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

**Volume II of IV
(Phase III Demonstration Results)**

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

Funded Through



Prepared by
**Tennessee Valley Authority
Resource Management
Muscle Shoals, Alabama 35662-1010**

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**U.S. Army Environmental Center
Pollution Prevention and Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401
POC: Ms. Darlene F. Bader**

Funded Through
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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 ₂ SO 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

SECTION 12.0
INTRODUCTION (PHASE III)

12.1 Phase III - Background and Objectives

During Phase II, it became apparent that the collection of additional data would be helpful to improve the design, operation, and economic success of scaled-up 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 alternate carbon sources in the anaerobic cell (cell A1)
- Establishing the anaerobic cell's performance at a lower flow rate (i.e., at a longer retention time)

These issues were addressed by extending the operating period of the existing large-scale demonstration program. This extension is referred to as Phase III.

The Phase III program was conducted from September 17, 1997, to July 21, 1998. During Phase III, the operation of the lagoon-based wetland was discontinued due to its poor performance in degrading RDX and difficulties in maintaining an adequate plant population within the lagoons. Changes to the operation of the gravel-based wetlands included:

- Using a less expensive carbon source (sucrose [cane molasses syrup] as opposed to milk replacement powder [MRS])
- Adding the carbon and nutrient sources more frequently (1 gallon of molasses syrup and 40 grams of diammonium phosphate each day versus 113.4 Kg of MRS every two weeks)
- Decreasing the amount of carbon added by one half
- Lowering the influent flow rate from 5 to 3 gpm.

Project objectives during Phase III 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 supplied carbon by one half
- Evaluate the gravel-based wetlands' ability to remove RDX and RDX by-products by increasing the groundwater's retention time in the gravel beds
- 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

In evaluating the information gathered during Phase III, data from both Phase II and Phase III were considered.

12.2 Approach

Evaluation of explosive remediation was assessed using the gravel-based system. The operational aspects of Phase III closely paralleled the approach previously reported in Phase II (see Volume I). Findings from the gravel-based system's first 16 months of operation indicated that a number of operational modifications could enhance explosive removal and lower operating cost. The intent of the Phase III work was to evaluate these modifications. The most significant system modification was the total reworking of the nutrient delivery system. In Phase II, a solution containing 113 kg of milk replacement powder (MRS) was injected into cell A1 every 14 days. Details of this system are described in Volume I, Section 2.4. As part of the Phase III program, the MRS system was totally replaced on September 10, 1997. Prior studies indicated that relatively soluble organic carbon sources, such as cane molasses syrup, were a better carbon source than less soluble sources like MRS and that cane molasses syrup costs an order of magnitude less than MRS.^{Ref. 12} Therefore, the system was modified to receive 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 70 ml of water. The method of delivering the nutrient solution was similar to that used in the MRS system and consisted of two delivery systems (Figure 12-1). The first system (unit 1) was located near cell A1's inlet header and the second system (unit 2) was located one third of the distance 'down' the anaerobic gravel bed.

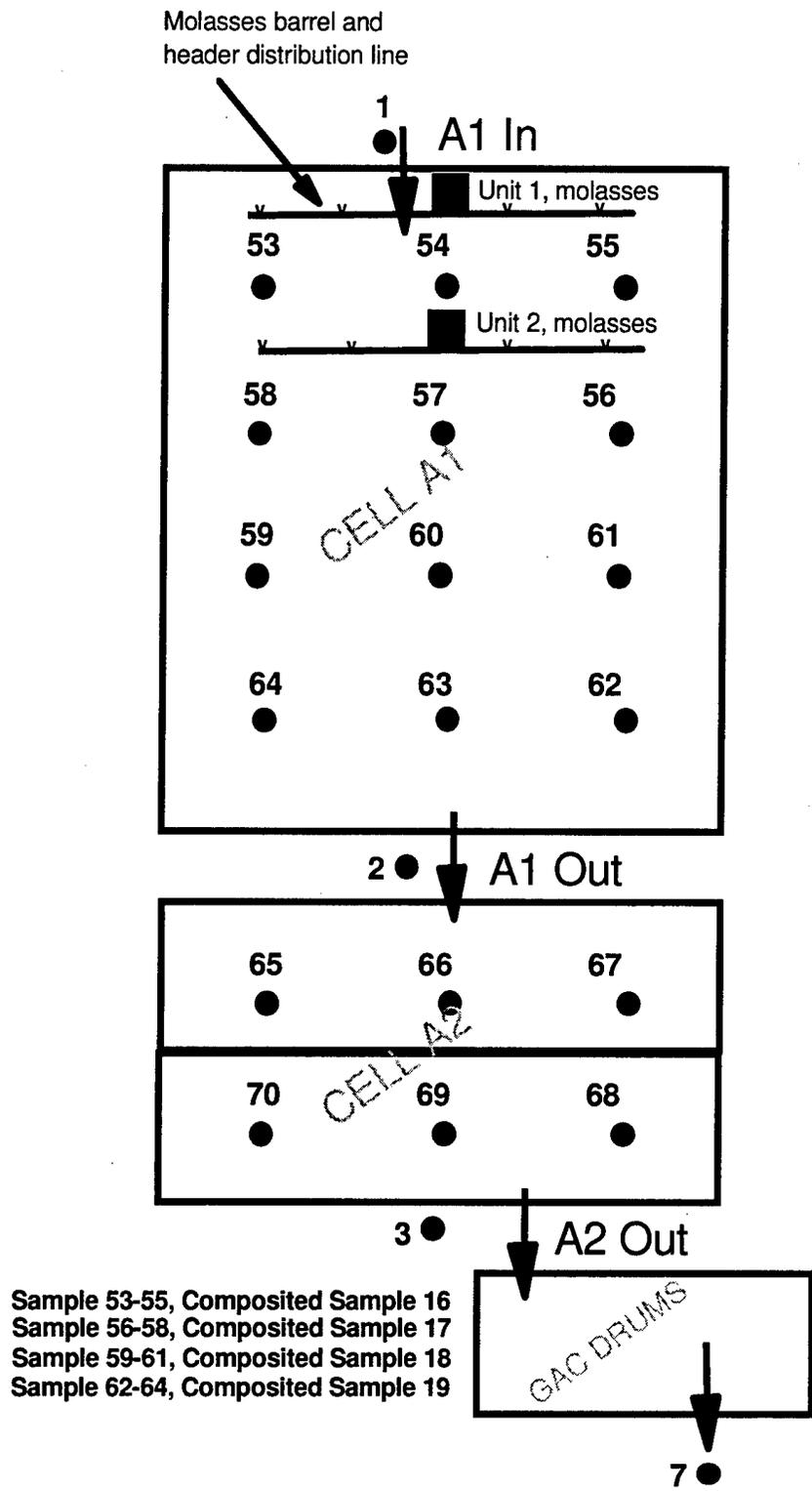


Figure 12-1

Diagram of Nutrient Solution Delivery System and Selected Sampling Points

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 at unit 2. Half a gallon of cane 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 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. As with 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.

The Phase II sampling protocol was modified to reduce the expenditure of time and manpower needed to evaluate these changes. It was also modified because a number of operational performance questions could be answered with the data gathered in Phase II or extrapolated from previous data. During Phase III, only water samples were collected. Phase III sampling consisted of one routine sampling program and one intensive sampling program each month (but, the routine and intensive programs were staggered two weeks apart). The routine sampling program was implemented at the beginning of Phase III and continued until the end of Phase III. The intensive sampling program was started in December 1997 and continued through April 1998.

12.3 Schedule

Phase III activities began on September 17, 1997, and continued through July 21, 1998 (see Gantt chart in Volume I, Table 1-1).

SECTION 13.0
SAMPLING PLAN (PHASE III)

13.1 Overview of Sampling Operations

The Phase III goals were to:

- Provide information on using a new carbon source to maintain anaerobic conditions in cell A1
- Evaluate winter performance of the system
- Test performance of a more mature system (i.e., conditions beyond the 1st year setup)
- Evaluate the impact of solids buildup on performance

These goals were met by exposing the gravel-based wetlands to explosives-contaminated water and monitoring explosive removal dynamics. Monitoring was expected to provide insight into:

- The wetlands' ability to remediate explosives-contaminated water
- The general condition of the wetlands
- The fate of explosives entering the wetland system

A list of characteristics monitored is provided in Table 13-1.

The wetlands' ability to remove explosives was evaluated by monitoring explosive 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 13-2. This table also provides a general outline of the plan used to analyze the gravel-based wetlands' ability 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 13-1
Sampling Goals for Phase III of 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	Monthly
	Retention Time Verification	Preferential Flow to Specific Wells Across a Cell	Intensive	Once
Monitor the General Condition of the Wetland	System Efficiency	Explosive Removal Efficiency	Routine	Monthly
	Water Chemistry	Various Analytes (see Table 3-3)	Routine	Monthly
	Physical Characteristics	Miscellaneous Characteristics (see Table 3-3)	Routine	Monthly
Determine the Fate of Explosives Entering the Wetlands	Fate in Water	Explosive and By-Product Concentrations	Routine	Monthly
		Additional Sample Points and Explosive By-Products	Intensive	Monthly

Table 13-2
Wetland Performance - Characteristics Measured During Phase III of 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 Volume I, Section 3.6.1)	Intensive/Monthly
Retention Time Verification	Preferential Flow to Specific Wells Across a Cell	Hydraulic Tracer Test: Results of Overall Mixing and Short-Circuiting Test	Intensive/Once
System Efficiency	Explosive Removal Efficiency	Calculated From Influent and Effluent Explosive Concentrations	Routine/Monthly

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

13.2 Description of the Phase III Sampling Program

To meet the Phase III objectives, portions of both the Phase II routine and a modified intensive sampling program were combined and implemented, as indicated in Table 13-3. The sampling plan for Phase III was less intensive than for Phase II. The toxicity testing, gravel sampling, and the plant analysis portion of the program were omitted. The same sampling procedures, sampling point locations (Figure 12-1), and sample point designations used in Phase II were used during the Phase III demonstration. A bromide (Br) tracer study was included in Phase III to verify system hydraulics. It was hypothesized that greater plant biomass may influence efficacy of explosive removal and it was deemed appropriate to verify the first year's results of hydraulic response, especially since a new flow rate was instituted in the second year of the demonstration.

The general water quality parameters were monitored throughout Phase III 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 13-3).

13.3 Description of the Hydraulic Mixing Tests

An overall mixing test, a short-circuiting test, and a supplemented short-circuiting test were conducted in cell A1 from April 26, 1998, to May 24, 1998. A mixing test was also conducted in cell A2 at that time. These tests were conducted to quantify hydraulic retention times, determine three-dimensional flow patterns, and illustrate the dynamics of preferential flow (short circuiting). The tests were designed and conducted to allow comparison to studies conducted during January, May, and August of 1997. General sampling procedures for the Phase II tests are provided in Volume I, Sections 3.7.7 and 3.7.8.

Table 13-3
Outline of the Phase III Sampling Plan

Water Quality Parameters	Frequency	Method ¹	Position Number ²
Regulatory Issues			
Explosives (Total Nitrobodyes)			
TNT	Every month	AP-0062	1-3,7,16-21
RDX	Every month	AP-0062	1-3,7,16-21
TNB	Every month	AP-0062	1-3,7,16-21
HMX	Every month	AP-0062	1-3,7,16-21
2,4-DNT	Every month	AP-0062	1-3,7,16-21
2,6-DNT	Every month	AP-0062	1-3,7,16-21
Explosives By-Products			
2A-DNT (TNT by-product)	Every month	AP-0062	1-3,7,16-21
4A-DNT (TNT by-product)	Every month	AP-0062	1-3,7,16-21
2,6-DANT (TNT by-product)	Every month	AP-0062	1-3,7,16-21
2,4-DANT (TNT by-product)	Every month	AP-0062	1-3,7,16-21
3,5-DNA (TNT by-product)	Every month	AP-0062	1-3,7,16-21
1,3-DNB (TNB by-product)	Every month	AP-0062	1-3,7,16-21
Mononitroso RDX (RDX by-product)	Every month	AP-0062	1-3,7,16-21
Trinitroso RDX (RDX by-product)	Every month	AP-0062	1-3,7,16-21
Azoxy Compounds	Every month	AP-0062	1-3,7,16-21
Other			
Biochemical Oxygen Demand (BOD-5)	Every month	405.1 Series	1-3,7,16-21
Total Suspended Solids	Every month	160.2 Series	1-3,7,16-21
Chlorides	Every month	AP-0300	1-3,7,16-21
Water Quality Parameters			
Dissolved Oxygen, pH, Electrical Conductivity, and Temperature	Every month	Meter ³ (YSI sonde)	1-3
Oxidation Reduction Potential	Every month	Method 2580	1-3
Dissolved Oxygen, pH, Electrical Conductivity, and Temperature	Four measurements a day, downloaded every 2 weeks	Meter ³ (YSI sonde)	53-64 at mid-depth
Total Flow Rate	Every month	Meter	1-3
Non-Purgeable Organic Carbon (NPOC)	Every month	415 Series	1-3,7
Chemical Oxygen Demand (COD)	Every month	410 Series	1-3,7
Plant Nutrients			
Ammonia Nitrogen (NH ₄ -N)	Every month	350 Series	1-3,7
Total Kjeldahl Nitrogen (TKN)	Every month	351 Series	1-3,7
Nitrate and Nitrite Nitrogen ((NO ₃ +NO ₂ -N)	Every month	353 Series	1-3,7
Orthophosphate (PO ₄ -P)	Every month	AP-0060	1-3,7

- 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.

As during Phase II, sodium bromide was used as the tracer of choice due to its inert chemistry and high solubility. However, two operating conditions were changed during the 1998 study. These changes included:

- Reducing the inlet flow rate into cell A1 from 5 to 3 gpm. This resulted in an increase in the theoretical hydraulic residence time in cell A1 from 7.5 to 12.5 days and the time in cell A2 from 1.7 to 2.7 days.
- Increasing the sodium bromide concentration by a factor of two to enhance analytical resolution. (In the Phase II tracer tests, it appeared that nitrate in the influent water interfered with detection of bromide.)

Other than the above noted changes, bromide tracer and sampling protocols used during Phase III were similar to those used during Phase II (see Volume I, Sections 3.5, 3.7.7, and 3.7.8). The sampling schedules for the Phase III tracer tests are summarized in Table 13-4.

To conduct the tracer studies in cell A1, a concentrated solution of sodium bromide was prepared by dissolving 1,896 g of NaBr into approximately 35 liters (9 gallons) of water. On April 26, 1998, five aliquots of the solution were equally distributed to the five sampling points of the influent manifold over a one-hour period. Bromide concentrations were monitored by collecting whole column water samples at sample points 2 (for mixing test) and 38-42 (for short-circuiting test). These sampling point locations are shown in Figure 3-3 (see Volume I). For the supplemental short-circuiting test (see description in Section 3.5.3), discrete water samples were also collected at sampling points 53-64 at depths of 8, 24, and 40 inches from the surface of the water. The samples at sampling points 38-42 (Figure 3-3) and 53-64 (Figure 12-1) were collected every 12 hours (0600 and 1800 hours) for a 28-day period. The effluent samples (sample point 2) were collected every 12 hours for the duration of the study using an auto-sampler.

To conduct the mixing test in cell A2, a concentrated solution was prepared by dissolving 560g of NaBr in approximately 15 liters (4 gallons) of water. The concentrated solution was added to the outlet sump of cell A1. As the tracer flowed through cell A2, water samples were

Table 13-4
Phase III Bromide Tracer Sampling Schedule

Date	Time	Sample Location ¹	Action	Samples
4/14/98	1200	2	Spike bromide in A-1 effluent sump	
4/14/98	1200	3	Start auto-sampler operation	
4/20/98	1200	3	Collect auto-sampler contents for analysis	24
4/26/98	1200	3	Collect auto-sampler contents for analysis	24
4/26/98	1200	1	Spike bromide in A-1 influent headers	
4/26/98	1200	2	Start auto-sampler operation	
4/27/98	0600	38-42 (B)	Collect discrete samples	5
		53-55 (T,M,B)	Collect discrete samples	9
4/27/98	1800	38-42 (B)	Collect discrete samples	5
		53-55 (T,M,B)	Collect discrete samples	9
4/28/98	0600	38-42 (B)	Collect discrete samples	5
		53-58 (T,M,B)	Collect discrete samples	9
4/28/98	1800	38-42 (B)	Collect discrete samples	5
		53-58 (T,M,B)	Collect discrete samples	9
4/29/98	0600	38-42 (B)	Collect discrete samples	5
		53-58 (T,M,B)	Collect discrete samples	9
4/29/98	1800	38-42 (B)	Collect discrete samples	5
		53-61 (T,M,B)	Collect discrete samples	9
4/30/98	0600	38-42 (B)	Collect discrete samples	5
		53-64 (T,M,B)	Collect discrete samples	9
4/30/98	1800	38-42 (B)	Collect discrete samples	5
		53-64 (T,M,B)	Collect discrete samples	9
5/1/98	0600	38-42 (B)	Collect discrete samples	5
		53-64 (T,M,B)	Collect discrete samples	9
5/1/98	1800	38-42 (B)	Collect discrete samples	5
		53-64 (T,M,B)	Collect discrete samples	9
5/2/98	1200	2	Collect auto sampler contents and restart	24
5/2/98	0600	38-42 (B)	Collect discrete samples	5
		53-55	Collect whole column samples	3
		56-64 (T,M,B)	Collect discrete samples	27
5/2/98	1800	38-42 (B)	Collect discrete samples	5
		53-55	Collect whole column samples	3
		56-64 (T,M,B)	Collect discrete samples	27
5/3/98	0600	38-42 (B)	Collect discrete samples	5
		53-58	Collect whole column samples	6
		59-64 (T,M,B)	Collect discrete samples	18
5/3/98	1800	38-42 (B)	Collect discrete samples	5
		53-58	Collect whole column samples	6
		59-64 (T,M,B)	Collect discrete samples	18

1) Abbreviations T,M,B refer to samples collected at the top, middle, and bottom of respective sampling points.

Table 13-4 (Continued)
Phase III Bromide Tracer Sampling Schedule

Date	Time	Sample Location ¹	Action	Samples
5/4/98	0600	38-42 (B)	Collect discrete samples	5
		53-61	Collect whole column samples	9
		62-64 (T,M,B)	Collect discrete samples	9
5/4/98	1800	38-42 (B)	Collect discrete samples	5
		53-61	Collect whole column samples	9
		62-64 (T,M,B)	Collect discrete samples	9
5/5/98	0600	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/5/98	1800	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/6/98	0600	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/6/98	1800	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/7/98	0600	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/7/98	1800	38-42 (B) 53-64	Collect discrete samples Collect whole column samples	5 12
5/8/98	1200	2	Collect auto sampler contents and restart	24
5/8/98	0600	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/8/98	1800	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/9/98	0600	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/9/98	1800	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/10/98	0600	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/10/98	1800	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/11/98	0600	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/11/98	1800	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/12/98	0600	38-42 (B)	Collect discrete samples	5
		53-64	Collect whole column samples	12
5/12/98	1200	2	Collect auto sampler contents for analysis	20
5/18/98	1200	2	Collect auto sampler contents for analysis	24
5/24/98	1200	2	Collect auto sampler contents for analysis	24

1) Abbreviations T,M,B refer to samples collected at the top, middle, and bottom of respective sampling points.

collected from sampling point 3 using an auto-sampler. The auto-sampler collected a 50-ml sample every 1.5 hours. Four samples were collected in each of the sampler's 200-ml storage containers; hence, each container held a 6-hour composite sample. The samples were collected over a 12-day period.

SECTION 14.0
FACILITY OPERATIONS (PHASE III)

14.1 **Description of Facility Operations**

Only the gravel-based system was operated during Phase III. As discussed in Volume I, the lagoon-based system was not operated during Phase III because it was ineffective at treating RDX and because it was difficult to maintain an adequate plant population in the lagoons. As in Phase II, the gravel-based system was run with limited operator intervention. Facility operations were chiefly conducted by TVA personnel and followed the same operational protocols used during Phase II. These duties included:

- Obtaining hand-held water data, including temperature, DO, pH, specific conductivity, and redox (performed monthly)
- Collecting water samples for analysis of explosives and other analytes, including BOD, COD, chlorides, total suspended solids, NPOC, TKN, NH₄-N, NO₃-N, NO₂-N, and PO₄-P (performed monthly)
- Recording flow meter readings and rainfall data (performed biweekly)
- Replenishing molasses syrup and diammonium phosphate (DAP) [done biweekly]
- Changing pump tubing on the molasses syrup pump (performed biweekly)
- Checking flow meters for blockage and cleaning them, if necessary, to provide the proper flow rate and adjusting the flow rate to 3 gpm, as needed (performed biweekly)
- In the winter months, replacing light bulbs in the insulated containers containing the nutrient feeding system. The light bulbs served as a source of heat for the nutrient feed system to prevent freeze damage to pumps and equipment (performed biweekly)

14.2 **Operational Problems and Solutions**

Operational problems encountered during Phase III were:

- Blockage of inlet and outlet headers
- Pump failures

- Weather-related interruptions
- Flow meter malfunctions
- Blockage of feeder lines from the molasses syrup feed system
- Lightning strikes

These setbacks were all temporary in nature and, overall, the system performed well during the Phase III demonstration. A detailed description of the problems encountered and corrective actions taken are listed below.

14.2.1 Blockage of Inlet and Outlet Headers

Blockage of both inlet and outlet headers occurred during Phase III, but at a slower pace than in Phase II and with less severe consequences. In October 1997, diminished flow was observed on each of the routine visits. Investigation indicated that slime (presumably bacteria, mold, or algae) had built up in the A1 distribution lines. This was corrected by dismantling the lines and cleaning them with a hypochlorite solution. During the following winter months, the headers were inspected by TVA during each biweekly visit. On February 17 and March 3, 1998, TVA personnel observed that flow from the A1 outlet header was restricted by the deposition of dead plant material. The header was cleaned by flushing it with water. No further problems were encountered after March 3, 1998.

14.2.2 Pump Failure

On November 12, 1997, it was discovered that only about one-half of the molasses syrup in the Unit 1 barrel (Figure 12-1) had been dispensed into cell A1. The peristaltic pump was found to be inoperable and a new pump was installed. On the next biweekly trip, the Unit 2 peristaltic pump was replaced. The old pumps were reconditioned and kept onsite to provide backup.

14.2.3 Weather-Related Interruptions/Failures

On November 25, 1997, a check valve (A1, Unit 2) was replaced due to freeze damage. This did not affect the unit's operability.

On January 20, 1998, an ice storm downed electrical lines resulting in a power interruption. This resulted in a one day loss of system power. Also on that day, it was observed that the molasses syrup feed rate appeared low (i.e., complete drawdown of the molasses reservoir was not accomplished). This was thought to be the result of low temperatures making the molasses syrup more viscous and, thereby, harder to pump. The system was restored the following day after a local power utility crew repaired the downed electrical lines.

14.2.4 Flow Meter Malfunction

On January 6, June 9, and June 23, 1998, the A1 outlet flow meter became clogged and the system reverted to gravity flow. The first two times, a simple cleaning of an internal mechanical wheel was adequate to restore operability of the units. During the June 23, 1998, incident, it was not possible to clean the unit sufficiently and, therefore, a spare flow meter was placed back in the system. In all instances, it appeared as if a silt deposit had bound up the internal flywheel.

14.2.5 Blockage of the Feed Lines From the Molasses Feed System

On February 3, 1998, and March 3, 1998, it was noted that the feed lines from the molasses syrup supply unit had become clogged with slime. Because residual amounts of molasses syrup were being left in the lines, TVA operating personnel felt that the slime was of microbial origin. Slime buildups appeared to be more severe during cold weather when it was more difficult to pump the molasses syrup due to its high viscosity.

To address this problem, the pump configuration was changed to include a water purge after injecting the molasses syrup. To purge the line, the sump pump was programmed to operate for 2 minutes after each 10-minute delivery cycle twice a day. This allowed for the removal of any molasses syrup in the lines. In addition, the molasses syrup feed lines were rotated so that control valves were in a vertical position to allow gravity drainage of the feed line and to lessen the likelihood of molasses syrup remaining in the line. These modifications were effective and the blockages did not reoccur.

14.2.6 Lightning Strikes

A lightning strike was the probable cause of the failure of a reciprocating pump in A2 and one of the A2 OUT pumps. The pump failures were discovered on July 7, 1998. The reciprocating pump was replaced. The A2 OUT pump was not replaced since the system was to be closed within two weeks and the remaining pump could be used. The float used to activate the A2 OUT pump was simply changed to the remaining working pump for the remainder of the demonstration.

SECTION 15.0
EXPERIMENTAL RESULTS (PHASE III)

15.1 **Routine Sample Test Results**

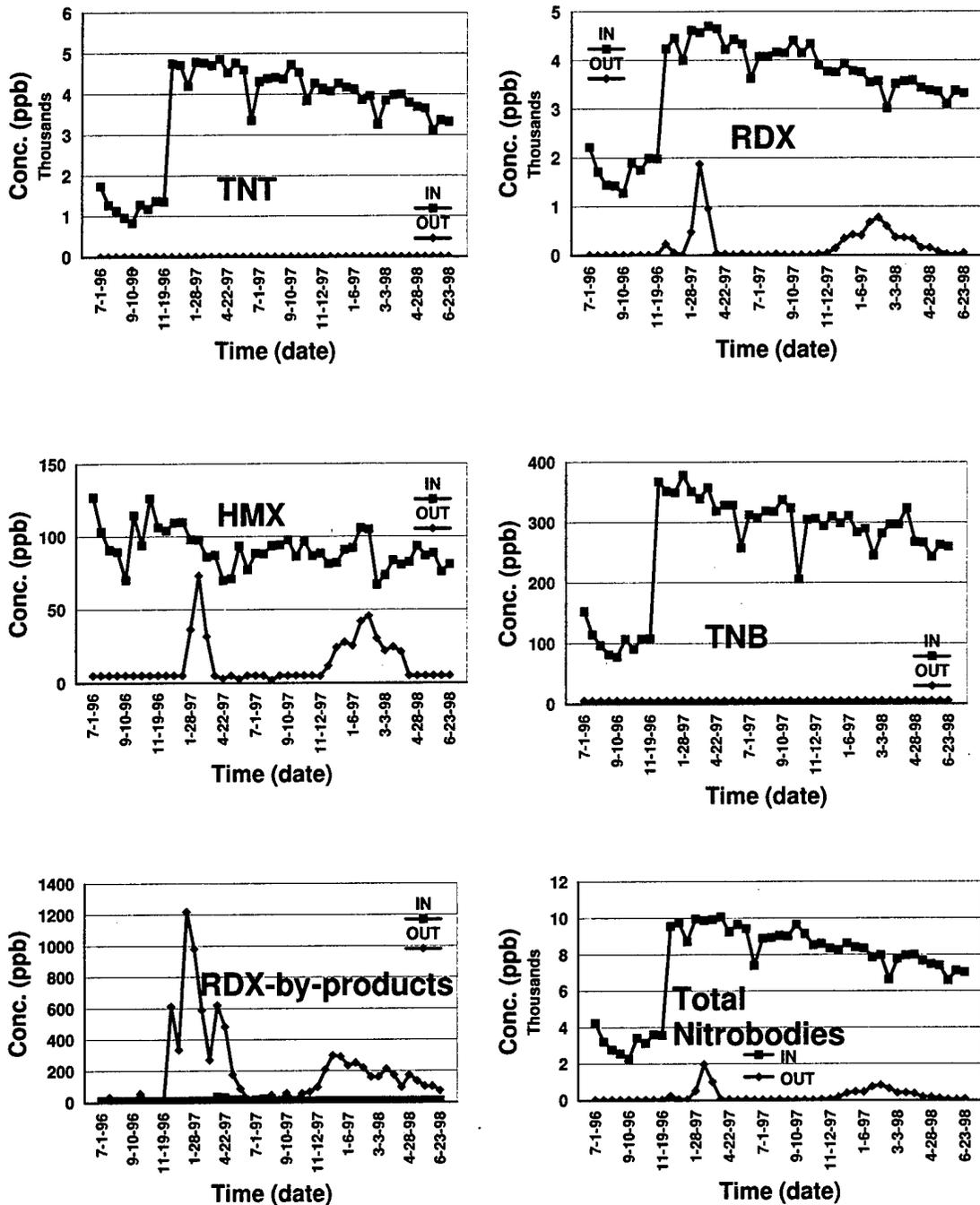
15.1.1 **Incoming Explosive Concentrations**

The total concentration of incoming explosives and explosive by-products are shown in Figures 15-1 and 15-2, respectively. Explosives-contaminated water from well MI-051 was used throughout Phase III. This water contained an average of 7,990 ppb total nitrobodyes including: 3,907 ppb TNT; 3,660 ppb RDX; 286 ppb TNB; 87 ppb HMX; 47 ppb 2,4-DNT; and 6 ppb 2,6-DNT. The explosive concentrations in the well water tended to decrease over the course of the demonstration (Figure 15-1). From the start of Phase III on September 16, 1997, to the end of Phase III, on July 21, 1998, the total nitrobody concentration decreased about 22%. This decrease was significant over the course of the demonstration. The statistical measure of the simple correlation coefficient, or R^2 , which is a measure of the degree of linear association between two variables, was 0.59 between time and nitrobody concentration. This correlation was similar to the decrease in nitrobody concentration with time observed in well MI-146 during Phase II. The slower rate of withdrawal, 3 gpm in Phase III compared to 5 gpm in Phase II, did not appear to influence the linear decrease in nitrobody concentration.

The other explosive by-products monitored (2,6-DANT, 2,4-DANT, 2,6-DNT, 1,3-DNB, and 3,5-DNA) were at or very close to the detection limits for both influent and effluent concentrations (Figure 15-3). In every instance, analysis revealed that effluent 2,6-DANT and 2,6-DNT concentrations were at or below minimum detection limits.

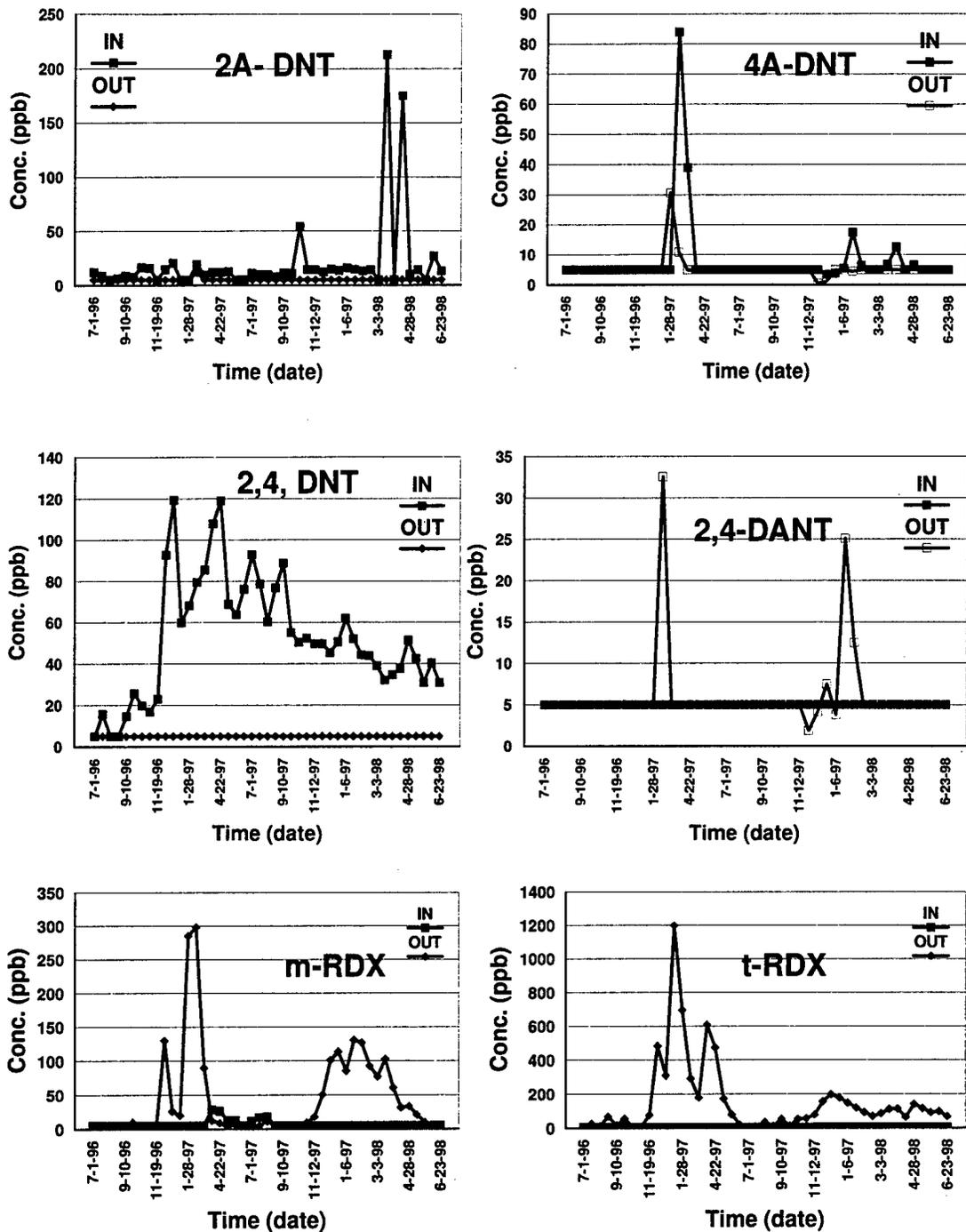
15.1.2 **Explosives Removal by the Gravel-Based Wetland**

Throughout Phase III, the gravel-based wetland met the demonstration goal of reducing TNT to less than 2 ppb. However, the goal of reducing the total nitrobody concentration to less than 50 ppb was not met (Figure 15-1). The total nitrobody concentrations in the gravel-based system's effluent exceeded the limit throughout the period between December 9, 1997, and June 20, 1998. The highest total nitrobody concentrations were encountered during the winter



Note: When a chemical was not detected, the Method Detection Limit was plotted instead.

Figure 15-1
Influent and Effluent Explosive Concentrations of the Gravel-Based Wetland
From June 17, 1996, to July 21, 1998



Note: When a chemical was not detected, the Method Detection Limit was plotted instead.

Figure 15-2
Influent and Effluent Explosive By-Product Concentrations of the Gravel-Based Wetland
From June 17, 1996, to July 21, 1998

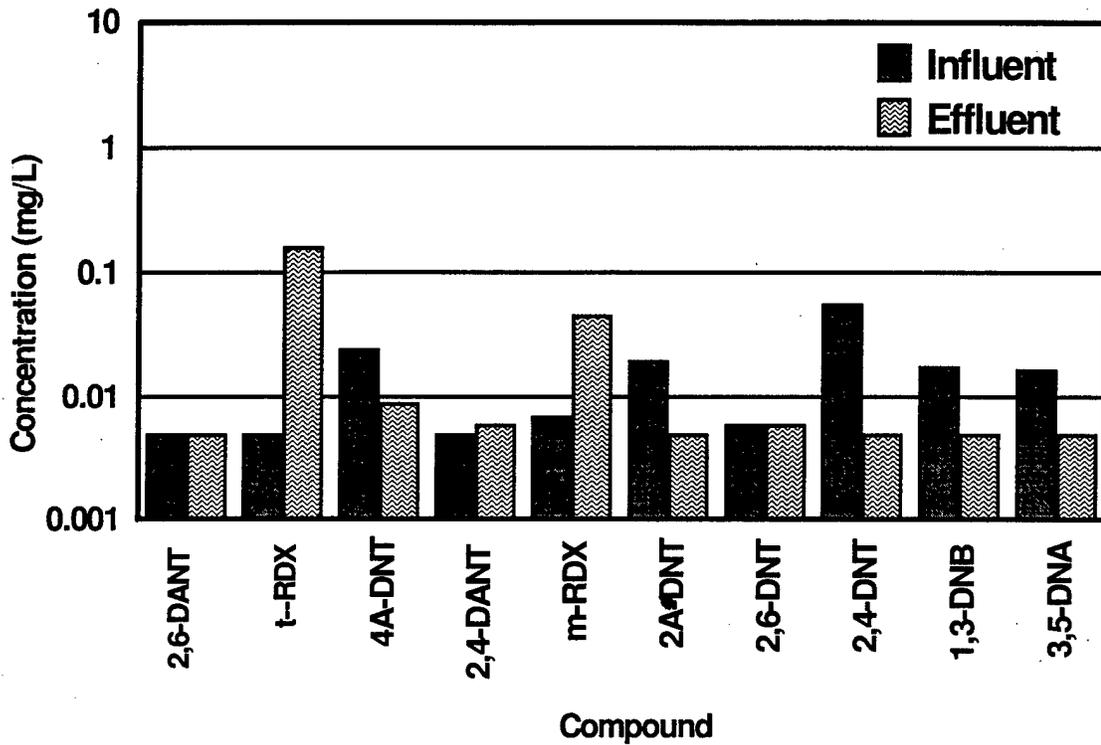


Figure 15-3
Average Influent and Effluent Explosive By-Product Concentrations From the
Gravel-Based Wetland From June 17, 1996, to July 21, 1998

months with the peak concentration (836 ppb) occurring on February 21, 1998.

Although there was a distinct increase in the concentration of most explosives and explosive by-products in the gravel-based system's effluent during the Phase III winter months, this increase was about half that experienced during Phase II. The increase in explosive and explosive by-product concentrations during the Phase II winter months could not be solely ascribed to lower temperatures since the system also experienced short-circuiting due to outlet header blockages due to the use of MRS. The Phase III change to a molasses-based carbon source and the reduction of the rate of carbon usage were part of an effort to avoid these blockages. The switch of carbon sources did reduce the number of outlet header blockages. However, the reduced carbon feed rate decreased the rate of contaminate removal (see Section 15.2.2.2). Consequently, despite a reduction in the influent feed rate from 5 gpm to 3 gpm, the system's overall performance during Phase III was only slightly better than in Phase II.

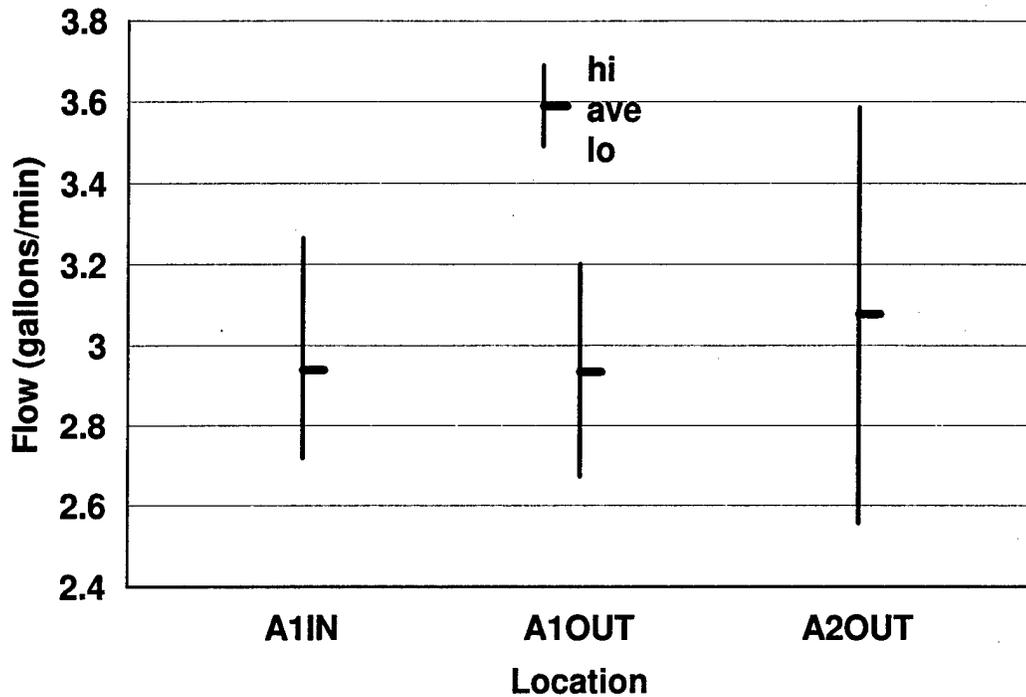
15.1.3 Flow Rate, Meteorological, and Water Quality

15.1.3.1 Influent and Effluent Flow Rates

The target flow rate of 3 gpm during Phase III was achieved. Flow rates for the A1 inlet, A1 outlet, and A2 outlet varied from 3.58 to 2.55 gpm (Figure 15-4). As noted in the Phase II report (Volume I), the flow variations detected are the result of the cumulative effects of several factors, including pump flow variations, mechanical flow meter variation, precipitation, evaporation, and evapotranspiration. Given the circumstances, the observed variation in flow was quite uniform, exhibiting an 11% coefficient of variation.

15.1.3.2 Meteorological Data

Average monthly rainfall and air temperature data were obtained from the NOAA Climatological Data Annual Survey (NOAA, Tennessee, 1996-1997, Asheville, NC). In comparison to long-term (30-year) averages for the site, the site experienced generally drier than normal conditions from September 1997 to March 1998 (Figure 15-5). However, wetter than normal conditions were experienced between April and June 1998.



The sample positions above are located at the:

- 1) A1 IN (inlet to anaerobic gravel bed)
- 2) A1 OUT (outlet from the anaerobic gravel bed)
- 3) A2 OUT (outlet from the aerobic gravel bed)

Figure 15-4

**Influent and Effluent Flow Rates for the Gravel-Based Wetland
From September 16, 1997, to July 21, 1998**

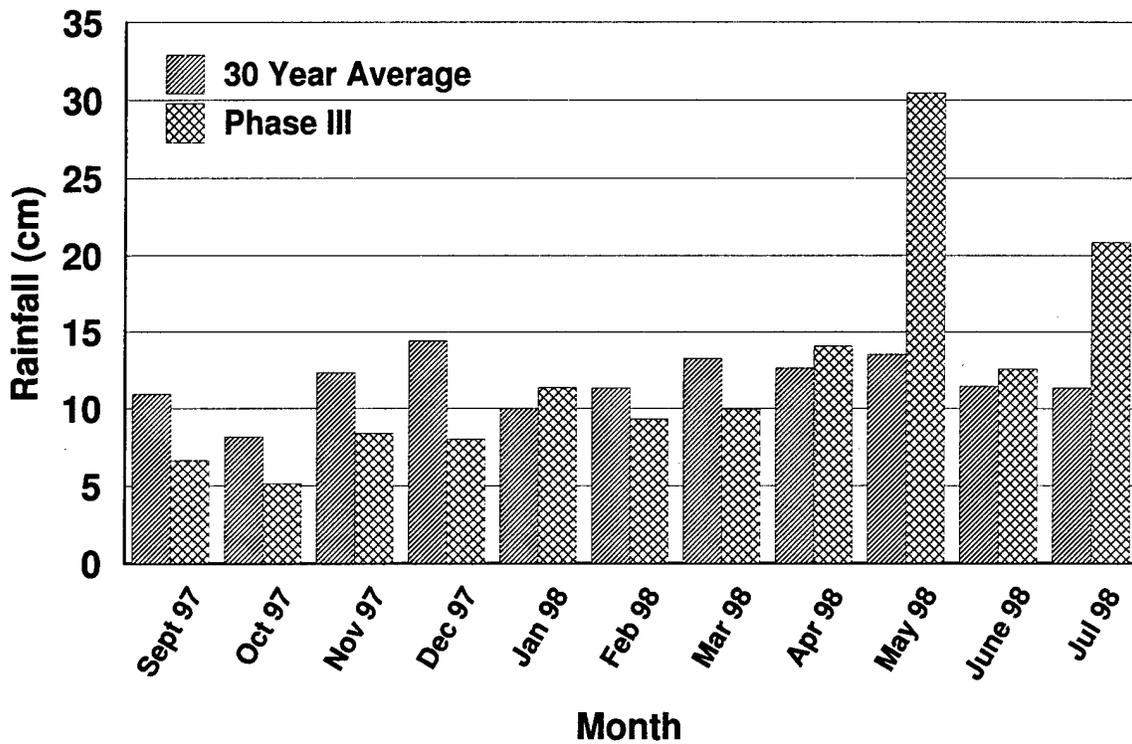
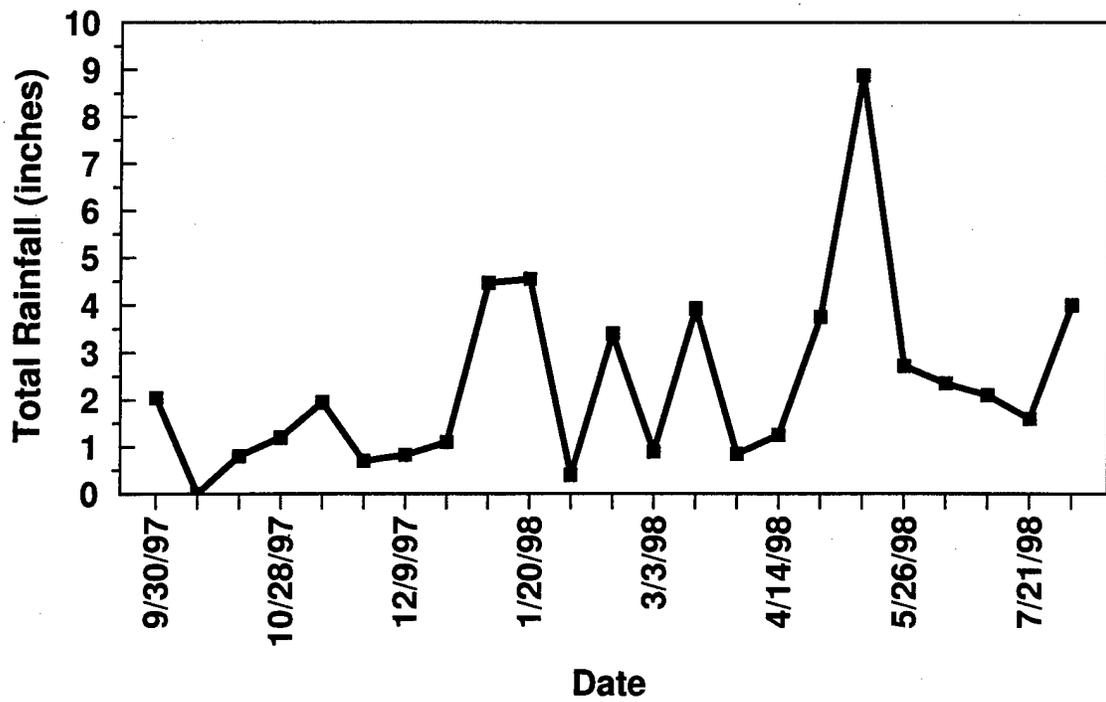


Figure 15-5
Rainfall From September 16, 1997, to July 21, 1998

Temperatures for both the Phase II and Phase III winter periods were above normal compared to the long-term (30-year NOAA data) average for the Milan site (Figure 15-6). During both phases, the winter temperatures were above the 30-year average.

15.1.3.3 Water Temperature

The temperature of the water entering and leaving the gravel-based wetlands showed seasonal declines in the cooler months, with the lowest temperature recorded being 7.3°C on March 17, 1998 (Figure 15-7). The incoming groundwater temperatures varied approximately 12°C, reflecting the effects of seasonal warming and cooling as the water moved from the well head to the wetland in a shallow buried pipe; a similar 10°C variation was observed in Phase II. The water temperatures within the anaerobic cell averaged 15.9°C, ranged between 7.3°C and 25.1°C, and varied minimally with location (Figure 15-8). The incoming and outgoing water temperatures for the anaerobic cell (cell A1) and the aerobic cell (cell A2) generally tracked within a few degrees of each other. Relative to the temperature of the water entering the anaerobic cell, the anaerobic and aerobic cells' outgoing water temperatures were depressed during the fall and winter months and tracked closer to the incoming water temperatures during the growing season.

15.1.3.4 Electrical Conductivity

Electrical conductivity (EC) is a measure of salt concentration which can be correlated with total dissolved solids. Throughout Phase III, the groundwater influent to cell A1 had the lowest electrical conductivity of the sample points measured (Figure 15-9). The electrical conductivity nearly doubled within the anaerobic cell and declined slightly in the aerobic cell. The mean electrical conductivity value within the anaerobic cell was about 0.5 mS/cm, varied from 0.85 to 0.3 mS/cm throughout Phase III, and increased down the length of the cell (Figure 15-10). This increase can be accounted for by several additive factors, such as the addition of inorganic fertilizer (diammonium phosphate) to the carbon source, evapotranspiration, and the dissolution of compounds in the gravel matrix, such as calcium carbonate (CaCO₃).

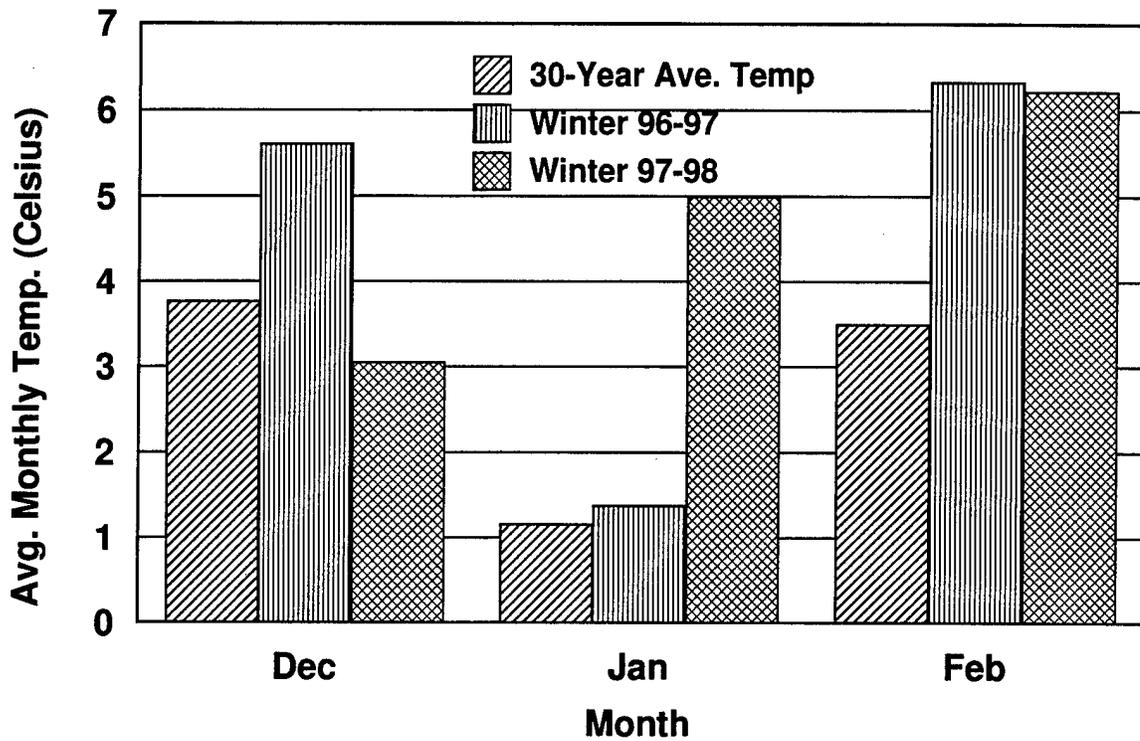


Figure 15-6
 Average Winter Air Temperatures During Phase II and Phase III

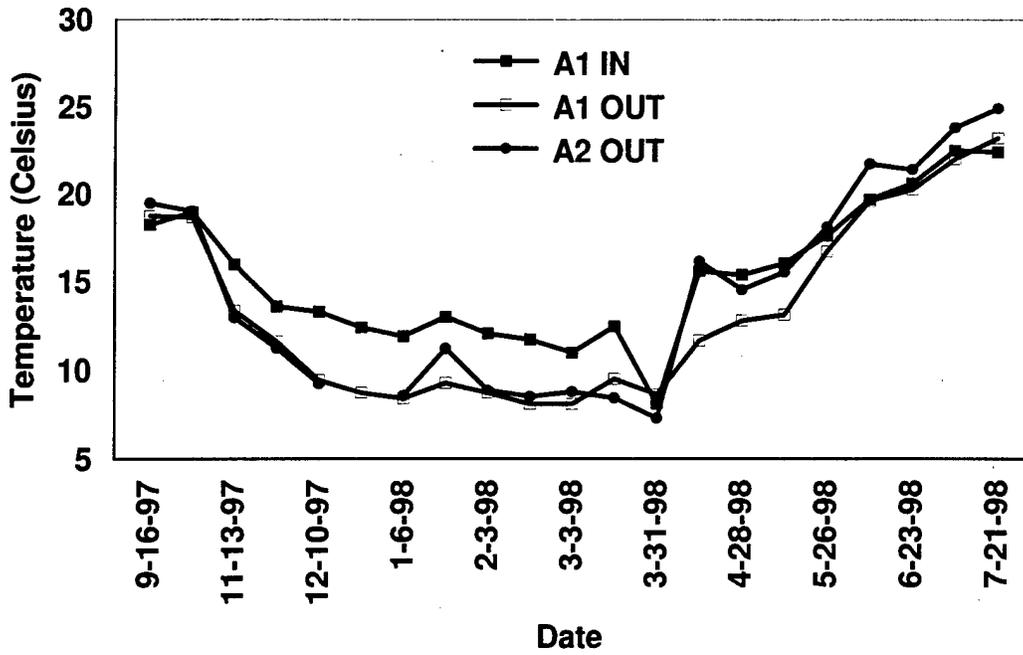


Figure 15-7

Average Wetland Water Temperatures in the Gravel-Based Wetland
From September 16, 1997, to July 21, 1998

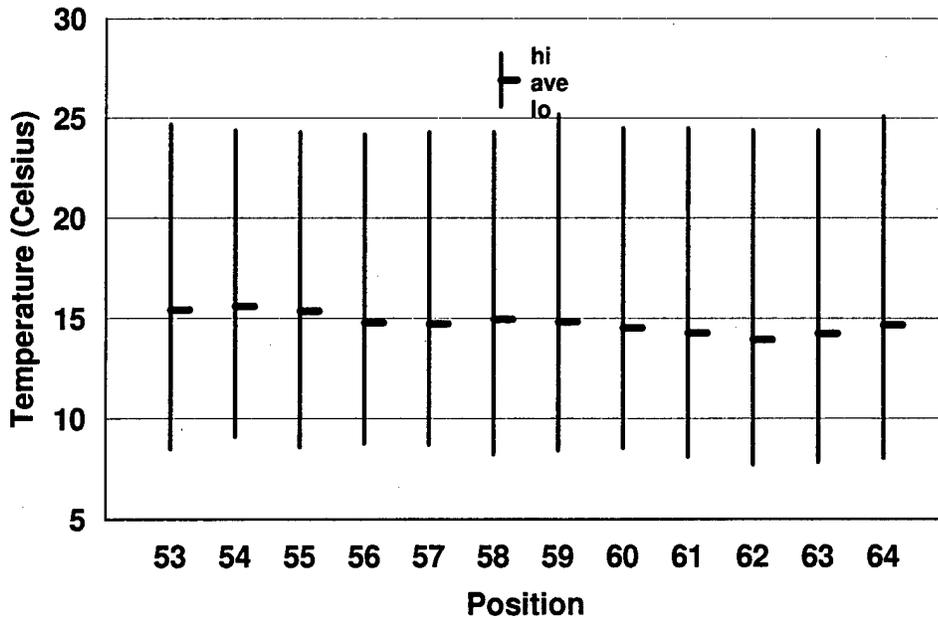
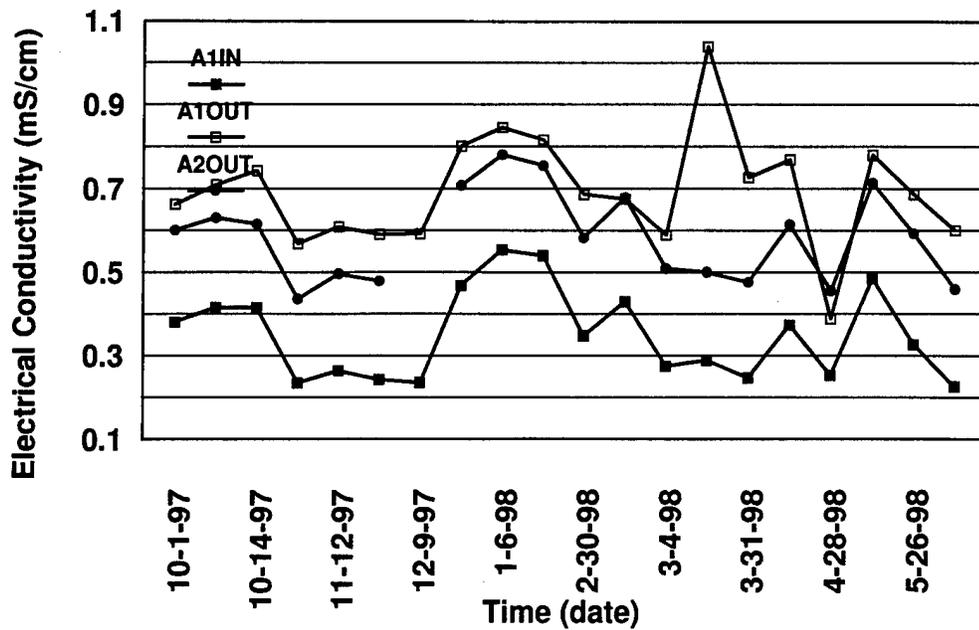


Figure 15-8

Annual Variation of Water Temperatures in Cell A1
From September 16, 1997, to July 21, 1998



Note: Break in A2 outlet due to an instrument malfunction.

Figure 15-9

Average Electrical Conductivity in the Gravel-Based System From September 16, 1997, to July 21, 1998

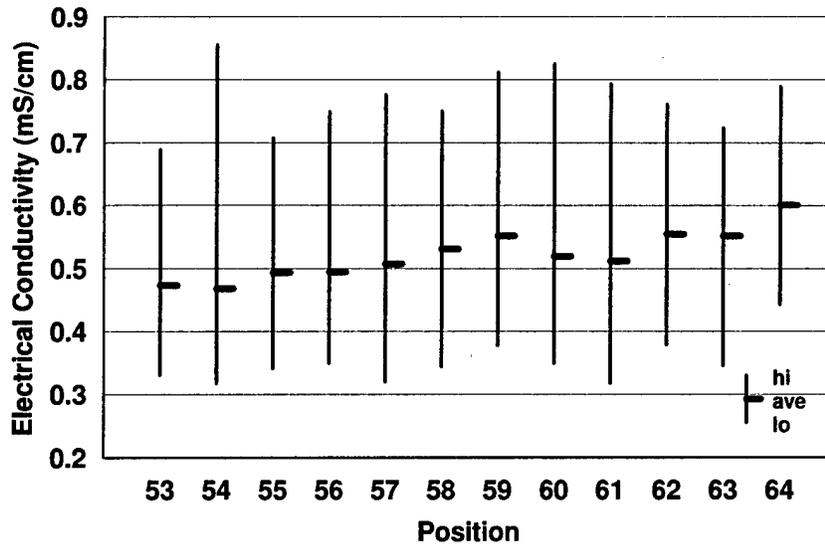


Figure 15-10

Annual Variation of Electrical Conductivity of Water in Cell A1 From September 16, 1997, to July 21, 1998

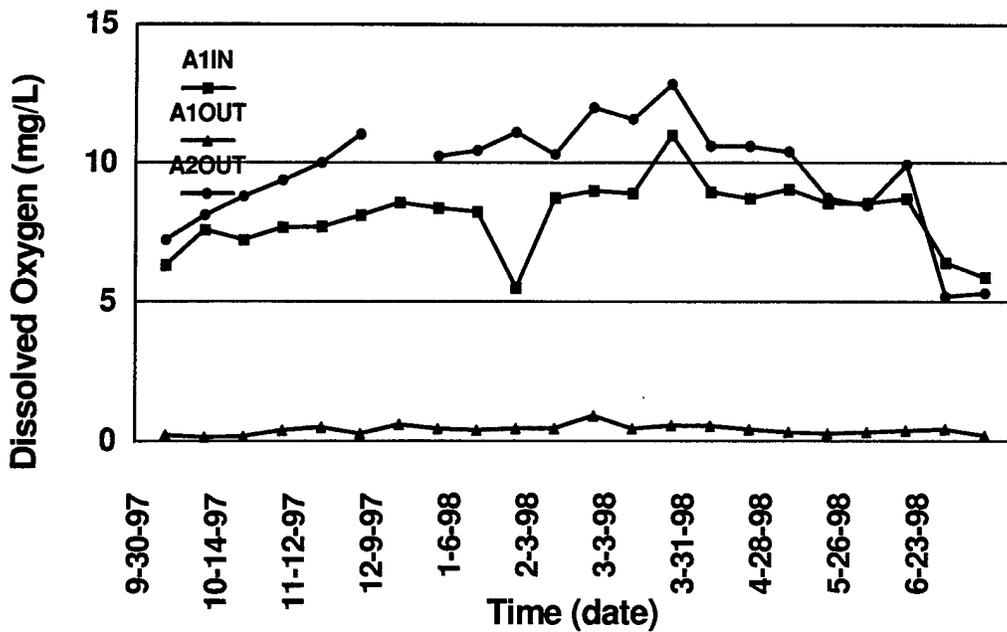
In contrast, the electrical conductivity of the water in the aerobic cell decreased from a mean of 0.69 mS/cm at the inlet to 0.58 mS/cm at the outlet. The decrease can be accounted for by degassing of CO₂ in the pore water of the gravel matrix and precipitation of calcium carbonate and metal ions such as manganese and iron. Precipitates of these and other ions will be formed due to carbon dioxide stripping and oxidation in the aerobic cell. Overall, the electrical conductivity increased from a mean of 0.38 mS/cm at the A1 inlet and to a mean of 0.69 mS/cm at the A2 outlet.

15.1.3.5 Dissolved Oxygen Concentration

A large drop in the dissolved oxygen concentration was observed between the anaerobic cell's inlet and outlet (Figure 15-11). Since both plant and microbes are responsible for oxygen consumption, these differences are thought to be due to respiration. The reduction was further increased by microbial activity promoted by additions of a carbon source (cane molasses syrup) and a nitrogen and phosphate source (diammonium phosphate). Seasonal changes in dissolved oxygen content are attributed to: (1) changes in community respiration as a function of temperature (high respiration in the summer; low respiration in the winter) and (2) changes in oxygen solubility as a function of temperature (higher solubility at low temperatures; lower solubility at high temperatures).

As a result of high organic fertilization rates (an average molasses syrup loading of 46 Kg ha/day), mean dissolved oxygen concentrations within the anaerobic gravel-based cell were very low (<1.0 mg/liter) during Phase III (Figure 15-12). These 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 a low surface-to-volume ratio. Low dissolved oxygen levels were also observed during Phase II (Volume I, Figure 6-10).

Aeration in the aerobic cell (A2) enhanced the removal of residual organic matter, as quantified by significant reductions in BOD₅ and COD and an increase of the dissolved oxygen content to moderate to high levels (Figure 15-11).



Note: Break in A2 outlet due to an instrument malfunction.

Figure 15-11

Annual Variation of the Gravel-Based Wetland's Dissolved Oxygen Content From September 16, 1997, to July 21, 1998

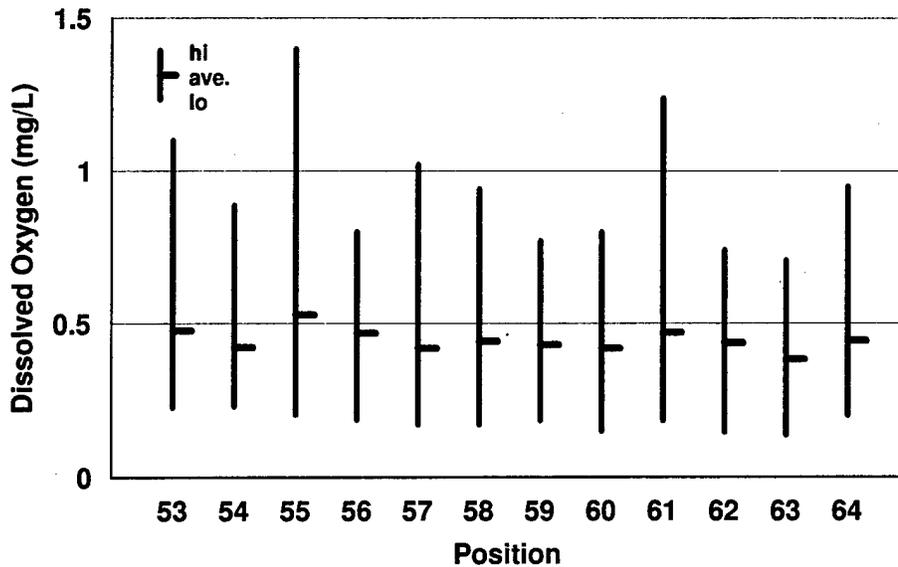


Figure 15-12

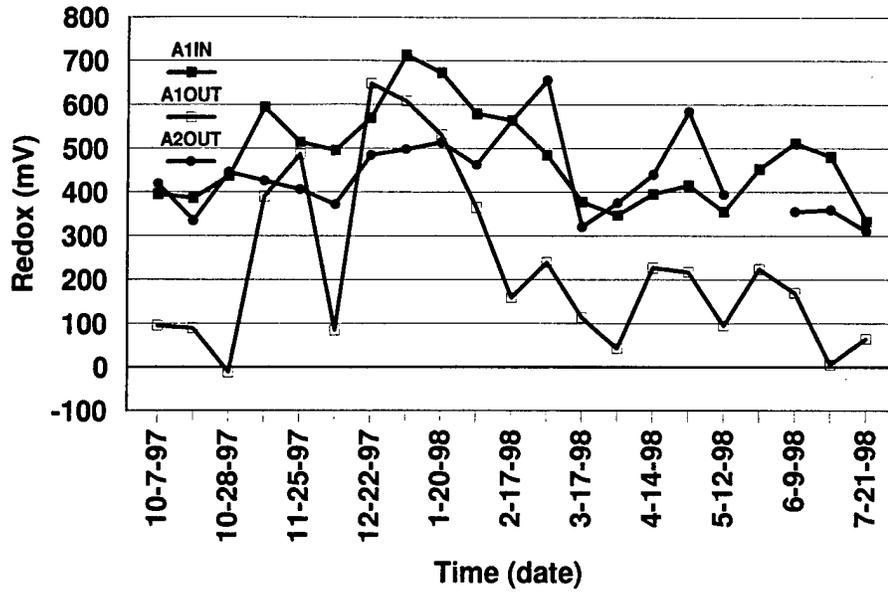
Average Dissolved Oxygen Content in Cell A1 From September 16, 1997, to July 21, 1998

15.1.3.6 Redox Potential

The mean redox potentials for the gravel-based system's influent and effluent streams in Phase III are provided in Figure 15-13. These redox values were not as low as those recorded in Phase II (compare Figure 15-13 with Figure 6-15, Volume I). For example, only two of the Phase III values at the A1 outlet indicate reducing conditions existed (i.e., had negative redox potentials); whereas in Phase II, over half the measured values were negative. The existence of higher redox values during Phase III suggests that the gravel-based wetland was not mature enough to supply a substantial portion of its own carbon during the second year. In addition, an increase in the influent nitrate concentration may have also effected explosives treatment. This is likely to have occurred because nitrates aggressively compete with explosives for the limited supply of electrons needed to reduce nitro-groups attached to explosives and explosive by-products. Thus, more carbon would have been required to maintain the same rate of explosives reduction than would have been required had the influent nitrate concentrations remained the same. The average nitrate concentrations in the anaerobic cell's influent increased from 6.4 mg/L during Phase II to 22.9 mg/L during Phase III. Given the combination of these factors and the fact that the amount of artificially supplied carbon substrate was halved compared to Phase II, it is understandable that the redox potential was higher in Phase III.

However, the higher Phase III redox potentials are thought to have had a negative effect on the system's ability to degrade explosive and explosive by-products. Prior studies indicated a strong correlation between low redox and high RDX removal rates.^{Ref. 9} Ideally, the anaerobic cell's redox potential should be maintained below -6 mV to ensure efficient system operation.^{Ref. 12} In practice, the mean redox values taken at sampling points within the anaerobic cell were +127 mV during Phase II and +500 mV during Phase III (Figure 15-14). Additional carbon was not added to the anaerobic cell 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 during any portion of the demonstration phase.

The mean redox values at each sampling point within the anaerobic cell were consistently positive and little variation in the mean redox potentials were observed throughout the cell.



Note: Break in A2 outlet due to a malfunctioning redox meter.

Figure 15-13

Annual Variation of Redox Potential of Wetland Waters From September 16, 1997, to July 21, 1998

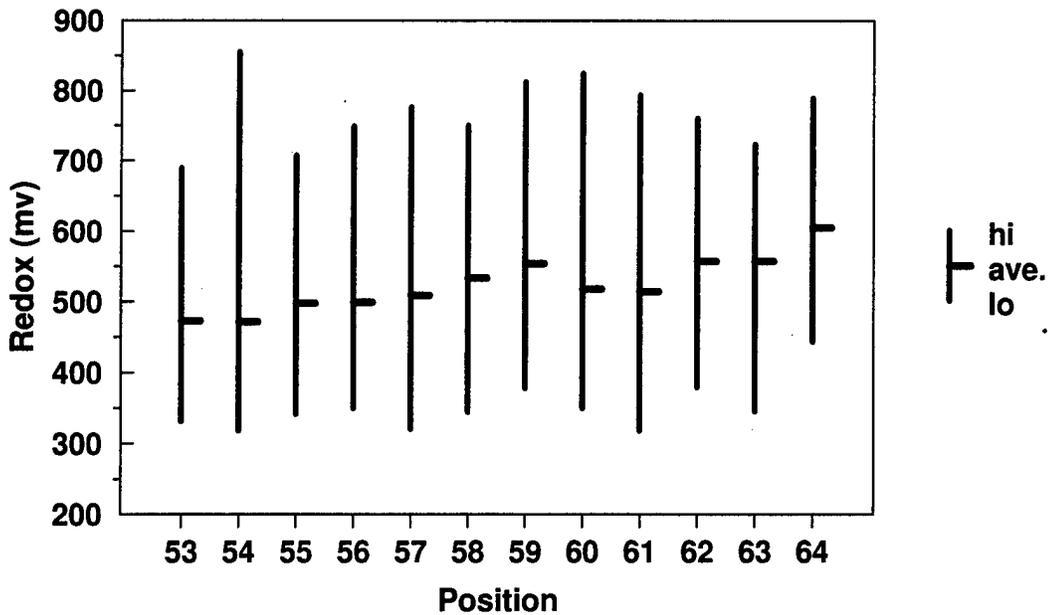


Figure 15-14

Average Redox Potential of Wetland Waters From the Anaerobic Cell (Cell A1) From September 16, 1997, to July 21, 1998

While precise comparisons with the Phase II results are not possible, it is likely that the more frequent addition of the carbon source and the higher influent nitrate concentrations are partly responsible for the greater uniformity in redox measurements in Phase III. The Phase III carbon source, a molasses-based nutrient solution, was added twice daily, whereas the Phase II source, MRS, was added every two weeks. Other factors include the fact that complete dissolution of MRS was not always achieved during Phase II, particularly in colder months.

The anaerobic cell's individual effluent redox values varied considerably while those for the aerobic cell exhibited less variation, typically ranging from +400 to +600 mV (Figure 15-13). There did not appear to be any clearly defined seasonal trends for either the anaerobic or aerobic effluents. High levels of variability in recorded redox measurements often occur in the field for reasons which include microbial fouling of the probes and sensitivity to rapidly changing conditions (e.g., convective currents and associated mixing of oxygen-rich and oxygen-depleted water due to changes in temperature).

15.1.3.7 pH

During Phase III, cell A1's mean influent and effluent pH values were nearly identical with a mean inlet pH of 6.48 and a mean outlet pH of 6.44 (Figure 15-15). The mildly acidic pH values in the respective influents were probably due to high ambient dissolved carbon dioxide concentrations, which are typical of many groundwater sources. Increases in pH for water exiting cell A2 (averaging 6.77 in Phase III) were due primarily to degassing of carbon dioxide 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}

In the anaerobic cell (cell A1), the mean pH at positions 53 through 64 was 6.33 and ranged from 5.53 to 7.85 (Figure 15-16). Similar values were obtained in the aerobic cell (cell A2), where the mean pH of samples taken at positions 65 through 70 was 6.9 (Figure 15-17). The samples taken from the aerobic cell showed less variation than for the individual sample points in cell A1.

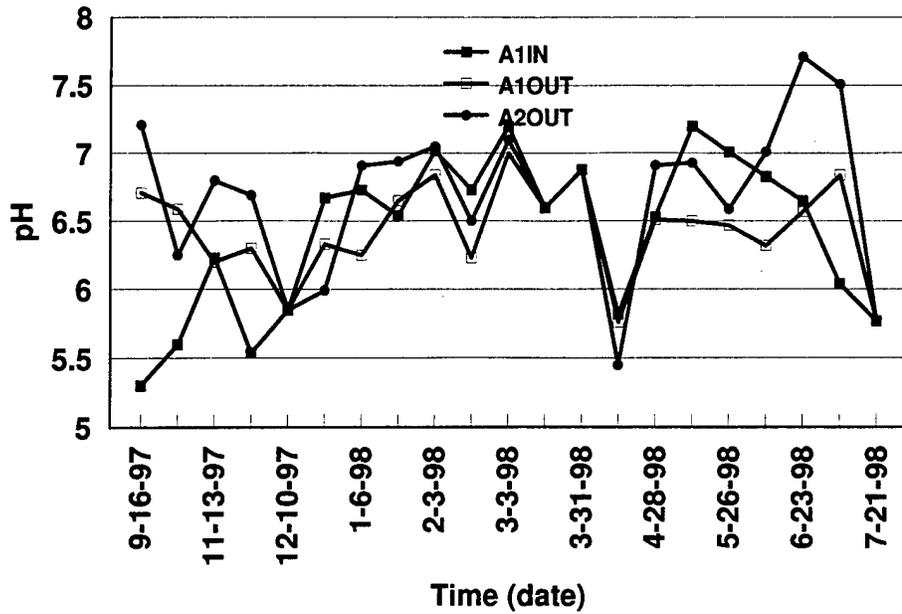


Figure 15-15

Average pH of Wetland Waters From
September 16, 1997, to July 21, 1998

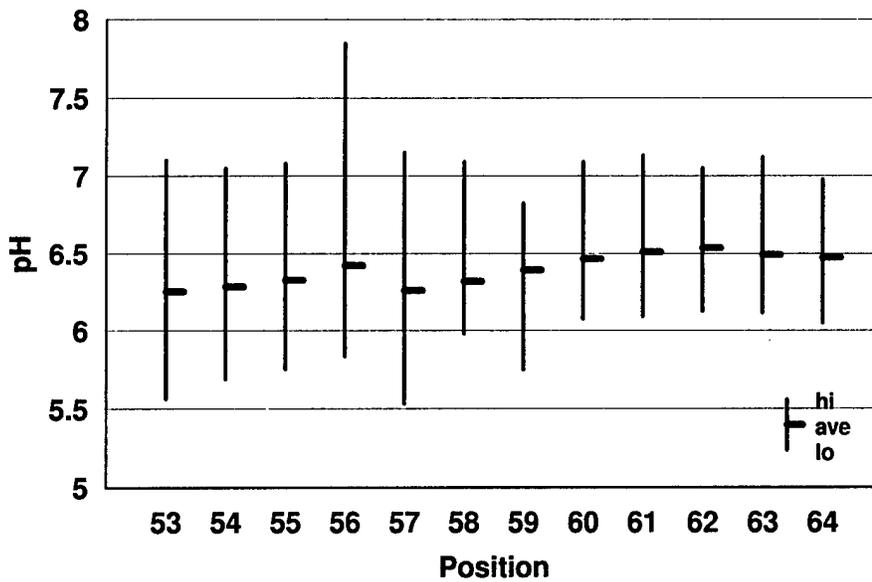


Figure 15-16

Annual Variation of pH of Water From the Anaerobic Cell (Cell A1)
From September 16, 1997, to July 21, 1997

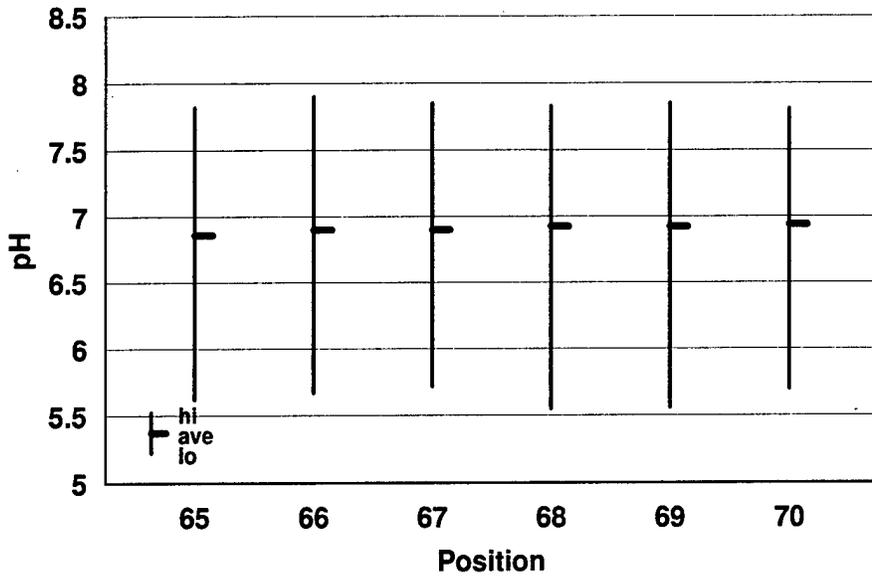


Figure 15-17

Annual Variation of pH in Composite Water Samples From the Aerobic Cell (Cell A2) From September 16, 1997, to July 21, 1997

15.1.3.8 Nutrients and Water Quality

Both the TKN and $\text{NH}_4\text{-N}$ concentrations increased as the water passed from the A1 inlet into cell A1 (Table 15-1). Total Kjeldahl nitrogen (TKN) was highly correlated with $\text{NH}_4\text{-N}$ since TKN is the sum of organic N and ammonia-N and does not contain nitrate. These increases were anticipated as the A1 cell was fertilized twice a day. Average orthophosphate (PO_4) tended to be higher during Phase III, but this was due to the higher concentrations in the incoming water and the addition of diammonium phosphate via the nutrient delivery system. Phosphate in incoming water (A1 inlet) increased from an average Phase II concentration of 0.02 mg/L to an average of 0.07 mg/L during Phase III. As the water moved across cell A1, the phosphate concentrations rose to an average of 0.14 mg/L and then dropped in cell A2. The average phosphate concentration at the A2 outlet was 0.06 mg/L. In addition to the increase in phosphate and NH_4 (from 7 to 10 fold) in cell A2, there were also increases in BOD-5 and COD. These increases are attributable to carbon additions, both in the form of molasses syrup and from plant materials in the cell. As observed during Phase II, the nitrates were denitrified in the anaerobic cell with nitrate concentrations falling from 23 mg/L to less than 1 mg/L during Phase III. In contrast, mean nitrate levels leaving the aerobic cell were increased to 5.08 mg/L. This increase was due to the aerobic conversion of ammonium (NH_4) to nitrate.

15.2 Intensive Sampling Test Results

15.2.1 Hydraulic Tracer Analysis

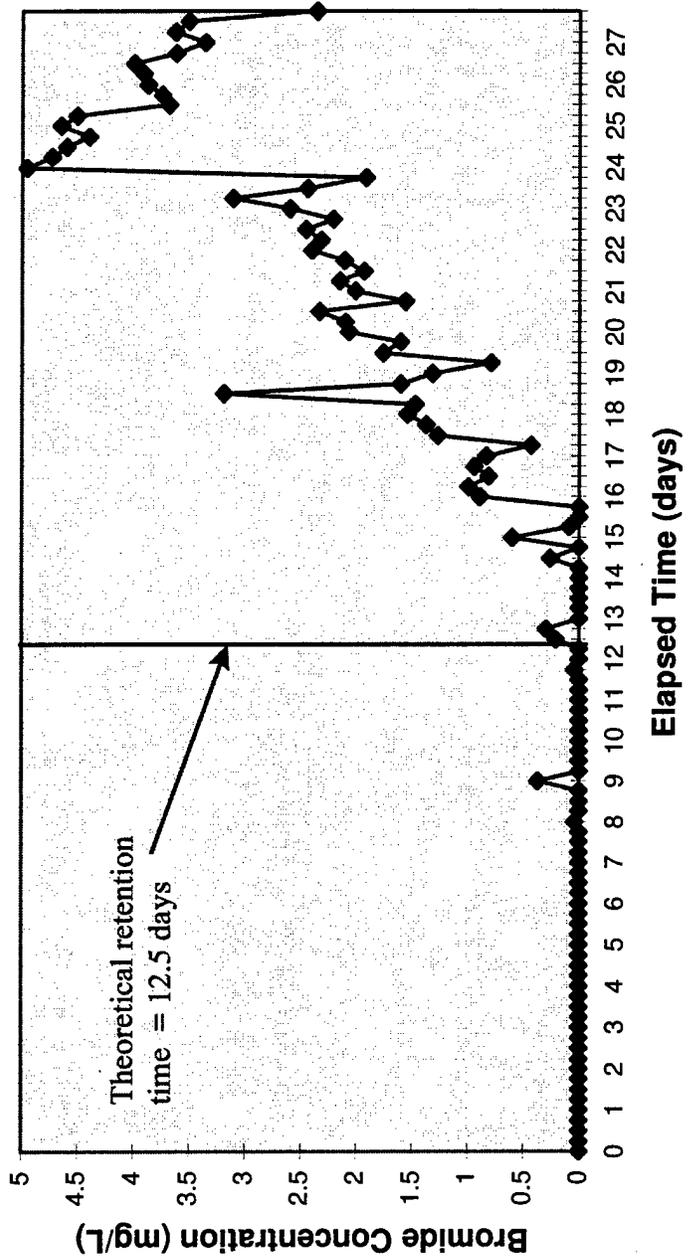
A series of bromide tracer studies conducted during the period of April 26 to May 24, 1998, provided additional information on flow and mixing characteristics of gravel cells A1 and A2. A detailed discussion of the methods used to conduct the hydraulic tracer test is provided in Section 3.5 (Volume I).

The mixing test results indicated that the bromide solution moved through the anaerobic cell (cell A1) at a significantly slower rate than anticipated. Figure 15-18 illustrates cell A1's effluent bromide concentration (mg/L) as a function of elapsed time. Theoretically, hydraulic retention time (HRT) in this cell should have been 12.5 days. However, the HRT obtained

Table 15-1
Nutrient Concentrations and Water Quality in the Gravel-Based Wetland
From September 16, 1997, to July 21, 1998

Sample Point Analysis	Detection Limit (mg/L)	Concentration (mg/L) at Sample Point												
		Gravel-Based Wetland						GAC System						
		1		2		3		7		7		7		
Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.	Avg.	SD	Num.
TKN	0.05	0.69	0.24	10	5.42	2.00	13	0.40	0.25	13	0.29	0.47	15	
NH ₄ -N	0.02	0.35	0.27	6	3.73	2.01	13	0.28	0.21	13	0.79	0.57	15	
NO ₃ -N	0.04	22.9	1.16	12	0.96	1.35	13	4.45	2.14	12	5.08	4.61	15	
PO ₄ -P	0.01	0.07	0.13	6	0.14	0.11	13	0.06	0.11	13	0.06	0.06	15	
Cl	0.1	3.43	0.45	2	5.39	1.13	2	6.79	2.29	2	5.06	0.735	2	
NPOC	0.9	0.66	1.44	4	4.06	2.19	12	0.44	0.36	12	0.45	0.37	2	
TSS	2.0	10.4	2.65	10	31.4	7.05	12	2.15	0.21	13	2	0.21	14	
COD	1.0	4.68	8.75	12	27.8	12.8	12	4.15	4.63	5	1.37	2.39	9	
BOD-5	0.1	4.41	1.61	12	42	39	20	0.89	0.67	18	1.2	0.7	20	

Avg = Average
SD = Standard deviation
Num = Number of observations for which analyte was above the Method Detection Limit
N/A = Not applicable



Note: Study was conducted from April 26 to May 24, 1998.

Figure 15-18
 Bromide Tracer Dynamics in Cell A1 as a Function of Elapsed Time

during the mixing test was approximately 25 days (Figure 15-18). There were small breakthroughs at days 9 and 13, representing minor short-circuiting, but the bulk of the bromide did not begin to appear until day 14. Peak concentrations (4-5 mg/L) were not observed until days 24 and 25. Analysis of this data indicated that the mixing testS undertaken in cell A-1 were compromised by the high specific gravity of the bromide solution coupled with negligible convective mixing. The aberrant results and relatively slow movement of the tracer can be explained as follows:

1. In previous tests, the concentration of nitrate in the influent groundwater interfered with the analytical technique used to analyze for bromide. To overcome this problem, it was decided to double the bromide concentration. However, due to the increased density of the bromide solution and abnormally low levels of convective mixing (seasonal phenomena), the bromide solution migrated to the bottom of the cell, where most of it stayed in bulk solution.
2. Diurnal convective mixing was at a minimum during the test period (April-May 1998) since the average daily air temperature was near the average groundwater temperature. For example, in April, the average differential between air and water temperature was 1.4°C, with air temperature averaging 13.7°C and water temperature averaging 12.3°C. With this small air/water temperature differential, thermal convective mixing was minimized.

These factors combined to impact test results accordingly: the heavy bromide solution stayed near the bottom and movement of bromide through the system was significantly slower than anticipated and provided an estimate of hydraulic retention time (25 days) that was twice the calculated value. The calculated hydraulic retention time (12.5 days) was determined based on total void volume of the anaerobic cell (M^3) divided by the average inlet flow rate (M^3/day).

A short-circuiting test was also conducted during this time period to evaluate the incidence of preferential flow (short-circuiting) and vertical mixing. The data set for the supplemental short-circuiting test is illustrated in four time series graphs (Figures 15-19 to 15-22). This data reveals minor changes in bromide concentration as a function of sampling point location

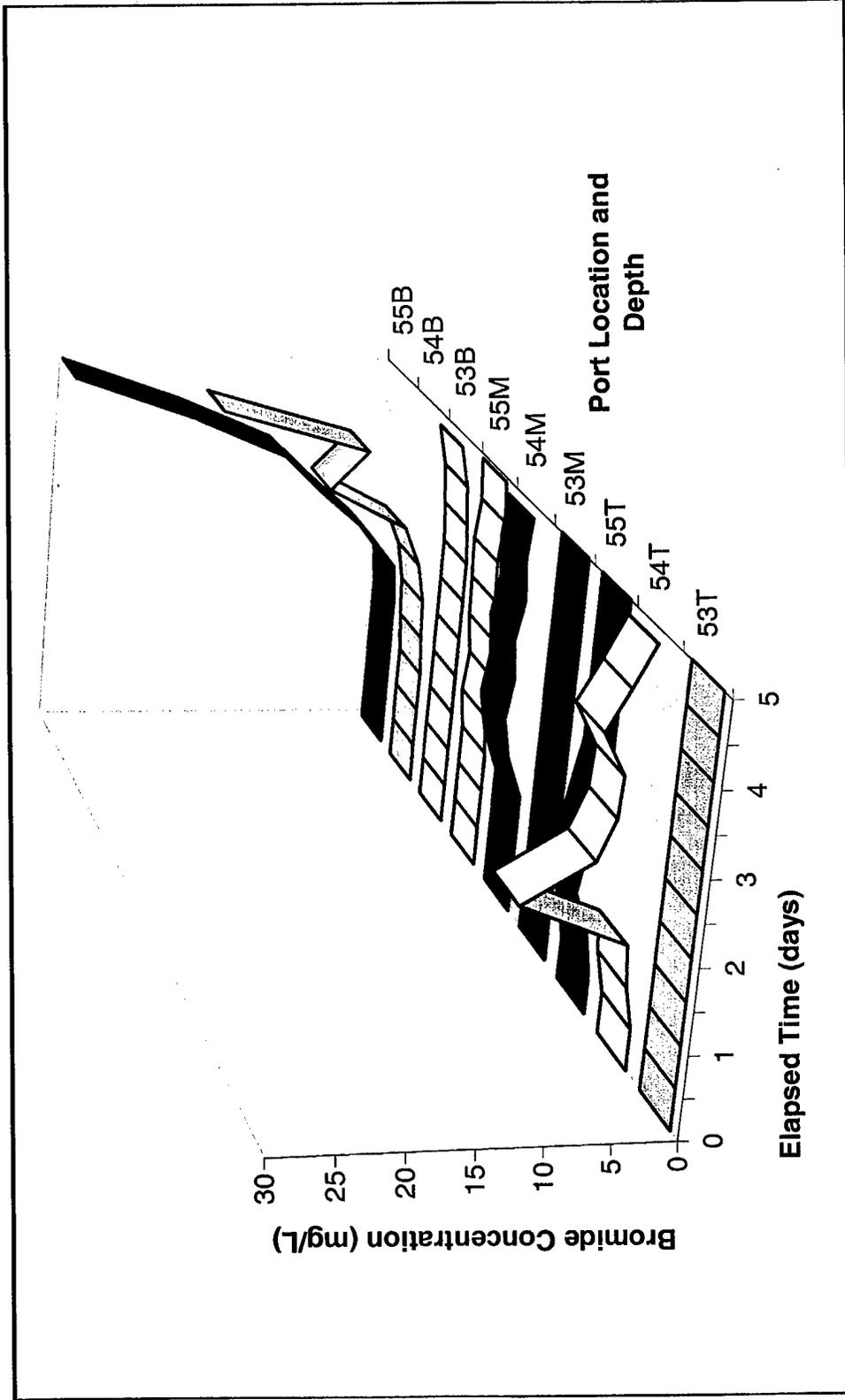


Figure 15-19
Bromide Concentration at Sample Locations 53, 54, and 55 as a Function of Depth and Elapsed Time

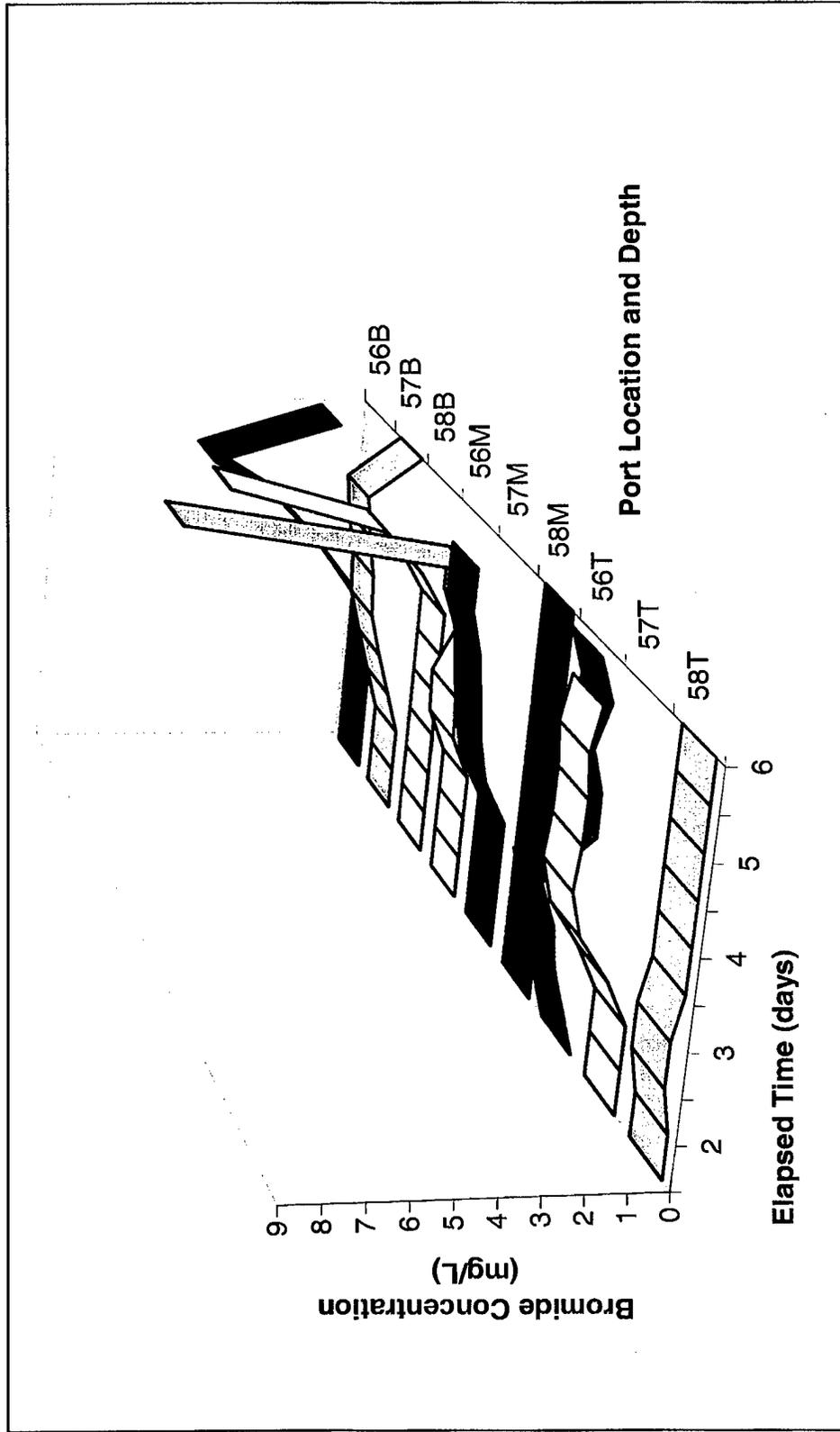


Figure 15-20

Bromide Concentration at Sample Locations 56, 57, and 58 as a Function of Depth and Elapsed Time

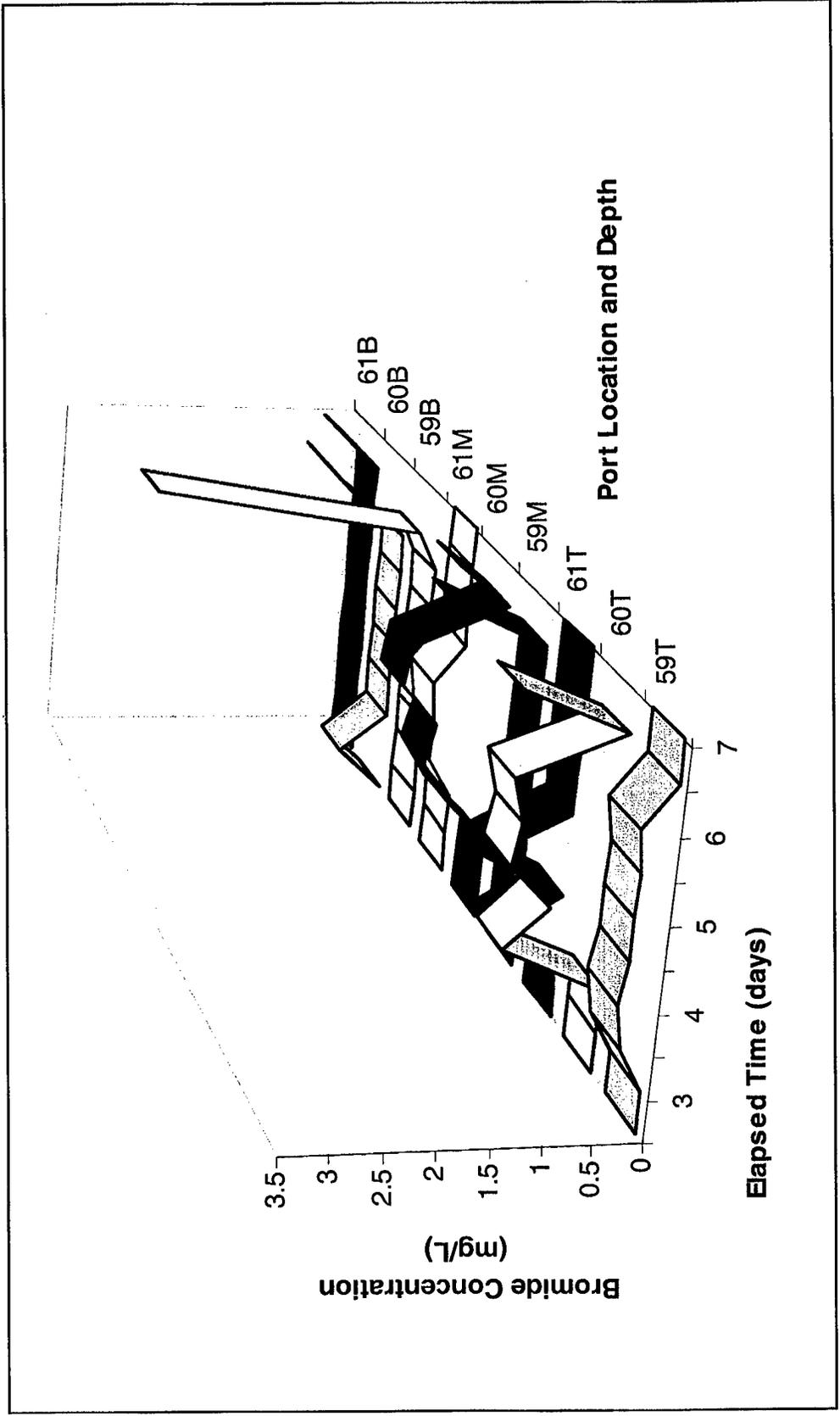


Figure 15-21
Bromide Concentration at Sample Locations 59, 60, and 61 as a Function of Depth and Elapsed Time

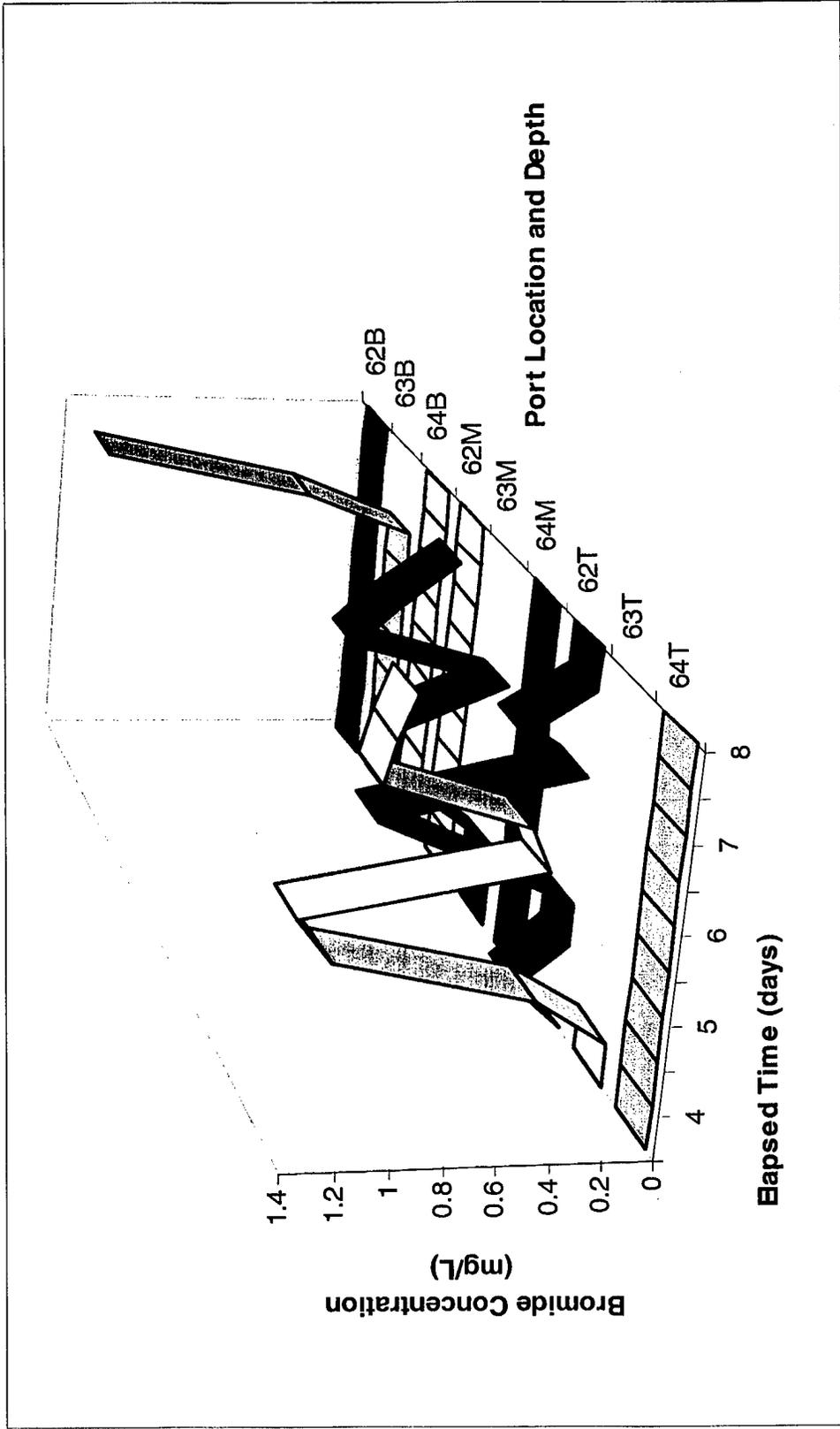


Figure 15-22
 Bromide Concentration at Sample Locations 62, 63, and 64 as a Function of Depth and Elapsed Time

and water depth over an eight-day period. As in the mixing test, the high specific gravity of the sodium bromide solution dramatically slowed the vertical and horizontal movement of bromide through the gravel cell. Mixing occurred due to: 1) simple diffusion (slow), 2) preferential flow (very fast), and 3) diurnal convective mixing (relatively fast).

Within half a day of adding the concentrated solution, bromide was detected near the top of sampling point 54, indicating early preferential flow (Figure 15-19). Five days after adding bromide to the anaerobic cell, the bromide concentrations in sampling points 53-55 ranged from <0.2 to 30 mg/L. The highest concentrations were located near the bottom, although sampling point 54 had concentrations exceeding 10 ppm near the top of the water column.

Three days post-application, low bromide concentrations (<1 mg/L) were observed at several locations within sampling points 56-58 and by the sixth day post-application, concentrations in several of these sampling points were ranging from <0.2 to 8 mg/L, with highest concentrations occurring near the bottom and at mid-water levels (Figure 15-20). Bromide concentrations at sampling points 59-61 (Figure 15-21) were less concentrated (<0.2 to 3.2 mg/L), but more uniformly distributed throughout the water column illustrating the impact of flow path and elapsed time on mixing.

Figures 15-20 and 15-21 revealed that the highest concentrations (5-8 mg/L) were in sampling points 58 and 59 (midway through cell A1) after 8-10 days of elapsed time. Lower concentrations observed in sampling points 53-55 (Figure 15-19) represented the trailing edge of the bromide front, while low concentrations in sampling points 61-64 (Figures 15-21 and 15-22) represented the leading edge of the bromide front. Data also indicates that the bromide was moving preferentially to the sides of the gravel cell (see data for sampling points 55, 56, 58, and 59), with less flow near interior sampling points (see data for sampling points 54, 57, and 60).

Findings of the short circuiting tests conducted during Phase II also indicated that the water tended to flow down each side of the gravel bed rather than through the middle. Preferential flow in the anaerobic cell may be due to a number of factors: 1) local channeling within the heterogeneous wetland substrates, 2) the impact of plant root development, and 3) the location and density of plant litter detritus within the pore spaces of the wetland substrate.

The regular short-circuiting test, in which bromide concentrations were measured from whole column water samples, provided additional information on water flow dynamics as a function of sampling point location and elapsed time (Figure 15-23).

A bromide tracer test was also conducted in cell A2 from April 14-26, 1998. Time series data (Figure 15-24) indicates that bromide was rapidly and uniformly mixed due to the reciprocating movement of water between contiguous cells. Results from the A2 study are very similar to results from similar studies completed during Phase II (see Figure 6-24 in Volume I), confirming that cell A2 performed like a completely mixed reactor while cell A1 functioned similar to a plug flow reactor.

15.2.2 Wetlands Efficiency

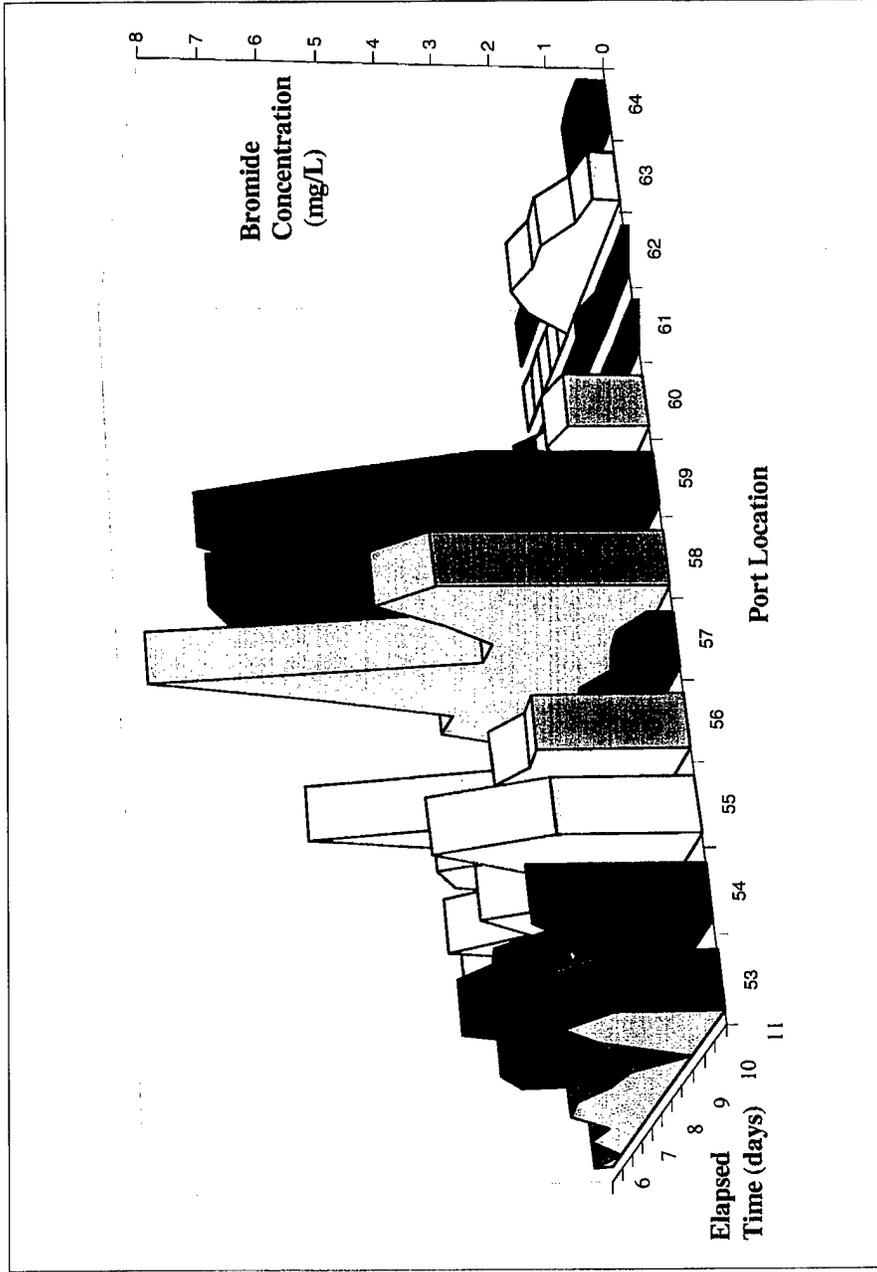
15.2.2.1 Efficiency of the Gravel-Based Wetlands

Explosive removal efficiency is a function of a number of factors including:

- The rates at which explosive and explosive by-products are degraded
- Incoming nitrobody concentrations
- Outgoing nitrobody concentrations
- Water retention time in the wetland cells

As discussed in Section 15.1.3.6, the redox potentials in the anaerobic cell were relatively high during Phase III and an increase in the influents nitrate concentrations during Phase III is thought to have the limited supply of electrons needed to reduce the nitro-groups attached to explosives and explosive by-products. Consequently, the rates of explosive and explosive by-product degradation are thought to have been reduced during Phase III, as evidenced by lower rate constants for TNT (see discussion in Section 15.2.2.2). However, this negative consequence was countered by various factors including:

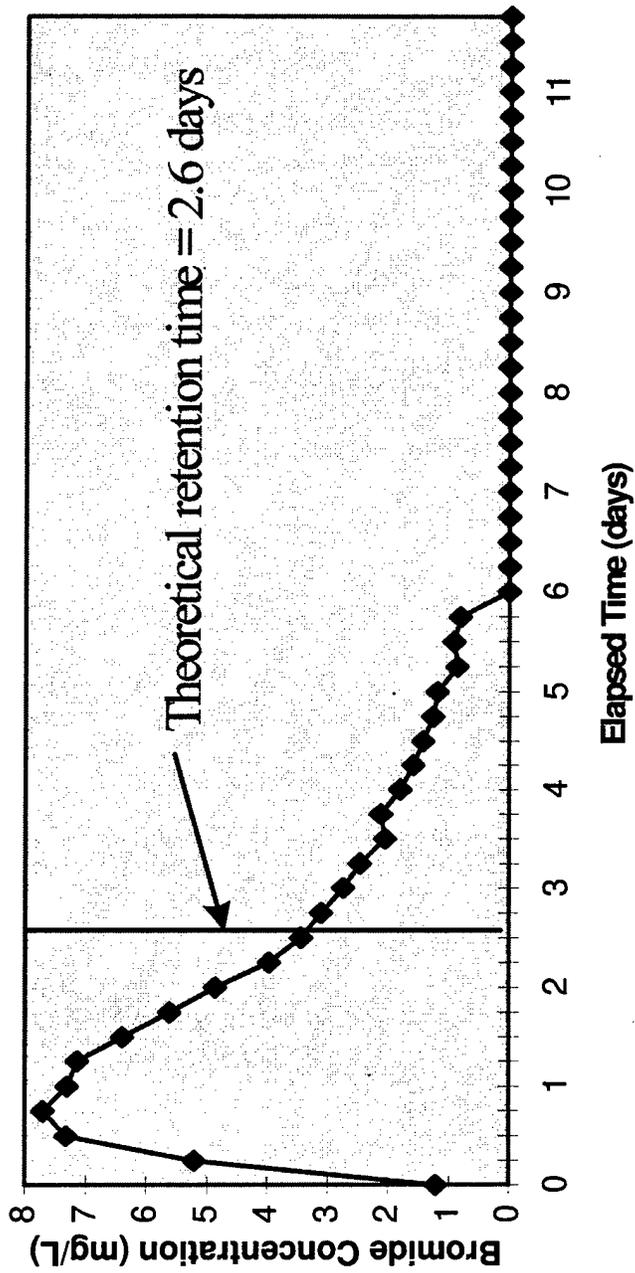
- The theoretical retention time in the gravel-based system was increased by about 40% above that for Phase II.



Note: A concentrated bromide tracer solution was added to the influent header of cell A-1 on April 26, 1998. Elapsed time (days) covers the time period May 2-12, 1998.

Figure 15-23

Bromide Tracer Concentration in Whole Column Water Samples as a Function of Sample Location and Elapsed Time



Note: Study was conducted from April 14 to April 26, 1998.

Figure 15-24

Bromide Tracer Dynamics in Cell A2 as a Function of Elapsed Time

- Total nitrobody concentrations entering the wetland were lower than in Phase II. (Total nitrobody concentration from the wells averaged 9,200 ppb during Phase II and 7,990 ppb during Phase III. These differences were statistically significant.)
- The average total nitrobody concentrations in the effluent were statistically the same during both project phases (57 ppb for Phase II and 44 ppb for Phase III.)

Consequently, the gravel-based system's total nitrobody removal efficiency remained about the same during both Phases II and III (Figure 15-25). Total nitrobody removal efficiency averaged 94.2% during Phase II and 94.5% during Phase III, respectively. Comparing the removal efficiency results of the two demonstration phases with the statistical technique of the unpaired t-test, indicates that there was no difference between the Phase II and Phase III results. The resultant t value of the test, -0.12, was not statistically significant at the 5% probability level.

15.2.2.2 Kinetic Rate Constants for TNT and RDX Removal

During Phase III, enough TNT was removed by the anaerobic cell to meet the project goal of reducing TNT concentrations to below 2 ppb (Figure 15-1). Indeed, the TNT concentrations dropped below the Method Detection Limit once the treated water was 40% of the way through the anaerobic cell (Figure 15-26). However, the rate constants for TNT removal were less than those observed during Phase II. This can be seen by comparing the rate constants for the same months of each Phase (Table 15-2). This data indicates that the anaerobic cell's capacity to degrade TNT was diminished during Phase III.

A month-to-month examination of the Phase II and Phase III RDX rate constants shows that they were consistently lower than those obtained during Phase II (Table 15-2). In December, for example, the rate constants for Phases II and III were 78 and 73 m/year, respectively. Nevertheless, the gravel-based wetland was unable to reduce the total nitrobody concentrations

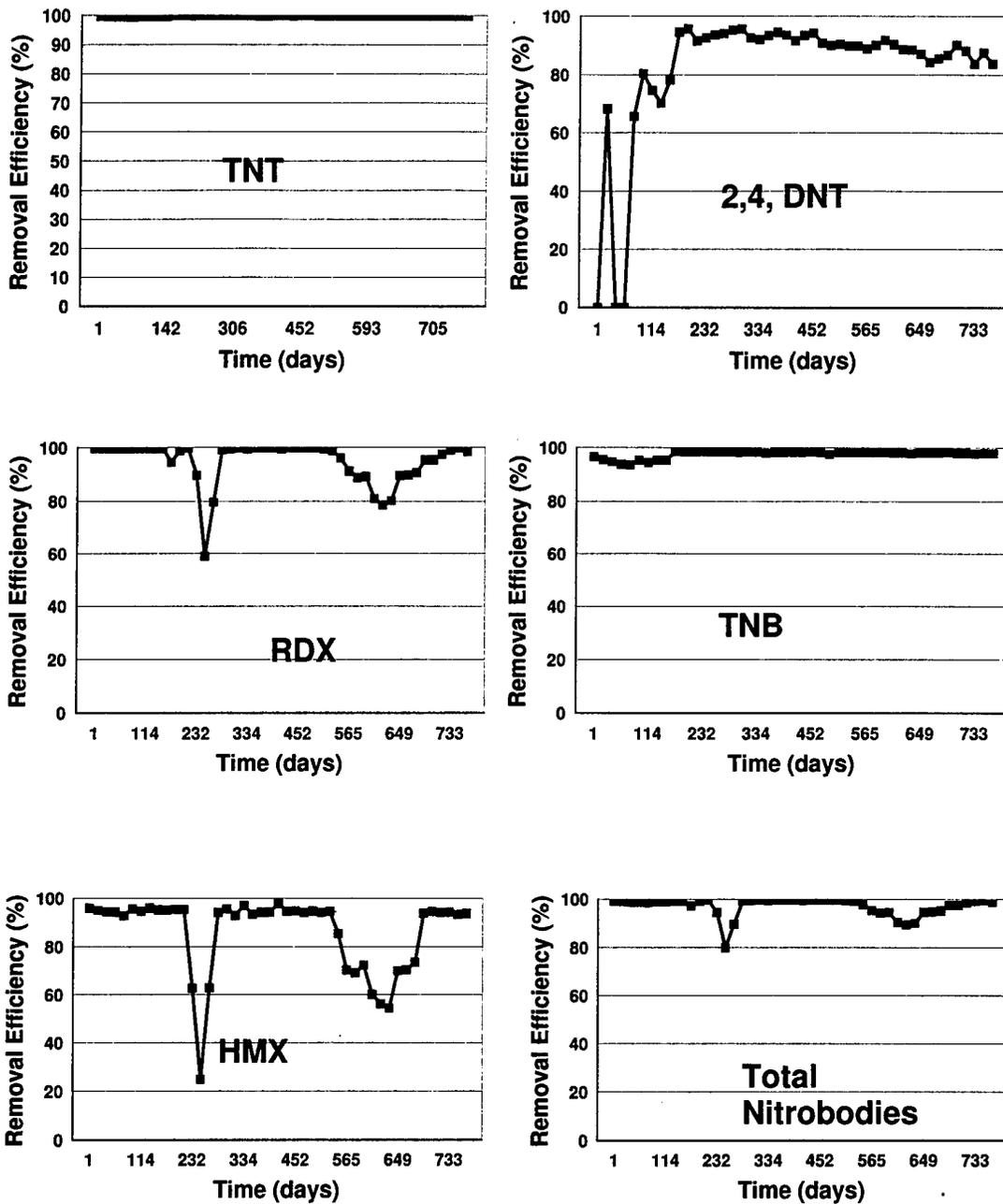


Figure 15-25
Removal Efficiencies of the Gravel-Based Wetlands
From September 16, 1997, to July 21, 1998

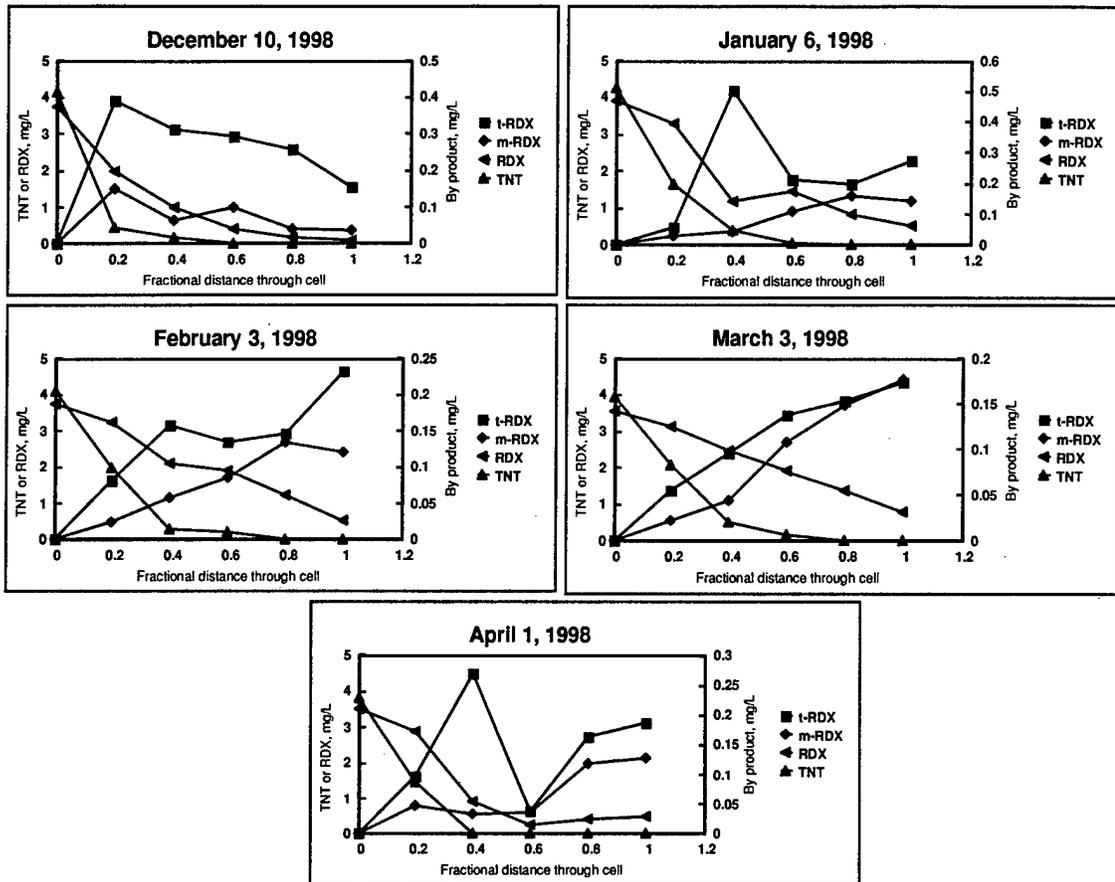


Figure 15-26
Concentration of TNT, RDX, and RDX By-Products in the Interior of Cell A1 From December 1997 to April 1998

Table 15-2

First-Order Rate Constants for TNT and RDX Removal in Gravel-Based Wetlands

Project Phase	Test Date (Month/Year)	Day of Operation (Day)	RDX k (m/yr)	TNT k (m/yr)
Phase II	8/96	49	259	773
	10/96	110	338	775
	12/96	171	78	925
	2/97	233	36	288
	4/97	292	66	392
	6/97	353	118	310
	8/97	414	216	342
Phase III ¹	12/97	541	73	236
	1/98	568	38	172
	2/98	596	30	147
	3/98	624	24	145
	4/98	652	51	349

- 1) During Phase III, the intensive sampling program used to obtain rate constants was only conducted during the winter months (December 1997 to April 1998).

below the 50 ppb goal during Phase III from December 9, 1997, to June 20, 1998. The 50 ppb goal was not met despite the fact that:

- The RDX concentration entering the anaerobic cell was lower than in Phase II.
- The anaerobic cell's peak effluent RDX concentrations did not reach the peaks experienced during Phase II.

In part, this goal was not reached because the effluent RDX concentrations remained at elevated levels over a longer time period than in Phase II (compare Phase II RDX and RDX by-product effluent concentrations in Figure 6-2 with Phase III concentrations in Figures 15-1 and 15-2).

A closer examination of the data suggests that the anaerobic cell's Phase II capacity to remove RDX during stable operating periods may have been higher than the rate constant data suggests. Several factors point to this possibility including:

- During Phase II, short circuiting in the anaerobic cell likely resulted in periodic spikes in the RDX effluent concentrations as a result of periodic pluggage of the anaerobic cell's outlet header. In contrast, little pluggage was experienced during Phase III suggesting that spiking was less likely to occur.
- The TNT rate constant data indicates that TNT removal rates were higher during Phase II than during Phase III suggesting better performance during Phase II. (TNT removal rates are thought to be a more sensitive indicator of system performance than those for RDX because TNT is easier to breakdown than RDX).
- The anaerobic cell's redox potentials were significantly lower in Phase II relative to Phase III (compare Figure 6-14 with Figures 15-13 and 15-14).

Of these factors, the anaerobic cell's low redox potential during Phase II is considered the most important indicator. Prior studies have indicated a strong correlation between low redox and high RDX removal rates.^{Ref. 9} Consequently, the anaerobic cell's capacity to remove TNT and RDX was higher during Phase II than Phase III. Ideally, the anaerobic cell's redox potential

should be maintained below -6 mV to ensure efficient system operation.^{Ref. 12} In practice, the average redox values within the anaerobic cell were +127 mV during Phase II and +500 mV during Phase III. The likely cause of the high Phase III redox potential was the reduction of the carbon loading rate in the anaerobic cell (Section 15.1.3.6). An increase in incoming nitrate concentrations may have also played a role in reducing explosive and explosive by-product degradation rates during Phase III as nitrates aggressively compete for the limited supply of electrons available for the reduction of nitro-groups attached to explosives and explosive by-products. The combination of these factors suggest that during Phase III, the anaerobic cell was operated under conditions which were physically more stable, but chemically less capable of explosive degradation.

Because of the strong correlation between low redox potential and high explosive removal rates, it was clear that the Phase III rate constants should not be used for design purposes. Keeping in mind the importance of carbon loading, as well as the above interpretation of the Phase II RDX rate constant data, the rate constants from Phase II were used to design the commercial-scale system (Section 8.0) and to develop the economic analysis (Section 9.0). Since system size primarily depends upon the RDX rate constant, use of the Phase II data is thought to have produced a reasonably conservative estimate of system size.

SECTION 16.0
OVERALL PHASE II AND PHASE III CONCLUSIONS

16.1 Background

During this demonstration of wetlands-based phytoremediation, groundwater was pumped to the surface and allowed to flow through wetlands where the natural plant and microbial processes degraded explosive compounds in the water. The demonstration was conducted after bench-scale tests indicated that gravel-based and lagoon-based wetlands could be used to remediate explosives-contaminated groundwater and that these technologies were worthy of demonstration. Use of the lagoon-based wetlands was based on the concept that plants alone could degrade explosives via plant production of nitroreductase enzymes. The use of gravel-based wetlands was based on the concept that explosive degradation occurred via both microbial and plant processes in gravel beds. Since both approaches had merit, a demonstration of both the lagoon-based and gravel-based systems was conducted at Milan Army Ammunition Plant, Milan, Tennessee. The systems were specifically designed to treat MAAP's groundwater which was contaminated with explosive residues.

During Phase II of this demonstration, the two wetland systems were operated and performance was compared. Each system received contaminated groundwater at a flow rate of 5 gpm. During Phase II, the average nitrobody concentration in the groundwater was 3,250 ppb from June to November 1996 and 9,200 ppb from November 1996 to August 1997. During Phase III, the total nitrobody concentration averaged 7,990 ppb from September 16, 1997, to July 21, 1998.

The first treatment system was a two-celled, lagoon-based wetland used to test the concept of explosive degradation via nitroreductase enzyme production from submergent plant species. 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 second treatment system was a two-celled, gravel-based wetland used to test the concept of explosive degradation via microbial and plant processes. 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 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.

At the conclusion of Phase II, it was determined that the gravel-based system was the most effective of the two types of wetlands demonstrated. The lagoon-based system only met the goal of reducing TNT concentrations below 2 ppb 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. As a consequence of the lagoon-based system's poor performance, operation of the lagoon-based system was discontinued at the end of Phase II. The gravel-based system continued to be operated through Phase III as a means of gathering additional information about the system. Prior to Phase III, the gravel-based system was modified so the system could be used to explore the system's operating envelope, gather additional winter information, and improve system performance. These changes included:

- Changing carbon sources from MRS to a molasses syrup

- Adding a nutrient solution containing diammonium phosphate (mixed with the molasses syrup)
- Shifting to an automated carbon source addition system
- Adding the carbon source more often
- Decreasing the amount of carbon added by half
- Reducing the incoming groundwater flow rate from 5 gm to 3 gpm
- Operating and maintaining the system similar to that required for a full-scale remediation system

Most of these modifications were related to the shift in carbon sources. During Phase III, cane molasses syrup was used as a carbon source because prior testing indicated that molasses syrup was easier to handle, an order of magnitude less expensive, and more effective at promoting the removal of explosives than other carbon sources.^{Ref. 12} Since molasses syrup contains less nutrients than MRS, a small amount of diammonium phosphate, a common fertilizer, was mixed with the molasses syrup to ensure microbial growth. One of the advantages of using molasses syrup is that it is more soluble than MRS and, therefore, more amenable to use in the automated feeding systems used during Phase III. Use of the automated feeding system allowed the carbon source to be added twice a day as opposed to once every two weeks during Phase II. Finally, the rate of carbon addition was reduced by half to determine if the gravel-based wetland plant community was mature enough to contribute to carbon loading. The term "carbon loading" refers to the amount of biologically available carbon which must be present to maintain the desired level of microbial activity. Decaying plant matter is not the only carbon source. With the exception of parrotfeather, the root systems of the plants in the gravel-based system were known to actively pump organic compounds (sugar like compounds) into the wetlands. The ability to actively supply this carbon was one of the selection criteria TVA used when it recommend the type of plants to be used in the gravel-based wetlands. With time, both live plants and decaying plant material are expected to contribute to the wetland's carbon loading. Hand calculations conducted at the end of Phase II indicated that biomass levels in the gravel-based wetland were approaching levels that could, in theory, supply a significant level of carbon. This could only be verified by reducing the artificial carbon inputs and measuring the system's response over an extended period of time.

The inlet flow rate was reduced to determine if higher system retention times would improve the gravel-based system's ability to remove explosives and explosive by-products in the winter.

At the new flow rate, the gravel-based system's theoretically hydraulic retention times in cells A1 and A2 were 12.5 and 2.7 days, respectively, for a total of 15.2 days. The theoretical hydraulic retention time was calculated by dividing the total void volume (M^3) of the cells by the average inlet flow rate (M^3/day).

16.2 Demonstration Results

Although the theoretical retention time in the gravel-based system was increased by about 40% above that for Phase II, the system's Phase III performance was mixed. The goal of the Phase III demonstration was to reduce TNT to concentrations less than 2 ppb and total nitrobenzenes to concentrations less than 50 ppb. The gravel-based demonstration system was able to reduce the TNT concentrations below 2 ppb and the total nitrobenzene concentration below 50 ppb from September 16, 1997, to December 9, 1997, and from June 20, 1998, to July 21, 1998, but was unable to reduce the total nitrobenzene concentration below 50 ppb from December 9, 1997, to June 20, 1998, due to a combination of low water temperatures and high redox potentials in the anaerobic cell.

A comparison of the Phase II and Phase III rate constants for TNT and RDX removal indicates that during the winter (December 1997 to April 1998), the rate of TNT removal was reduced during Phase III while the rate for RDX removal remained about the same. However, TVA concluded that the degradation rate data should be interpreted cautiously (see Section 15.2.2.2) since system redox potentials were high and prior testing indicates that there is a strong correlation between low redox potential and high TNT and RDX removal rates.^{Refs. 9 and 12}

TVA also concluded that the April 1997 rate constant for RDX should be used for commercial design purposes (see discussion in Section 8.5.1) and that neither the Phase II nor Phase III winter data should be used for design purposes. During both phases of this project, the gravel-based system was experiencing difficulties in the winter. 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 microbial growth. These problems led to ponding (short circuiting), flow restrictions, and a periodic interruption of MRS addition. During Phase III, the carbon source was changed from MRS to molasses syrup, the carbon source was added more frequently, and the carbon loading rate was halved. As a consequence of these changes,

flow rates through the gravel-based system were more stable and the system did not experience ponding (short-circuiting). However, the reduced carbon loading resulted in a significant increase in the anaerobic cell's redox potential which, in turn, substantially decreased the anaerobic cell's ability to degrade explosives. An increase in incoming nitrate concentrations may have also played a role in reducing explosive and explosive by-product degradation rates as nitrates aggressively compete for the limited supply of electrons available for the reduction of nitro-groups attached to explosives and explosive by-products. As a consequence, the Phase III data do not accurately reflect the gravel-based system's capacity to remove explosives and explosive by-products from contaminated waters under optimum conditions. To ensure efficient operation of the anaerobic cell, the cell's redox potential should be maintained below -6 mV.^{Ref. 12}

16.3 Summary

The Phase III demonstration was conducted from September 17, 1997, to July 21, 1998. During this period, it was concluded that:

- The total nitrobody concentration in the incoming groundwater averaged 7,990 ppb.
- The gravel-based system was able to reduce TNT concentrations below 2 ppb over the entire demonstration period.
- Between December 9, 1997, and June 20, 1998, the gravel-based system was unable to reduce the total nitrobody concentrations below 50 ppb.
- The gravel-based system's efficiency at removing total nitrobodies remained high during Phase III, averaging 94.49%.
- The anaerobic cell's redox potential rose to an average of +500 mV during the demonstration period. As a consequence, the cell's ability to degrade explosives and explosive by-products was substantially reduced.

- The wetland was not able to supply a sufficient amount of its own carbon to support an adequate level of explosives and explosive by-product degradation. Ideally, sufficient carbon should be added to the system to lower the redox potential in the anaerobic cell to below -6 mV to ensure efficient explosives degradation. Additional carbon was not added to the gravel-based 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.
- The presence of higher nitrate levels in the influent may have also contributed to reduced rates of explosives and explosive by-product degradation because nitrates aggressively compete with the nitro-groups attached to explosives and explosive by-products.
- Due to the reduced microbial activity, the Phase III degradation rate data should be interpreted cautiously since prior studies indicate that there is a strong correlation between low redox potential and high TNT and RDX removal rates.^{Refs. 9 and 12}
- The Phase III data shows that the gravel-based system was somewhat less effective than in Phase II. The system was less effective in Phase III because some of the operational parameters were changed to evaluate system performance. As a result, the data from Phase II was used for design purposes since it appeared to have the most optimum operating conditions.
- As a consequence of the use of molasses syrup, flow rates through the gravel-based system were more stable, the system did not experience ponding, and the carbon source could be added more frequently using an automated system.

Overall, the gravel-based system performed well during both Phases II and III. The project results indicate that the gravel-based wetlands was more effective at reducing hard-to-degrade compounds like RDX and HMX than was the lagoon-based system. During both phases of the project, it was demonstrated that wetlands' effectiveness at reducing explosive and explosive by-product concentrations is reduced during the winter months. Furthermore, the Phase III results illustrated the importance of maintaining the low redox potential in the anaerobic cell to ensure efficient explosives removal. Ideally, redox potentials should be maintained below

-6 mV. The need to maintain low redox potential should be taken into account when full-scale systems are designed.

The overall demonstration results indicate that while both the lagoon- and gravel-based systems could degrade 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, was only able to meet the TNT reduction goal of 2 ppb during the initial stages of the demonstration, and had difficulty in maintaining a sustainable plant-based ecosystem. In contrast, the gravel-based system was able to degrade both HMX 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 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 and operated to overcome the winter performance issues.

These results indicate that the gravel-based system is an economical and efficient alternative to remediate explosive-contaminated groundwater.

SECTION 17.0

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