundary Groundwater Focused Feasibility Study (June 1994), Table 7-2, page 7-13.
(b) Original capital cost converted to 1996 dollars using the CE index [i.e. new cost = original cost * (382.5/368.1).]
(c) Building included in wetland estimate.
(d) Included in capital cost for wetland.
(e) Original capital cost converted to 1996 dollars using the CE index and converted to a 200 gpm equivalent [i.e. new cost = original cost * (382.5/368.1) * (200 gpm/600 gpm).]
(f) Original O&M converted to a 200 gpm equivalent [i.e. new cost = original 600 gpm cost * (capital invest at 200 gpm/ capital investment at 600 gpm)]
(g) From battery limits cost sheet (Table 3-1).
(h) One operator at 20% of his time. Operator cost based on $79,000/year per operator as per the original GMF/GAC estimate.
(i) Effluent Monitoring only, residual monitoring not required.
(j) Original O&M converted to a 200 gpm equivalent [i.e. new cost = original 600 gpm cost * (200 gpm/ 600 gpm)]

Table 9-4
Estimated Battery Limits Cost for a Commercial-Scale Wetland With Discharge by Groundwater Reinjection

	Battery Limits Cost, $
Direct Cost	
Excavation and Fill	$95,080 [1]
Gravel Fill	$1,057,374 [1]
Liner	$927,814 [1]
Pumps	$12,115 [1]
Tanks	$8,754 [1]
Instruments	$28,079 [1,2]
Insulation	$16,351 [1]
Piping	$167,178 [1]
Walls and Structures	$175,164 [1]
Foundations	$58,719 [1]
Electrical	$37,726 [1]
Cleanup and Painting	$1,188 [1]
Planting	$42,663 [1]
Misc. (survey, soil tests, overheads, etc.)	$305,850 [1]
Total Direct Cost	$2,934,053
Indirect Cost	
Additional System Cost	
Health and Safety	$12,474 [3]
Bid Contingency, 15% of Direct Cost	$440,108 [4]
Scope Contingency, 15% of Direct Cost	$440,108 [4]
Subtotal	$892,690
Construction Subtotal (system cost + direct costs)	$3,826,743
Implementation Cost	
Engineering Services During Construction	$150,328 [3]
Engineering & Design	$147,332 [3]
Total Battery Limits Investment	**$4,124,403**

1) Based on TVA assessment of a conceptual design of a commercial-scale facility.

2) Includes the cost of sixteen oxygen meters for monitoring the anaerobic cell's performance as well as other instrumentation.

3) Based on TVA's assessment of actual needs for site construction.

4) Used the same method outlined in previous U.S. Army Corps of Engineers' Focused Feasibility Studies.

- Construction of the anaerobic and aerobic cells
- Planting of initial emergent macrophytes and seeding of microbes
- Installation of a carbon/nutrient feeding system
- All instrumentation needed to operate the facility
- An operating manual
- Electrical utility lines to 100 feet from the base of the wetland at the influent end
- 100 feet of 4-inch PVC line from the base of the wetland at the influent end (inlet for the contaminated water)
- 100 feet of 4-inch PVC line from the base of the wetland at the discharge end (outlet for normal groundwater discharge)
- 100 feet of 3.5-foot I.D. (minimum) culvert from the base of the discharge end of the wetland (outlet for emergency discharge)

The battery limits cost provided do not include:

- Groundwater extraction wells
- A facility for pumping treated water to the injection wells. (A 6-foot-diameter sump has been provided within the aerobic cell to allow the placement of a submersible pump, if MAAP so desires.)
- Utilities other than electricity (none expected)
- Post-construction sanitation facilities (none expected)
- Equipment for collecting and monitoring effluent
- Roads or parking lots
- Operator training

Estimated operation and maintenance costs are provided in Table 9-5. A description of related operator duties is outlined in Section 9-4. Assuming a 95% system availability and 30-year life, the total cost (operation and maintenance cost plus capital cost) for treating groundwater with this gravel-based system is estimated to be $2.06 per thousand gallons of groundwater.

Table 9-5

Operation and Maintenance Cost for a Gravel-Based Wetlands With Groundwater Reinjection

Item	Annual Cost, $/year	Basis
Maintenance		
Berms	$4,920	$400 per acre * 12.8 acres[1]
Pumps	$485	4% of direct cost
Tanks	$350	4% of direct cost
Walls and Structures	$7,007	4% of direct cost
Pipes	$6,687	4% of direct cost
Electrical Equipment	$1,509	4% of direct cost
Instruments	$1,123	4% of direct cost
Total Maintenance	$22,081	
Raw Materials		
Carbon Source[2]	$17,630	439 lb/day * 365 day * $0.11/lb
Phosphate Source[2]	$1,200	$220/ton fertilizer * 5.45 ton/year
Electricity	$6,400	106,670 kWh per year * $0.06 per kWh[3]
Total Raw Materials	$25,230	
Subtotal Maintenance & Operations	**$47,311**	
Operator	$15,800	One $79,000/yr operator at 20%[3]
System Effluent Monitoring	$5,200	52 samples at $100 per sample[3,4]
Total O&M	**$68,311**	

1) Rough cost from "Treatment of Wetlands" by Robert H. Kadlec and Robert L. Knight, 1996, page 607.

2) Bioavailable carbon and nutrient sources provided to encourage anaerobic microbial activity.

3) Cost from "Milan Army Ammunition Plant: Northern Boundary Groundwater Focused Feasibility Study," June 1996.

4) Cost for obtaining one inlet and one outlet water sample and analyzing each sample for explosives each month. Other analytical cost associated with operating the system are included in the figures for capital cost, maintenance, and operating labor. This includes the cost of installing, monitoring, maintaining, and operating dissolved oxygen probes in the anaerobic cell.

9.4 Operator Duties for Typical Gravel-Based Wetland

Maintenance requirements of gravel-based wetland systems are minimal. Operator functions are limited and include:

- Ensuring that the source carbon is being fed properly into the wetlands
- Refilling the liquid sucrose and 10-34-0 tanks
- Ensuring that the anaerobic cell's dissolved oxygen levels remain low
- Ensuring that water continues to flow subsurface and is below the gravel surface for extended periods of time
- Inspecting the leak detection system for evidence of leakage
- Inspecting the aerobic cell pumps, distribution channels, dams, and outlet headers to ensure proper operation and to identify and rectify maintenance issues
- Annual weeding of the occasional tree sapling or noxious weed

Annual weeding need not be extensive since most non-aquatic plant species do not find the wetland's environment attractive and most seedlings have a difficult time establishing themselves in gravel beds. However, certain tree species (Willows, Sycamore, etc.) are able to establish a foothold. These species must be removed since their long roots might perforate the liner. Removal of noxious weeds (rapidly growing vines, for example) should be limited to those species which might choke out desirable plants.

SECTION 10.0
QUALITY ASSURANCE

10.1 Introduction

The Analytical Laboratory (AL) at Muscle Shoals, Alabama, provided analytical chemistry support for the demonstration by performing analyses for explosives, nutrients, metals, bromide, and non-purgeable organic carbon. AL also developed and improved existing analytical procedures for use in this project.

Chemical oxygen demand and biochemical oxygen demand analyses were performed at the Wetlands Laboratory at Muscle Shoals, Alabama.

10.2 General Information

10.2.1 Project Organization and Responsibilities

The Project Manager provided overall direction for the demonstration.

The engineering staff reported to the Project Manager and were responsible for performing detailed design engineering and construction.

The Wetlands Manager reported to the Project Manager and was responsible for providing technical direction and staff for development of processes and experimental design. He also provided oversight of field operations and produced the final data evaluation.

Wetlands Facility staff members (Muscle Shoals) reported to the Wetlands Manager and were responsible for designing field experiments and bench-scale tests. The staff also provided technical expertise in design, operation, and assessment of the field test facility.

TVA's Field Operation Team (Milan) reported to the Wetlands Manager and were responsible for the operation of test facilities and documentation of experiments. The team provided for

calibration and operation of test equipment. The team performed field sampling, packaged samples for shipment to the analytical laboratory, and documented sampling activities.

The Laboratory Manager was responsible for providing oversight of activities in the analytical laboratory and for review of analytical laboratory data.

The Quality Assurance Officer of AL reported to the Laboratory Manager and was responsible for auditing actions and documentation to ensure adherence to this plan. The QA Officer was responsible for providing quarterly quality control data reports to the Laboratory Manager.

10.2.2 Research Records

Laboratory records from the project consist of data reports, bound research logbooks, instrument logs, worksheets, machine printouts with annotations, chromatograms, plots, review notes, and data summaries. These records have been accumulated by the work order number assigned by the laboratory's database and will be archived in the TVA RM records storage facility in Muscle Shoals, Alabama, for three years following the end of the project. Records are available for review at the request of USAEC.

10.2.3 Field Quality Control Samples

For every sampling event for water, a field blank and field duplicate sample were taken. The field blank was made by pouring deionized water into the same type sample container as used for field samples. The deionized water was taken from the working stock used in the field operations. The field duplicate was taken at random from routine sampling points by pulling an additional sample.

10.2.4 Sample Custody

Field samples were handled in accordance with AL Procedure SP-0001, "Sample Chain of Custody." Samples were taken in accordance with procedures provided in the sampling plan. Sample custody sheets were completed at the time of sampling and delivered to the laboratory

with the samples. Any problems involving broken or missing samples were handled with the sampling team and documented on the custody sheets or other receiving records.

10.3 Analytical Procedures

A written procedure for explosives analysis was produced in the course of earlier phases of this project and is attached as Appendix A-1. It involved analysis by HPLC.

10.3.1 Nutrients, Oxygen Demand, and Metals

Other analyses for nutrients, oxygen demand, and metals were performed in accordance with standard EPA procedures, as documented in the project plan (see also procedures listed in Appendix A).

10.3.2 HPLC Analysis

The starting point for analysis of explosives and explosive degradation products for this project was EPA Method 8330, a high performance liquid chromatography (HPLC) analysis method which utilizes a methanol/water mobile phase and a UV detector. Method 8330 specifies confirmation of compounds by analyzing them on two different columns. Compounds found to be present on both columns at the correct retention time are reported as present.

Modifications to this procedure by TVA included the use of a concentration step with a Waters Porapak® RDX Sep-Pak® Vac cartridge. The dual column confirmation was replaced by analysis on a system with a photodiode array (PDA) detector, as well as on a system with a UV detector. The PDA provides an ultraviolet spectrum which can be used to confirm the identity of a compound, but it is not as sensitive as the UV detector. A single type analytical column is used on both systems.

Some compounds studied in this project were additions to the analyte list in Method 8330. It was found they could not be analyzed without modification to 8330 because of co-elution problems. Scientists at CRREL had developed an HPLC gradient method for analysis of explosives which is a modification to 8330 which uses an isocratic mobile phase. This

gradient method is able to separate the target compounds for this project with one exception, so it was adopted. Tri-RDX and 2,6-DANT were found to co-elute, but they may be differentiated by their UV spectra. On the occasions when they were both found in a sample, the tri-RDX was quantified since the detector's response is more sensitive to this compound and 2,6-DANT was reported as "present."

Water samples were either directly injected or passed through a RDX Sep-Pak column and eluted with acetonitrile which was diluted 1:1 with water, depending on the initial concentration of target compounds. All sample fractions run on the PDA were passed through RDX Sep-Pak and eluted with acetonitrile which was diluted 1:1 with water. Sediment was treated, as called for in Method 8330 for soil. Gravel was extracted by a scaled-up version of the sediment process.

10.4 Data Reduction, Validation, and Reporting

10.4.1 Data Reduction

Data from HPLC analysis of explosives and degradation products were calculated and reduced on Varian's Star workstation software which provided peak identification and peak-height calculations. Photodiode-array spectra were analyzed and compared with the same software package. Curve fitting for calibration curves was performed on an Excel spreadsheet using linear regression functions provided with that program. The resulting coefficients were applied to peak heights in a QBASIC program written at TVA RM which also reformats information to be placed into the Laboratory Information Management System (LIMS) for calculation of percent recovery of quality control samples. The LIMS software also calculates percent recovery of matrix spikes and relative percent difference between duplicate analyses.

Data from the flow injection analyzer (nitrate, ammonia, total nitrogen, etc.) were reduced and calculated using the Omnion software package on the QuikChem analyzer. These results were interfaced directly with the LIMS. This software package measures peak area and automatically applies linear regression analysis of calibration curves to determine concentrations. Percent recovery and relative percent difference for quality control samples were calculated on a spreadsheet developed at TVA RM.

Data from metals analysis were analyzed using Thermo Jarrell Ash's Enable software package which measures photomultiplier response and automatically applies linear regression analysis of calibration curves to determine concentrations. Percent recovery for quality control samples was calculated on the LIMS in the same manner HPLC data were calculated.

Data from bromide analysis were evaluated using Dionex chromatography software package which measures peak area and applies calibration curves.

Data from simple instrumental methods, such as total suspended solids, 5-day BOD, and chemical oxygen demand, were reduced by hand or on simple spreadsheets.

10.4.2 Data Validation

Throughout the course of the project, analytical measurements were first reviewed by the chemist producing them and then by another chemist before being interfaced with the LIMS. If quality control samples fell outside limits, associated project samples were coded as "qualified" data or the samples were scheduled for reanalysis. After questions were resolved, results were passed to the Laboratory Manager for final review and validation of the data packages. Additional reviews were performed by the Quality Assurance Officer.

10.4.3 Data Reporting

After approval, data were reported to the Wetlands Manager from the LIMS.

10.4.4 Records Retention

Records of laboratory measurements and analyses will be maintained for a period of three years after the end of the project in TVA's Muscle Shoals Records Center. This is a federal agency record center with access control, retrieval, and fire protection, as described in 36 CFR 1228 Subpart K.

All analytical data were accumulated as packages from each sampling event. Each package included, as a minimum, sample descriptions or identification information, a copy of the chain of custody record, sample analytical results, quality control sample results with percent recovery of the added compounds, worksheets, chromatograms, raw data, and a copy of the final report. Data from failed attempts at measurement were stored along with other records for samples.

Support records were also accumulated which include determination of Method Detection Limits, records of purchase of standard materials, and records of use of standard materials.

10.4.5 Qualification Codes

The following codes may be found in data packages.

- NA - Compound not analyzed.
- <MDL - Compound not detected [analysis value falls below the Method Detection Limit (MDL)].
- TR - Compound was present at trace level. Indicated but less than MDL.
- Q - "Qualified" - For a sample in which an analyte was found, the measurement for an associated quality control sample for that same analyte fell outside control limits.

10.5 Internal Quality Control

10.5.1 Initial Quality Control

AL routinely ran blank samples to demonstrate that glassware and reagents were free of interferences.

Initially, and as methods were developed, quality control check sample sets of known concentration were run to ensure method precision and accuracy were known.

For automated analytical equipment, such as flow injection analyzers and high performance liquid chromatography, retention time windows or timing windows were established in order for analytes to be properly identified by analytical software.

Each analyst demonstrated the ability to generate acceptable results with the methods before working alone on project samples.

10.5.2 Cross-Check and Blind Quality Control Samples

The laboratory routinely participated in nationally promulgated cross-checks to demonstrate the laboratory's ability, as compared to national performance of commonly performed methods.

10.5.3 Batch Quality Control

For automated methods, a variety of quality control samples were analyzed routinely with each batch. These included reagent blanks, midpoint calibration standards, laboratory control samples, matrix spikes, and duplicates. Percent recovery was calculated for midpoint calibration standards, laboratory control samples, and matrix spikes. Relative percent difference was calculated for duplicate samples. In all, thousands of quality control analyses were performed for this project. Typical analytical quality control for a HPLC run was as indicated in Table 10-1.

Typical results for percent recovery of two types of known samples are included in Tables 10-2, 10-3, and 10-4.

As chromatography systems age, performance changes. Columns deteriorate and detectors become less responsive with time. Such analytical performance was monitored with data like those in Tables 10-2 through 10-4. When quality control samples fell outside 85%-115% recovery, samples were qualified with a "Q" code or reanalyzed. It should be noted that some analytes, such as the azoxytoluene compounds, fell outside these limits consistently, but were

Table 10-1

Typical Analytical Quality Control for an HPLC Run

Sample Type	Frequency
Laboratory Control Sample (made from a separate stock than the calibration standards)	Every 20 field samples[1]
Method Blank	Every 20 field samples
Matrix Spike	Every 20 field samples
Matrix Spike Duplicate	Every 20 field samples
Initial Calibration Check[2]	At beginning of run
Continuing Calibration Check[2]	After every 10 injections[3]
Final Calibration Check[2]	At end of run

1) Analytical batch quality control samples were run for every 20 samples (or subset thereof) of the same matrix prepared with the same reagents on the same day.

2) Calibration check samples were injected as two solutions because of peak overlap.

3) Calibration check samples were run after every 10 injections counting field samples, method blanks, matrix spikes, matrix spike duplicates, and laboratory control samples.

Table 10-2

Percent Recovery of Quality Control Check Samples Mix 1 - April - June 1998

2,6-DANT	HMX	2,4-DANT	RDX	TNB	TNT	4-ADNT	2-ADNT	2,6-DNT	2,4-DNT	T-2,2'-AZT	T-2',4-AZT	T-4,4'-AZT	D-4,4'-AZT	1,3-DNB	3,5-DNA
91.6	88.8	112	105	111	110	104	104	101	107	80.4	66	60.9	98.2	106	107
91.6	91.8	112	102	105	109	109	109	106	107	83.1	68.3	60.1	99.1	106	108
92.3	90.4	111	106	107	107	110	109	107	110	80.1	66.2	59	98.2	106	108
92.1	94.1	113	104	107	113	116	115	110	112	82.4	66.7	60	102	106	107
90.2	89.7	111	103	107	109	109	110	106	110	81.7	65.3	61.3	100	106	106
89.4	94.4	104	105	109	111	114	112	108	112	81.8	64.9	60.5	100	106	107
91.8	90.4	111	103	108	111	110	111	107	110	85	71.9	61.3	103	106	108
91.6	88.1	109	105	107	110	111	109	105	111	83.4	72.8	60	101	107	106
89.7	87.8	106	103	105	111	112	113	106	109	85.4	63.3	54.4	99.1	106	104
91.1	87.1	108	103	107	109	115	116	115	115	83.1	65.3	60	102	107	106
90.6	84.9	105	105	107	108	105	103	97.5	106	81.6	69.6	56	102	107	107
88.5	88.1	102	101	104	108	108	104	103	107	82.3	68.9	58.8	98.2	107	106
85.5	81.2	92.9	103	108	111	111	106	102	107	81.8	67.7	59.2	103	105	105
83.4	96.9	98.5	100	104	107	106	105	107	103	80.4	63.9	60.4	96.5	103	101
86.2	91.4	98.5	102	105	108	109	107	102	105	78.1	60.8	60.7	96.5	105	105
81.3	92.7	101	101	104	107	107	107	105	107	80.3	61.7	57.8	98.2	104	104
84.1	84.2	100	101	105	108	107	105	103	107	80.6	65.3	57.5	99.1	105	105
88.5	85.5	101	101	104	107	104	105	101	106	80.4	63.1	56.7	98.2	105	105
82	90.1	93.3	100	104	107	112	111	106	109	78.7	59.9	52.5	97.4	104	103
89.2	93.4	110	100	105	106	108	106	100	105	78.2	55.9	54.4	96.5	105	103
83	90.1	100	100	108	107	106	105	103	105	82.4	65.5	54.1	100	105	104
85.7	95.7	97.9	99.4	105	106	103	105	101	104	80.2	60.5	58.3	98.2	105	102
80.6	83.2	84	101	104	107	106	108	105	107	82.3	63	57.6	100	106	104
85.3	80.2	90.4	104	107	107	112	110	102	109	80.1	66.8	53.7	101	107	106
81.1	83.8	85	102	106	108	106	107	104	107	78.6	63.6	52.4	95.6	105	104
87.4	84.5	95.8	102	106	109	106	109	105	108	78.7	63	53.1	97.4	105	105
101	109	107	94	94.4	96.4	94.6	99.1	110	99.3	97.4	98.3	96.9	98.2	97.9	98.6
98.9	97.9	87.3	99.4	99.9	104	106	108	104	104	100	111	102	108	103	106
91.3	103	84.8	94.7	97.2	101	97.1	99.1	98	100	94.7	94	96.1	0	102	102
98.9	104	106	92	87.6	94	95	97.9	108	97.4	94.7	94.8	96.8	101	97.9	98.3
94.3	91	85.4	92	93	99.6	98.8	99	97.6	98.4	96.5	122	102	97.4	96.9	101
93.8	89.6	93.5	94	94.6	98.6	100	103	104	100	107	122	91.7	95.6	98.8	99.9
96.4	89	94.4	96.6	96.2	102	98.8	100	99	99.3	98.2	114	102	104	98.8	101
102	102	106	96.6	97	104	102	103	103	104	102	106	97.6	107	103	104
97.6	90.7	98.1	97.5	98.9	106	111	111	110	107	110	118	100	107	101	103
98.9	87.6	100	97.5	98.9	103	101	101	104	103	101	106	105	104	101	106
98.9	93.4	107	96.6	99.9	105	112	111	113	104	106	116	105	107	101	99.9
98.9	102	112	97.5	97.6	102	111	110	112	105	100	105	95.5	106	98.8	97.6
96.7	95.2	109	98.5	98.9	101	93	95.4	101	101	94.7	103	99	102	98.8	98.6
99.9	103	113	98.5	99.9	101	95	98.2	102	100	105	122	102	107	101	99.9
101	97.9	109	97.5	98.9	98.6	90.5	93.1	99	96.4	95.6	92.2	98	101	99.8	97.3
103	105	113	94.5	97.6	98.6	96.4	98.7	102	97.4	104	105	101	107	98.8	99.1
99.9	91	103	96.6	97.7	103	103	101	102	101	98.2	109	97.7	102	97.9	99.8
92.6	90.7	96.8	98.5	97.9	102	102	105	106	102	98.2	109	97.7	104	99.8	99.9
96.2	91.4	95	96.6	97.9	99.6	99.1	100	106	101	104	110	100	106	97.9	98.3
103	101	112	98.5	99.9	102	103	103	108	102	103	117	102	104	101	100
95.4	101	104	97.5	98.9	97.7	101	100	107	100	96.5	97.4	93.8	100	99.8	97.8
94.1	105	105	94.2	96.6	101	95	96.1	97.3	95	93.9	94.8	93.9	99.1	97.9	95.8
103	90.7	105	97.5	97.9	101	104	104	99	101	95.6	106	97.2	103	101	99.1
103	93.8	107	98.5	97.9	101	92.6	96.1	93.2	97.4	98.2	116	100	103	101	100
101	88.3	102	98.5	97.8	102	107	112	123	110	93.9	109	101	100	99.8	99.8
103	91	106	96.6	97.5	102	104	103	104	100	94.7	105	96.4	101	99.8	97.1
102	93.8	110	95.6	97.8	104	112	112	117	105	126	183	94.6	82.3	98.8	97.8
105	96.9	108	95.6	97.7	102	91.9	92.6	92.8	94.8	93	102	93.4	100	98.8	98.4
79.7	90.8	101	92.7	91.9	90.7	90.7	88.1	87	88.6	64	46.9	37.4	77.5	89	88.6
84.6	91.8	114	94.7	92.3	87.5	90.4	87.6	87.6	86.5	63.2	45.8	38.8	76	90.7	88.9
82.3	90.4	106	93.4	92	89	88.8	87.9	89.6	88.3	63.2	46.8	38.1	76.9	88.9	88.7
87.2	87.5	111	93.2	91.2	88.6	89.5	89.1	87.6	87.3	62.9	44.9	39.5	76.8	88.3	88.4
84.3	82.2	119	96.6	92.3	92.4	93	93.1	89.2	92	64.6	51.4	39.5	78.9	91.6	92.3
85.3	87.5	114	94	91.5	92	94.9	91.4	93.8	91.7	62.6	48.2	37.7	77.8	90.5	90.6
86	84.5	120	96.6	93.4	91.8	92	92.4	91.2	89.2	62.9	51.6	36.9	76.8	90.8	90.9

Table 10-3

Percent Recovery of Quality Control Check Samples Mix 2 - April - June 1998

Tri-RDX	Mono-RDX
94.4	104
94.4	105
94.8	104
93.3	104
95	102
92.1	102
91.9	103
94.6	105
94.6	105
93.9	103
92.7	108
93.9	105
94.8	104
94.2	104
95.4	107
94.6	100
95	104
93.7	103
93.1	101
94.8	103
95.2	103
93.7	103
93.1	107
89.6	103
91.6	102
92.9	103
110	109
111	109
102	102
103	93.3
103	103
102	84
105	103
113	107
104	104
104	108
103	106
106	108
102	107
101	103
105	106
101	108
102	108
105	108
103	107
102	107
106	110
105	112

Table 10-4

Percent Recovery - Laboratory Control Samples - April - June 1998[1]

2,6-DANT	HMX	2,4-DANT	RDX	TNB	TNT	4-ADNT	2-ADNT	2,6-DNT	2,4-DNT	1,3-DNB
85.8	90.7	93.9	107	105	108	108	110	76	90.6	85.6
87.7	92.6	95.9	105	106	108	107	109	81	94.6	90.6
	76		82	80	86		87		86	85
	86		101	98.5	103		106		103	102
88.1	89.2	104	105	108	110	110	110	94	105	103
	81.5		99	94	102		105		102	100
	83.4		88.9	88.2	96.4		96.4		93.6	92.8
	66.9		88.3	87.1	96.4		96.9		95.4	94.2
	71.1		98.1	89.4	95.7		94.9		89.7	94.3
	90		90	90	90		100		90	100
	97		91.5	89	95.5		100		99	100
	78.5		83.5	67.5	85		86.5		84.5	85
	99.5		93.5	87.5	93.5		96.5		94	96
	100		100	90	100		100		100	100
	91.5		92.5	78	85		89		84	88

1) Laboratory control samples for water were made from a stock purchased from a commercial supplier which did not have all the analytes of interest to this project. Laboratory control samples for vegetation were mixed at TVA and contained eleven compounds of interest.

Table 10-5

Typical Method Detection Limits for Explosives and Explosive By-Products

Analyte	Influent (mg/L)	Effluent (mg/L)
2,6,Diamino-4-nitrotoluene	0.005	0.0004
Trinitroso RDX	0.005	0.0004
HMX	0.005	0.0004
2,4-Diamino-6-nitrotoluene	0.005	0.0004
Mononitroso RDX	0.005	0.0004
RDX	0.006	0.0005
1,3,5-Trinitrobenzene (TNB)	0.005	0.0004
2,4,6-Trinitrotoluene (TNT)	0.005	0.0004
4-Amino-2,6-dinitrotoluene	0.005	0.0004
2-Amino-4,6-dinitrotoluene	0.005	0.0004
2,6-Dinitrotoluene	0.006	0.0005
2,4-Dinitrotoluene	0.005	0.0004
Tetranitro-2,2'-azoxytoluene	0.005	0.0004
Tetranitro-2',4-azoxytoluene	0.011	0.0008
Tetranitro-4,4'-azoxytoluene	0.008	0.0006
Dinitro-4,4'-azoxytoluene	0.014	0.001
1,3-Dinitrobenzene	0.005	0.0004
3,5-Dinitroaniline	0.005	0.0004

never routinely found in field samples. These compounds fall in a region with complex background chromatograms and are more difficult to quantify. Over the course of the project, when analytes which did occur routinely in field samples consistently fell outside limits, the system was cleaned, adjusted, or recalibrated.

Quality control for non-automated methods (BOD-5, COD, and TSS) was more limited. Runs included duplicates, blanks, and knowns.

10.5.4 Calibration

Calibration of ion chromatographs, flow injection analyzers, carbon analyzers, chemical demand analyzers, and inductively coupled plasma devices were made with each analytical run using software provided by the manufacturer of the device.

Calibration of the HPLC device was done initially when the column was changed and when quality control sample response indicated that recalibration was required. Calibration was done at five concentrations. Data were fit to three models: slope only ($y = mx$), linear ($y = a + bx$), and quadratic ($y = a + bx + cx^2$). The choice of the model was made based on back-calculation of the calibration standards for each analyte.

10.6 Method Detection Limits

AL determined Method Detection Limits as defined in 40 CFR Part 136, Appendix B, Revision 1.11. Detection limits were documented in internal memoranda. Limits were reported with analytical results. Detection limits for HPLC were found to be a function of column age and detector stability.

Typical Method Detection Limits for analytes of interest in this project are listed in Tables 10-5 to 10-7. For explosives, effluent water and other low-concentration samples were concentrated before analysis to lower the detection limits.

Table 10-6

Typical Method Detection Limits for Other Analytes in Water

Test Description	Limit	Units
Ammonia	0.02	mg NH_3-N/L
Chloride	0.1	mg/L
Cadmium	0.03	mg/L
Calcium	0.03	mg/L
Copper	0.02	mg/L
Iron	0.02	mg/L
Lead	0.3	mg/L
Magnesium	0.2	mg/L
Manganese	0.008	mg/L
Nitrate Plus Nitrite Nitrogen	0.08	mg NO_3-N/L
Nickel	0.07	mg/L
Phosphate as Phosphorus	0.01	mg PO_4-P/L
Zinc	0.009	mg/L
Total Kjeldahl Nitrogen	0.05	mg N/L
Bromide	0.2	mg/L
Total Organic Carbon	0.9	mg/L

Table 10-7

Typical Method Detection Limits for Explosives and Explosive By-Products in Gravel and Sediment

Analyte	Gravel (mg/kg)	Sediment (mg/kg)
2,6,Diamino-4-nitrotoluene	0.002	0.025
Trinitroso RDX	0.002	0.025
HMX	0.002	0.025
2,4-Diamino-6-nitrotoluene	0.002	0.025
Mononitroso RDX	0.002	0.025
RDX	0.0025	0.03
1,3,5-Trinitrobenzene (TNB)	0.002	0.025
2,4,6-Trinitrotoluene (TNT)	0.002	0.025
4-Amino-2,6-dinitrotoluene	0.002	0.025
2-Amino-4,6-dinitrotoluene	0.002	0.025
2,6-Dinitrotoluene	0.0025	0.03
2,4-Dinitrotoluene	0.002	0.025
Tetranitro-2,2'-azoxytoluene	0.002	0.025
Tetranitro-2',4-azoxytoluene	0.002	0.025
Tetranitro-4,4'-azoxytoluene	0.003	0.04
Dinitro-4,4'-azoxytoluene	0.002	0.025
1,3-Dinitrobenzene	0.002	0.025
3,5-Dinitroaniline	0.002	0.025

10.7 Performance and System Audits

The AL QA Officer performed internal audits, surveillances, and reviews. Results were reported in writing to the Laboratory Manager. Suitable corrective actions were instituted in response to concerns and findings of these audit reports. The corrective action tracking system utilized by the laboratory was employed to track these items to closure, as appropriate.

The QA Officer also inspected control charts, logs, records, printouts, results of quality control checks, and other quality-related documents from the project.

USAEC staff also reviewed procedures, interim data, and project reports. Findings and concerns from these reviews also resulted in corrective actions by the laboratory staff. As appropriate, some of these were tracked to completion on the corrective action tracking system.

SECTION 11.0
CONCLUSIONS (PHASE II)

11.1 Background

Phytoremediation has been reported to be a potentially successful method for removing explosive compounds in groundwater by pumping the water to the surface and letting natural plant and microbial processes degrade explosives. There was some research supporting the fact that plants alone could degrade explosives via production of nitroreductase enzyme. Other research on gravel-based wetlands indicated that degradation of explosives in constructed wetlands occurred via both microbial and plant processes. To determine the effectiveness of phytoremediating explosives-contaminated groundwater, a demonstration was conducted at Milan Army Ammunition Plant to treat groundwater contaminated with explosives. The demonstration included two types of wetlands, each receiving a 5 gpm flow of contaminated groundwater. The concentration of nitrobodies in the groundwater was 3,250 ppb from June to November 1996 and 9,200 ppb from November 1996 to September 1997. The first wetland was a two-celled, lagoon-based wetland used to test the concept of explosive degradation via nitroreductase enzyme production from submergent plant species. The second type was a two-celled, gravel-based wetland used to test the concept of explosive degradation via microbial and plant processes. The lagoon-based wetland's two cells were identical with each having a 5.7-day retention time for a total retention time of 11.4 days. The first cell of the gravel-based wetland was maintained as an anaerobic reactor by adding carbon on a biweekly basis. The second cell was maintained as an aerobic reactor using a TVA RM-patented technology (patent number 5,863,433) to remove excess carbon, nutrients, and explosive by-products released from the first cell. The retention times in the first and second gravel-based cells were 8.4 and 1.7 days, respectively, for a total of 10.1 days.

11.2 Study Results

11.2.1 Explosives Degradation

The ability of the wetland systems to remediate groundwater contaminated with explosives was evaluated by measuring the explosives concentration in water leaving the wetlands and

comparing the values with the influent concentrations on a biweekly basis. The goals of the demonstration were to reduce TNT to concentrations less than 2 ppb and total nitrobodies to concentrations less than 50 ppb. The gravel-based wetlands met these goals except for wintertime reduction of nitrobodies.

The lagoon-based wetlands only met the goal of reducing TNT to less than 2 ppb during the initial stages of the demonstration. Removal efficiencies for TNT and TNB were greater than 85% during most of the demonstration period. The removal efficiencies decreased below 85% during the colder winter months. The lagoons were effective at removing TNT and TNB in contaminated water, but were ineffective at removing RDX and HMX. Removal efficiencies for RDX and HMX in the lagoons did not reach levels greater than 30%.

The gravel-based wetlands did a good job removing all of the explosives. Removal efficiencies for TNT and TNB were greater than 90%. Removal efficiencies for RDX and HMX were 90% during most of the demonstrations and from 20%-80% during the colder winter months. Critical parameters monitored in the gravel-based wetlands were redox and dissolved oxygen. Organic carbon was added to the first cell to maintain an anaerobic environment for optimum microbial degradation of the explosives. The mean saturated dissolved oxygen and redox were less than 1 mg/L and 0 mV in the set of sampling wells located four-fifths down the length of the wetland during the demonstration period.

The rate of explosive degradation and the formation of TNT and RDX by-products during degradation was monitored by sampling water at interior locations within the wetlands, in addition to influent and effluent samples from each wetland cell. The rate of RDX removal in the lagoons was very slow with no observable formation of RDX by-products. The rate of TNT removal in the lagoons was greater than RDX removal and was dependent on temperature with lower removal rates occurring in the winter. The TNT by-products 2A-DNT, 4A-DNT, 2,4-DANT were observed to occur at concentrations less than 5% of the influent TNT concentration. Removal of TNT and RDX occurred at quicker rates in the gravel-based wetlands compared to the lagoon-based wetlands. As in the lagoon, RDX removal rate was less than TNT removal rate. The removal rates for RDX and TNT in the gravel bed were dependent on temperature with slower removal occurring in the winter months. The TNT by-products 2A-DNT, 4A-DNT, 2,4-DANT were observed in the gravel bed at maximum

concentrations approximately equal to 15% of the influent TNT concentration. The RDX by-products, mononitroso and trinitroso RDX, were also observed in the wetlands. Trinitroso RDX was more predominant than mononitroso RDX. The maximum trinitroso RDX concentration found was 28% of the initial influent RDX concentration.

11.2.2 Hydraulic Tracer Analysis

The bromide tracer studies were conducted in January, May, and August of 1997. The tracer analyses revealed that hydraulic movement through the gravel-based system's anaerobic cell was a combination of plug-flow and complete-mix. The hydraulic movement through the gravel-based system's aerobic cell was almost entirely complete-mix due to the manner in which the system creates an oxidative environment. Both of the lagoon-based system's cells exhibited complete-mix hydraulics.

11.2.3 Toxicity Testing

Water samples were collected for toxicity analyses. Samples collected were the contaminated groundwater entering the wetlands and effluent waters from each of the wetland systems. Organisms used for toxicity testing were minnows and daphnids. The analyses showed the untreated contaminated groundwater to be toxic to the test organisms. Both wetlands systems were observed to remove the toxic effects of the contaminated groundwater.

The gravel and sediment samples were also examined for toxicity to sediment invertebrates. Test organisms used in the sediment toxicity tests were amphipods and midge larvae. Amphipods were used to test gravel toxicity. Amphipod toxicity was observed in the anaerobic gravel cell closest to the influent header at one sampling date and in the aerobic gravel cell closest to the effluent header at another sampling date. The toxicity of the gravel obtained near the anaerobic cell's influent header was probably due to explosives. Possible causative agents for toxicity in the aerobic cell could not be identified. Death by starvation has been hypothesized since the amphipods were competing with the high aerobic metabolism of the local bacteria for nutrient resources.

Amphipod and midge larvae toxicity were observed in all sediment samples collected from the lagoon wetlands. Sorption of explosives and explosive by-products onto sediments in lagoon wetlands occurs to a point that is toxic to ecological life. Conclusions regarding gravel and sediment toxicity should be considered preliminary in nature due to the limited scope of the tests conducted.

11.2.4 Explosives in Gravel, Sediment, and Plants

Gravel, sediment, and plants were collected throughout the course of the demonstration to determine if explosives and explosives by-products accumulated in these wetland components. Explosives and explosive by-products were observed on the gravel and sediments of the gravel-and lagoon-based wetlands. Concentrations were generally greater in samples collected closest to the influent. The quantity of total nitrobodies (RDX, TNT, TNB, HMX, 2,4-DNT, and 2,6-DNT) and total explosives (nitrobodies plus measured by-products) on the gravel and sediments were always less than 1.3% to 1.0% of the mass of nitrobodies entering the gravel- and lagoon-based wetland, respectively. The percent accumulation was greatest in the winter of 1996/1997 and declined during the summer of 1997.

Plants were observed to contain explosives and explosive by-products. The explosives, TNT, RDX, and HMX, were the predominant forms found in the submergent plants in the lagoon-based wetlands. The explosive RDX and its by-products, m-RDX and t-RDX, were the predominant forms found in the emergent plants in the gravel-based wetlands. Concentrations of the explosives in the emergent plants were greatest in the winter and declined in the summer. The decline in concentrations could have been due to increased growth and biomass of the plants causing a dilution of the explosives or increased metabolism of the explosives by the plants.

11.3 Recommendations for Future Work

During the course of this project, it became apparent that the gravel-based wetland's performance was better than that of the lagoon-based wetland and that acquiring additional data would be helpful to improve the design, operation, and economic success of scaled-up systems. Areas of interest included:

- Continuing to establish the effect of long term plant growth on explosive remediation
- Continuing to examine nitrobody remediation at cold temperature
- Examining the use of alternate carbon sources in the anaerobic cell (cell A1)
- Establishing the anaerobic cell's performance at a lower flow rate

To examine the use of alternate carbon sources, and to establish a maximum flow rate for the anaerobic cell, a supplemental test program was developed in July 1997. This program is referred to as the "Alternate Carbon Source and Higher Flowrate Study." In this study, small-scale cells were installed above the gravel bed at the Milan demonstration site. The use of the small-scale system was desirable because of the smaller system's operating conditions. Steady state conditions were maintained in the demonstration system during Phase II. A copy of the test plan for this study is provided in Appendix C.

The remaining issues were addressed by extending the operating period of the existing large-scale demonstration program. This extension is referred to as Phase III. In addition, the results of the "Alternate Carbon and Higher Flow Rate Study" were to be verified in Phase III. The Phase III program ran from September 1997 to July 1998. During Phase III, the operation of the lagoon-based wetlands was discontinued due to its poor performance in removing RDX and HMX. Changes to the operation of the gravel-based wetlands included using a less expensive carbon source (sucrose [cane molasses] as opposed to MRS), decreasing the amount of carbon added by one half, and modifying the influent flow rate. The change to a less expensive carbon source was done to evaluate system performance under improved economic cost of operation. Reducing the amount of carbon by one half was done to evaluate the ability of the wetland plants to supply carbon to the gravel substrate, thus, reducing exogenous carbon inputs. The decrease in the influent flow rate was done to evaluate the performance of the gravel-based wetlands to completely remove the RDX by-products, in addition to RDX

removal. Some operational problems existed during the winter of 1996/1997 which may have affected wintertime treatment performance. Operating the demonstration through another winter season was deemed critical in understanding the viability of the technology for continuous groundwater treatment.

11.4 Summary

Two types of wetland systems were evaluated for treating groundwater contaminated with explosives at the Milan Army Ammunition Plant during the Milan demonstration (Phase II of this project). One type was a lagoon-based wetland containing submergent plants. The second type was a gravel-based wetland in which contaminated water flowed through gravel planted with emergent wetland plants. Each wetland treated 5 gpm of contaminated groundwater from June 17, 1996, to September 16, 1997. The nitrobody concentration in the groundwater was 3,250 ppm from June to November 1996 and 9,200 ppm from November 1996 to August 1997.

Demonstration results indicate that while both the lagoon- and gravel-based systems could remove explosives, the gravel-based system was clearly superior. The lagoon-based system was unable to satisfactorily remove RDX, HMX, or meet the total nitrobody removal goals and was only able to meet the TNT reduction goal of 2 ppb during the initial stages of the demonstration. In contrast, the gravel-based system was able to degrade both HMX and RDX and was able to meet the demonstration goals during all but the coldest months. During winter operations, the gravel-based system had difficulty meeting the total nitrobody reduction goals due to a decrease in treatment efficiencies at low water temperatures. Design and cost analysis indicates that a gravel-based system can be economically resized to overcome the winter performance issues. To verify these conclusions, additional winter performance data will be collected from the gravel-based system during Phase III. Phase III will be conducted during the winter of 1998.

Based on these demonstration results, the gravel-based system would make an economically and technically sound alternative for the remediation of explosives-contaminated groundwater.