U.S. Army Environmental Center

PHYTOREMEDIATION OF EXPLOSIVES CONTAMINATED GROUNDWATER IN CONSTRUCTED WETLANDS: II - FLOW THROUGH STUDY

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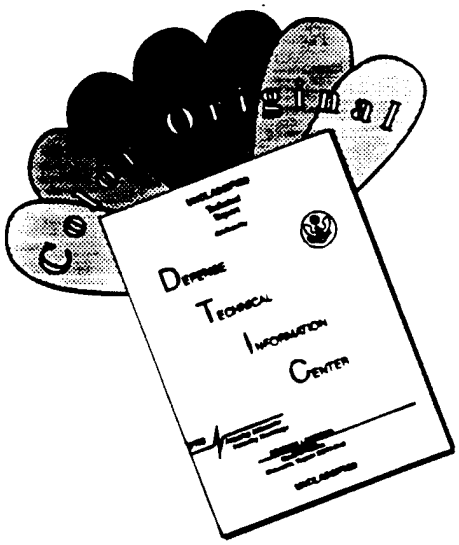

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Phytoremediation of Explosives-Contaminated Groundwater In Constructed Wetlands: II - Flow Through Study

Prepared for
U.S. Army Environmental Center
Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401
POC: Ms. Darlene Bader

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Prepared by
L.L. Behrends
F.J. Sikora
W.D. Phillips
E. Baily
C. McDonald
and
H.S. Coonrod
of the
Tennessee Valley Authority
Environmental Research Center

AND

D.F. Bader
of the
U.S. Army Environmental Center
Environmental Technology Division

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This study evaluates the utility of constructed wetlands for remediating explosives contaminated groundwaters using bench scale flow-through type reactors. Specifically the study examines: the degradation of TNT, TNB, RDX, and HMX in contaminated waters in plant lagoons and gravel-based wetlands. The study also provides design recommendations for the wetland demonstration project to be located at the Milan Army Ammunition Plant (MAAP), in Tennessee.

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ABBREVIATIONS

2A-DNT	-2-Aminodinitrotoluene
4A-DNT	-4-Aminodinitrotoluene
CO_2	-Carbon Dioxide
°C	-Degrees Centigrade
cm	-Centimeters
cm^2	-Centimeters square
COD	-Chemical Oxygen Demand
D.O.	-Dissolved Oxygen
DoD	-Department of Defense
g/l	-Grams per liter
g/cm^2	-Grams per centimeter square
g/m^2	-Grams per meter square
mg/l	-Milligrams per liter
NPDES	-National Pollutant Discharge Elimination System
HMX	-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	-High Performance Liquid Chromatography
I.U.	-International Units
mL/min	-Milliliter per minute
MIRP	-Military Interdepartmental Purchase Request
MRS	-Milk replacement starter
N	-Nitrogen
ORP	-Redox potential
P	-Phosphorus
ppb	-Parts per billion
RDX	-Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNB	-Trinitrobenzene
TNT	-2,4,6 Trinitrotoluene
TVA	-Tennessee Valley Authority
U.S.	-United States
USAEC	-United States Army Environmental Center

SECTION 1.0

INTRODUCTION

This study is a follow-up to a batch study (Study I), which was undertaken to evaluate the utility of constructed wetlands, both surface and subsurface flow, for remediating explosives contaminated groundwater. The present study, (Study II), a 30 day microcosm study was conducted for the Army Environmental Center as part of a continuing technology demonstration program. Objectives of Study II included validating findings of Study I and evaluating an expanded range of experimental wetland environments in flow-through system mode with respect to their abilities to remediate contaminated groundwater containing low concentration of TNT, RDX, HMX, and TNB.

SECTION 2.0

MATERIALS AND METHODS

Twenty microcosms were used in this study, each of which consisted of an opaque glass aquaria (38 liters) partitioned with glass into either 4 or 2 cells (see Figures 2-1 a and b respectively). They were located within a large research greenhouse at TVA's Constructed Wetlands R&D Center. The experimental design was completely randomized in factorial arrangement to test three main factors at two levels. Main factors and their respective levels were:

- Wetland species (parrot feather *Myriophyllum aquatlcum,* vs. canary grass, *Phalaris arundinacea*;
- Initial planting density (25 g/l versus 50 g/l on a wet weight basis);
- Level of fertility (350 mg/l versus 700 mg/l milk replacement starter).

Table 2-1 summarizes treatment designation and treatment factors. The experimental design, in factorial arrangement, included three factors, each at two levels for the subsurface flow design. The surface flow (lagoon system) evaluated fertility rate and plant density, but only for the plant species parrot feather. Treatment designations followed the convention as follows:

- The first letter refers to the species designation (C = canary grass, P = Parrot feather);
- The second letter refers to the planting density (L = low, H = high);
- The third letter refers to the fertility level (L = low, H = high).

Systems designation are in parenthesis following treatment designations and are as follows: (W) = wetlands, subsurface flow; and (L) = lagoon, surface flow.

Plants were apportioned to microcosm cells on a unit area basis (g/cm^2), such that all cells within a treatment had similar biomass per unit area. Canary grass and parrot feather were planted in the rock based wetlands (W), such that the crown was above the water level. In the

Table 2-1
Treatment Designations and Summary of Treatments.

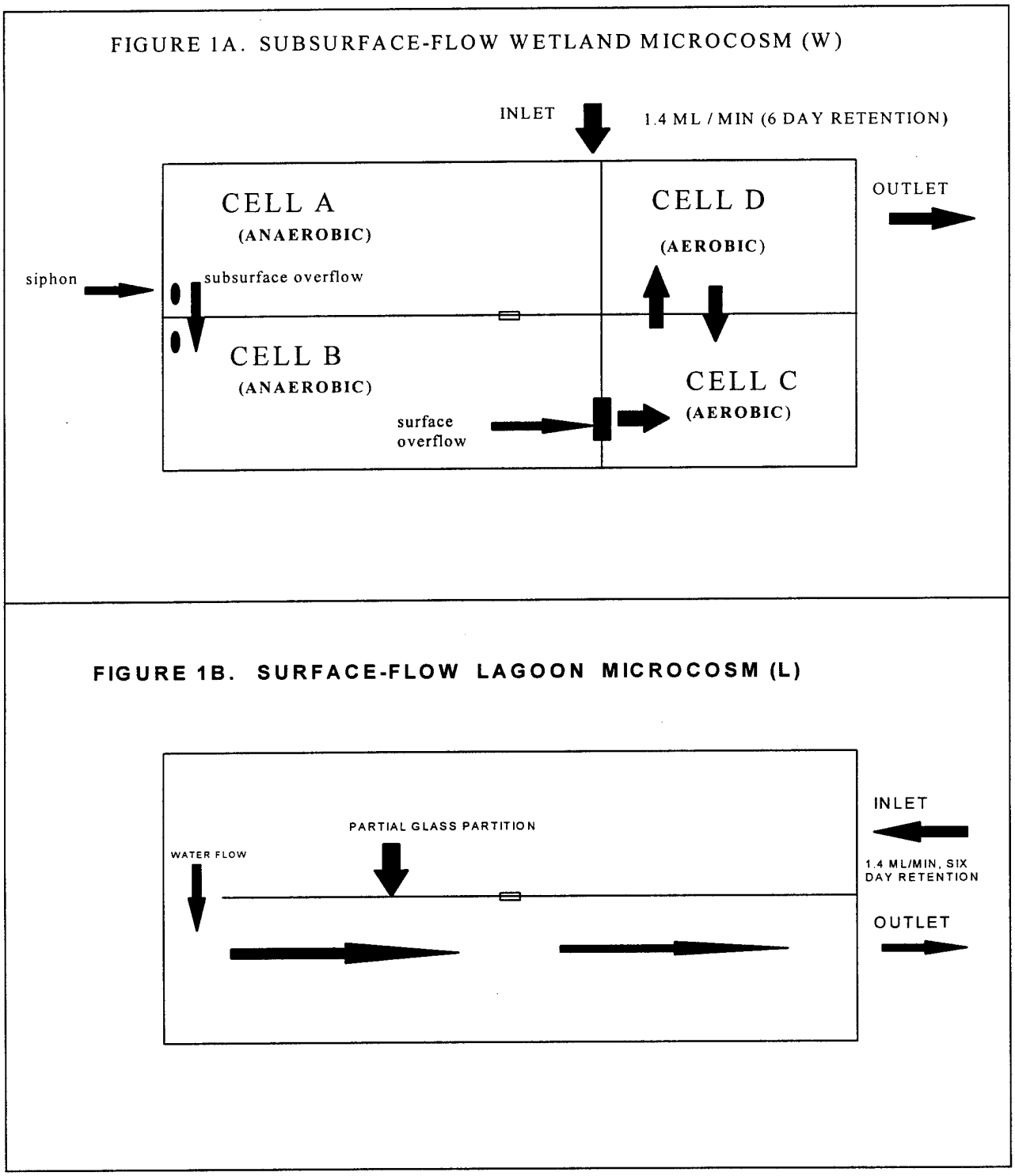
TREATMENT DESIGNATION	REPS. (N)	MICROCOSM (type)	CELLS[1] (#/microcosm)	SPECIES[3]	DENSITY (g/microcosm)	FERTILITY LEVEL (mg/l)
PLL (W)	2	WETLAND[2]	4	P. FEATHER	300	350
PHL (W)	2	WETLAND	4	P. FEATHER	600	350
PLH (W)	2	WETLAND	4	P. FEATHER	300	700
PHH (W)	2	WETLAND	4	P. FEATHER	600	700
CLL (W)	2	WETLAND	4	CAN. GRASS	300	350
CHL (W)	2	WETLAND	4	CAN. GRASS	600	350
CLH (W)	2	WETLAND	4	CAN. GRASS	300	700
CHH (W)	2	WETLAND	4	CAN. GRASS	600	700
PLL (L)	1	LAGOON	2	P. FEATHER	300	350
PHL (L)	1	LAGOON	2	P. FEATHER	600	350
PLH (L)	1	LAGOON	2	P. FEATHER	300	700
PHH (L)	1	LAGOON	2	P. FEATHER	600	700

+

1 Cells A and B in rock filters maintained anaerobic, cells C and D maintained aerobic via air-lifts (recurrent reciprocation at two hour intervals).

2 Wetlands operated as subsurface flow with terminal reciprocating cells.

3 Parrot feather (*Myriophyllum aquaticum = brazilience*); canary grass (*Phalaris arundinacea*).



Figures 2.1 A and B
Plan view of wetland (W) and lagoon (L) microcosms
illustrating cell partitions, flow rates, and water treatment flow-paths.

lagoon systems (L), parrot feather was placed into the shallow water and distributed to ensure even surface coverage. On a dry matter basis the high and low biomass treatments were planted at densities equivalent to 899 and 449 g/m2 (canary grass) and 971 and 485 g/m2 (parrot feather), respectively. Microcosms were planted, fertilized, and operated under experimental conditions for 15 days prior to experimentation to allow plants and microbial populations to become established and acclimatized.

Initial water volume in all treatments was equal to 12 liters. Contaminated groundwater used in this study was pumped from Milan well MI 146 (Milan Army Ammunition Plant, Milan, Tennessee), transported to TVA and stored on site in large stainless steel tanks until used in experiments. Average concentrations of explosives (mg/l), as measured in the storage containers were as follows: TNT, 2.153; RDX, 2.732; HMX, 0.160; and TNB, 0.154.

Flow rate of contaminated water to each microcosm was maintained at approximately 1.4 ml/min with peristaltic pumps, for a calculated hydraulic retention time of 6 days. This retention time was selected based on an earlier study that was designed to evaluate explosives remediation in batch loaded (static non-flow-through), rock biofilters and shallow planted lagoons (see Batch Study I).

The four cell aquaria, simulating subsurface-flow wetlands (W), were back-filled with bacteria-laden river gravel (void space = 35-40 %) to a depth of approximately 22 cm. Gravel was collected from an outdoor anaerobic subsurface flow wetland which had been in operation for over 1 year, transported to the greenhouse and placed into microcosms. Care was taken to maintain the "harvested" rocks under anaerobic conditions so that the anaerobes were not exposed to aerobic conditions.

Figure 2-1a illustrates a plan view of the wetland microcosms detailing flow paths and position of inlet, subsurface siphon and outlet. Cells A and B of each wetland microcosm (W), each had surface areas equal to 416 cm^2 and were designed to maintain anaerobic conditions (no aeration); cells C and D each had surface areas equal to 214.5 cm^2 and were designed to remain aerobic.

Cells C and D of wetland microcosms were aerated using paired air lifts which were operated sequentially at two hour intervals; this process of sequential and recurrent aeration is referred to as reciprocation. For example, during reciprocation cycle one, water in each C cell was air-lifted to and stored in the contiguous D cell. Water in excess of cell D's freeboard was allowed to leave the system via an external standpipe. The process was reversed every two hours. The process of air-lifting water facilitated mild aeration and as water was removed from the pumped cell, the rock backfill material, plant roots, and fixed-film microbial populations were exposed to atmospheric oxygen for approximately two hours. Sequential anaerobic-aerobic environments have been found to be useful in remediating recalcitrant compounds and their byproducts, and to facilitate removal of excess carbon and nutrients which are often used to fertilize microbial/plant remediation ecosystems.

The 2-cell aquaria (Figure 2-1 b), simulating shallow lagoons (L), were designated as "controls" (no rock substrate, no aeration) and were stocked with parrot feather *Myriophyllum aquaticum,* either at 25 g/l or 50 g/l. Two fertility treatments were also imposed on each plant stocking density (350 versus 700 mg/l fertility, milk replacement starter). These non-replicated treatments were not a part of the factorial experiment, but were included to allow comparisons between rock-based wetlands and lagoon systems.

Organic fertilizer consisting of a commercial grade of milk replacement starter (MRS), was used as the sole source of exogenous carbon and macro / micro-nutrients (Table 2-2). At the initiation of the experiment, time = 0, contaminated water was batch fertilized with MRS. Twelve liters of the fertilized munitions-contaminated water mixture was apportioned to each microcosm. Subsequently, unfertilized contaminated groundwater was pumped via peristaltic pumps at a rate of 1.4 ml/min into the inlet of each microcosm. Based on void space, water volume, and flow rate this was equivalent to a six day retention time; two days in each of cells A and B and one day in each of cells C and D. With respect to the shallow lagoons (L), the six-day retention time was equally divided between cells A and B. On day 20 of the experiment, following collection of water samples, all microcosms were refertilized with a concentrated slurry of MRS equivalent to 4.2 or 8.4 grams of the powder. These rates of fertilization were based on the initial fertilization rates, i.e. 350 and 700 mg/l. The concentrated slurry was injected with syringes into each microcosm near the inlet (below the surface), to simulate a plug-flow situation. Subsequent sampling of TNT, RDX, HMX and byproduct compounds

Table 2-2
Proximate Composition of Milk Replacement Starter Used as Organic Fertilizer in TNT MICROCOSM STUDY II.

Crude protein, not less than	22.0%
Crude fat, not less than	20.0%
Crude fiber, not more than	0.5%
Calcium (Ca), not less than	0.75%
Calcium (Ca), not less than	1.25%
Phosphorus (P), not less than	0.70%
Vitamin A, not less than	20,000 I.U./lb
Vitamin D3, not less than	5000 I.U./lb.
Vitamin E, not less than	100 I.U./lb.
INGREDIENTS: Dried whey, dried whey protein concentrate, dried whey product, dried skim milk, dried milk protein, protein modified soy flour, animal fat (preserved with ethoxyquin), lecithin, dicalcium phosphate, calcium carbonate, vitamin A acetate, D-activated animal sterol (source of vitamin D-3, vitamin E supplement, thiamine mononitrate, pryridoxine hydrochloride, folic acid, vitamin B-12 supplement, choline chloride, sodium silico aluminate, manganese sulfate, zinc sulfate, ferrous sulfate, copper sulfate, cobalt sulfate, ethylenediamine dihydriodide and sodium selenite. oxytetracycline (125 g per ton), neomycin base (250 g per ton.	

were sampled on day 6, 10, 20, and 30. Analysis of munitions and by-products was via HPLC. On each sampling date, 20-50 ml samples were collected from the 4-cell microcosms at the:

- Inlet,
- Overflow of cell A (siphon location),
- Adjacent to overflow of cell B, and
- Outflow of cell D.

In the two-cell microcosms, 20 ml samples were taken at the inlet, and at points in the flow path to approximate 2, 4, and 6 day retention. Samples collected for explosives determinations were stored and frozen in amber glass vials until analyzed. Analyses were conducted using HPLC.

Water samples were also sampled on a routine basis for COD (Hach Method), dissolved oxygen (D.O.), pH, conductivity and temperature using a water quality sonde (Yellow Springs Instruments, Yellow springs, Ohio). Redox potential (ORP), was measured via insitu probes (platimum electrode and calomel reference electrode) located near the inlet and outlet of each microcosm. Measurement of ORP was conducted at regular intervals to monitor changes in ORP as a function of treatment and location within the microcosms.

After 45 days of culture (15 days acclimation and 30 days of experiment), plant biomass was harvested from each microcosm, dissected into root and shoot portions (canary grass), or root, subsurface stem, and aerial shoot portions (parrot feather), allowed to "drip-dry", and weighed to the nearest 0.1 gram. Subsequently, the samples were placed into tarred paper bags and dried for 48 hours in a forced-air oven operated at 60 degrees centigrade. Oven-dried samples were reweighted to the nearest 0.1g and yields and standing crops were calculated on a g/m^2 basis.

For the purpose of this report, data has been compiled, averaged, and summarized in either table of graphical format. Simple correlation was used to demonstrate the relationship between redox potential and remediation of RDX.

SECTION 3.0

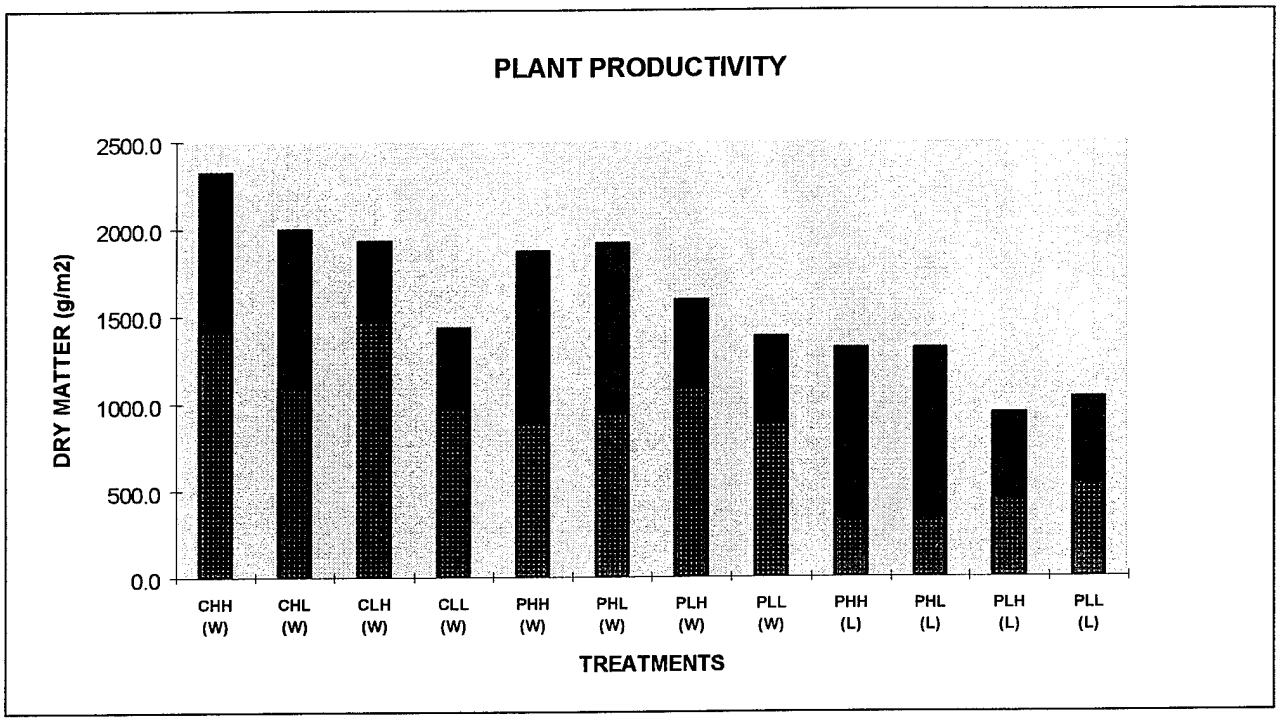
RESULTS AND DISCUSSION

3.1 Plant Productivity, Growth, and Treatment Implications

Gross biomass of whole plants (roots, shoots and stems) expressed as g/m^2 dry matter, ranged from 881 to 2260 g/m^2. In wetlands treatments (W), canary grass responded in an additive manner to both increased density and fertility and under high density-high fertility conditions yielded 2203 g/m^2. In contrast, parrot feather tended to have higher yields (2262 g/m^2), in the low fertility-high density treatment. In the lagoon systems (L), parrot feather yields were not additive, indicating possible yield by treatment interactions. Parrot feather production (gross), in the lagoon treatments were relatively low (825 to 1237 g/m^2) except in the high density / high fertility treatment (20 81 g/m^2).

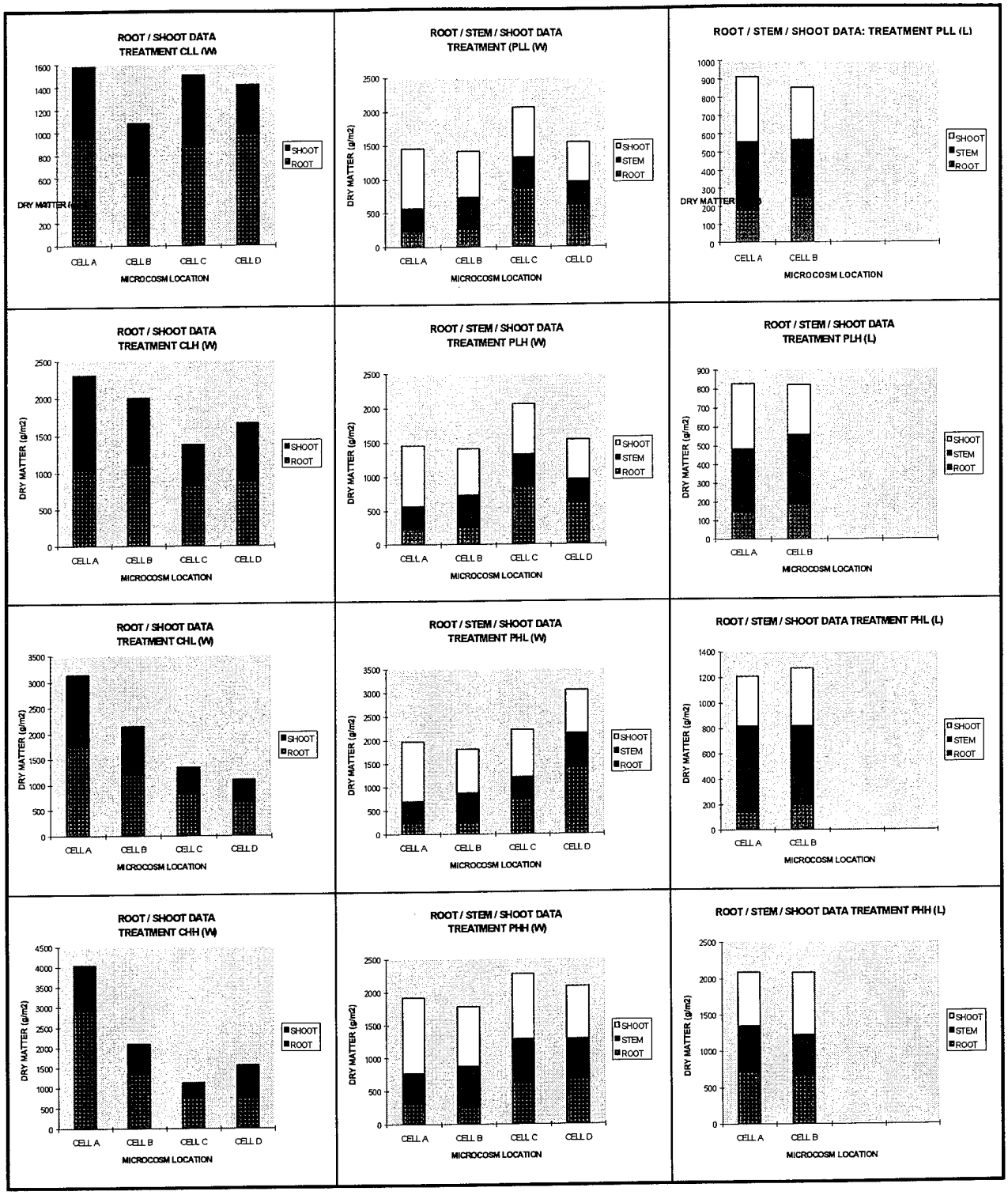
Figure 3-1 illustrates gross production on a dry matter basis (initial biomass plus net production) as a function of treatment. Bottom bars, colored in blue, represent initial biomass at time of planting; while the top bars, colored in black, represent net production or yield. Notice that canary grass production responded to increases in fertility, but very little to increases in density. Parrot feather yields in the wetland systems also showed a strong response to fertilization at the low density, but a negative response to fertilization at the high density. These responses both indicate that at the high density, plant biomass may have been near carrying capacity. Parrot feather yields in the lagoon systems were significantly less than yields in the wetland systems, irrespective of fertility or plant density (Figure 3-1). Yields (g dry matter/m^2), averaged over levels of fertility and density for canary grass and parrot feather were: canary grass (1244), parrot feather (wetlands, 958; and lagoons, 421).

Closer examination of plant production data as a function of location (Cells A, B, C, D) and tissue type (root, sub-surface stem, and aerial shoot), reveals significant differences in species responses to density, fertility, and treatment system (Figure 3-2). Values are based on gross biomass production over a 45 day period during September and October, 1995 (15 day acclimation period and 30 day study).



Initial planting density represented by upper bars, net production by lower bars, and gross production by sum of grass. Plant type are designated by the first letter of the treatment designation. The letter C designates canary grass; P designates parrot feather. Values represent production over a 45 day period (September - October 1995).

Figure 3-1
Initial Planting Density, Net Production, and Gross Production for Canary Grass and Parrot Feather as a Function of Treatment.



Note: Y-axes have not been standardized across treatments).

Figure 3-2
Mean dry matter production of roots, stems, and shoots as a function of location, plant species, plant density, level of fertility, and treatment system.

Canary grass yields tended to decrease from cell-A to cell-D mostly as a result of nutrient limitations. Also, shoot biomass tended to decrease relative to root biomass (root/shoot ratios), as fertility and density increased. In contrast, parrot feather yields in similar wetland environments (W), tended to increase from cell A to cell D irrespective of fertility and density inputs. Also, the root to shoot ratio of parrot feather increased dramatically in the aerobic portions of the wetlands (cells C and D contrast cells A and B, Figure 3-2). Plant yield data and tissue growth partitioning are potentially important with respect to sustainability and treatment efficacy of the proposed treatment system(s). In start up operations, it will be necessary to augment with organic fertilizers to promote anaerobic conditions. However, over time the carbon fixed in the plants (plant tissue contains approximately 50% carbon on a dry matter basis), should become available to the microbial populations as the plants grow, senesce, and die. Plant leaf litter and dead roots and their attendant high oxygen demands will also decrease the impact of atmospheric diffusion of oxygen into the treatment wetlands.

With respect to plant growth patterns and tissue partitioning, it may be important to have planting schemes and treatment environments that promote high root to shoot ratios. Roots provide tremendous surface area for both microbial attachment and for direct uptake of nutrients, explosives and explosives by-products. Plant production data in this study would support planting canary grass near the inlet (strong response to high fertility) and parrot feather in the distal areas of the wetlands, including the reciprocating cells, (high root to shoot ratios at low fertility and in aerated environments).

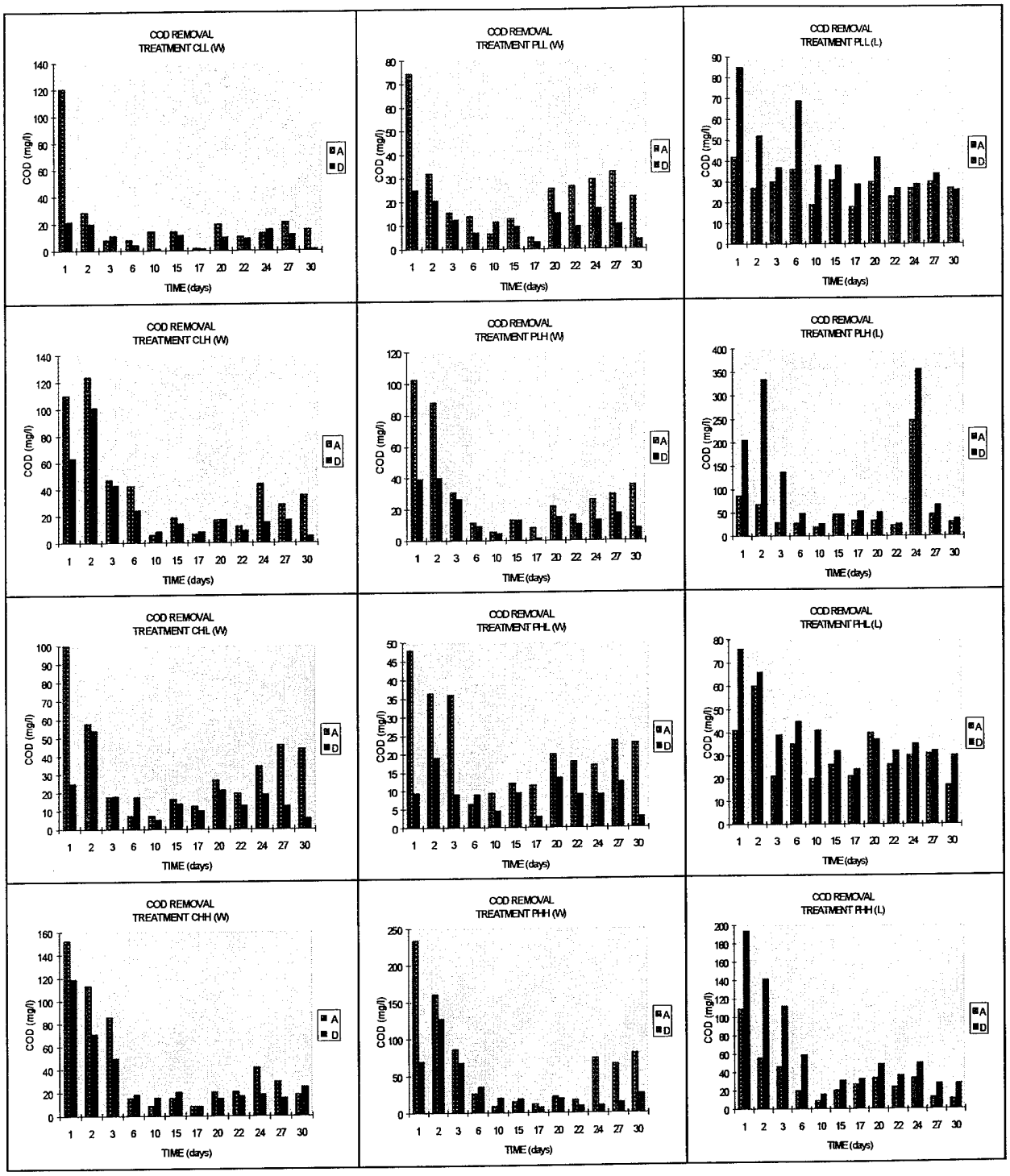
3.2 Water Quality

Water quality parameters were averaged by treatment over sample dates (n = 15) for the 30 day trial. Means and standard deviations are summarized by in Table 3-1. Neither temperature nor pH values differed significantly among treatments and were relatively stable throughout the study. Notable differences in pH between A and D locations within the wetland systems were assumed to be due to reciprocation, subsequent off-gassing of CO_2 and a shift in the carbonic acid buffer system.

TREATMENT DESIGNATION	TEMPERATURE (°C)		ELECTRICAL CONDUCTIVITY (mS/cm)		DISSOLVED OXYGEN (mg/l)		pH (unitless)		REDOX POTENTIAL (mV)[1]	
LOCATION	A[2]	D[2]	A[2]	D[2]	A[2]	D[2]	A[2]	D[2]	A[2]	D[2]
CLL (W)	**22.5**	**21.5**	**185.3**	**222.9**	**1.7**	**5.6**	**6.4**	**6.9**	**-154.9**	**61.5**
	(3.7)	(3.5)	(33.4)	(42.5)	(1.0)	(1.7)	(0.3)	(0.3)	(165.9)	(72.2)
CHL (W)	**22.0**	**20.8**	**224.4**	**266.8**	**1.5**	**5.3**	**6.4**	**7.0**	**-194.9**	**54.2**
	(3.6)	(3.5)	(55.3)	(41.9)	(1.6)	(2.1)	(0.2)	(0.3)	(185.2)	(45.8)
CLH (W)	**22.0**	**20.9**	**239.0**	**276.7**	**1.0**	**5.0**	**6.2**	**6.9**	**-250.0**	**-3.5**
	(3.6)	(3.5)	(69.1)	(59.3)	(0.5)	(2.4)	(0.2)	(0.2)	(158.0)	(138.1)
CHH (W)	**22.3**	**21.1**	**216.1**	**270.7**	**1.1**	**4.2**	**6.2**	**6.9**	**-248.8**	**52.0**
	(3.6)	(3.5)	(83.9)	(60.6)	(0.5)	(2.2)	(0.2)	(0.2)	(160.7)	(291.0)
PLL (W)	**22.3**	**21.3**	**156.7**	**188.6**	**1.4**	**5.2**	**6.4**	**6.9**	**-169.5**	**65.8**
	(3.8)	(3.6)	(45.3)	(41.1)	(1.3)	(2.1)	(0.2)	(0.2)	(157.0)	(123.9)
PHL (W)	**22.2**	**21.1**	**173.5**	**176.9**	**0.8**	**6.2**	**6.4**	**6.9**	**-238.8**	**87.6**
	(3.9)	(3.6)	(55.3)	(38.9)	(0.5)	(1.9)	(0.2)	(0.2)	(175.6)	(84.4)
PLH (W)	**22.0**	**21.0**	**208.4**	**219.5**	**1.1**	**5.2**	**6.4**	**6.9**	**-279.5**	**35.6**
	(3.9)	(3.7)	(71.3)	(66.5)	(1.3)	(2.0)	(0.3)	(0.2)	(150.3)	(143.4)
PHH (W)	**22.2**	**21.2**	**228.4**	**241.0**	**0.9**	**4.2**	**6.2**	**6.8**	**-292.6**	**77.2**
	(3.9)	(3.6)	(90.4)	(75.0)	(0.7)	(2.5)	(0.2)	(0.2)	(123.2)	(175.0)
PLL (L)	**22.3**	**21.8**	**67.7**	**45.8**	**5.5**	**6.8**	**6.4**	**6.5**	**25.3**	**10.8**
	(3.7)	(3.6)	(40.0)	(37.6)	(2.7)	(3.1)	(0.4)	(0.3)	(46.6)	(27.9)
PHL (L)	**22.5**	**21.9**	**69.3**	**44.7**	**5.3**	**6.0**	**6.4**	**6.3**	**87.7**	**23.3**
	(3.8)	(3.7)	(39.1)	(35.1)	(2.7)	(2.8)	(0.4)	(0.3)	(82.3)	(39.4)
PLH (L)	**22.3**	**21.9**	**96.9**	**80.1**	**3.0**	**4.4**	**6.4**	**6.4**	**-34.3**	**-17.7**
	(3.8)	(3.7)	(50.0)	(57.5)	(1.6)	(2.9)	(0.4)	(0.4)	(79.5)	(67.8)
PHH (L)	**22.5**	**21.9**	**109.5**	**87.2**	**3.5**	**4.0**	**6.5**	**6.4**	**-49.2**	**7.8**
	(3.9)	(3.9)	(56.1)	(51.9)	(2.2)	(2.1)	(0.3)	(0.4)	(75.6)	(68.4)

1. Redox values are uncorrected. Add 255 for corrected values.
2. Location A was proximate to the inlet, while location D was near the outlet of each microcosm, irrespective of system

Table 3-1
Water Quality Parameters: Means and Standard Deviations, (+/- 1 stdev) as Monitored During the 30 Day Trial (September / October 1995).



Notes: 1). Cells were fertilized with milk replacement starter on days 0 and day 20 (see text for rates and methods).

2). Y-axes are not standardized across treatments.

Figure 3-3
COD Removal Rates as a Function of Treatment, Location (Cell), and Days Post-Fertilization

treatment, time and location. Three important aspects of this graph should be noted:

- The relatively rapid decline in COD within the first six days in wetland treatments versus lagoon treatments,

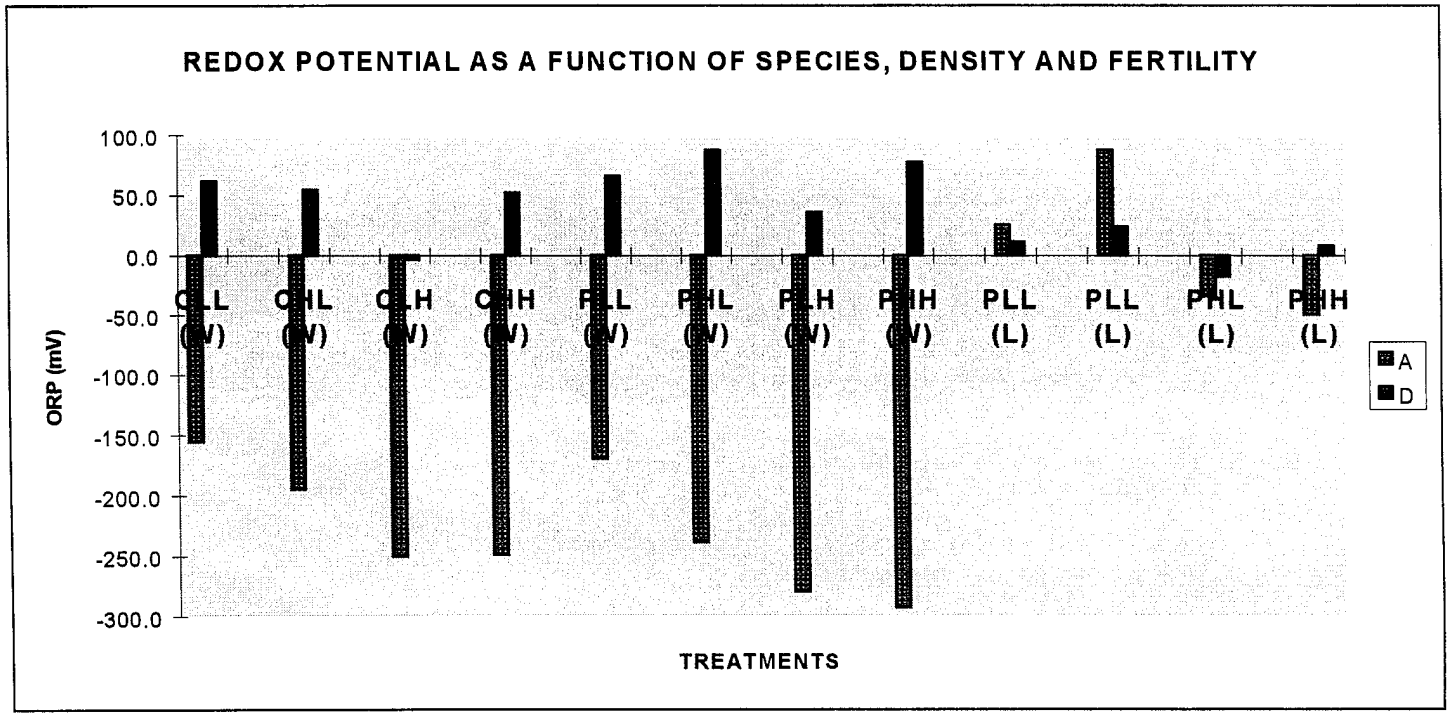
- The relative difference in COD values among locations (A versus D) within wetland treatments,

- And the small but perceptible increase in COD between location A and B within the lagoon treatments.

The increase in COD is an indication that parrots feather in lagoon environments is "leaking" organic matter back into the water in excess of the systems ability to oxidize the organic matter. Under extreme conditions, this could be considered pollution, as it has an inherent biological oxygen demand that may violate NPDES permit limits.

Redox potential plays an important role in explosives bioremediation technologies. Establishing a wide range of redox zones within the treatment train allows for a diversity of microbial populations which can effectively oxidize and/or reduce munitions, their by-products and organics. Figure 3-4 compares average redox potentials of the various treatments with respect to location (near inlet A versus near outlet D). The figure illustrates the relative contribution of plant species, plant density and fertility to negative redox values (see stair step pattern of negative values). Also, the figure vividly illustrates the differences in performance between subsurface-flow wetlands (W) and surface-flow lagoons (L). At low fertility, average redox values for the lagoon systems were positive in both cells A and B. At high fertility, the lagoon systems exhibited average values that were slightly negative, but still significantly less negative than comparable wetland cells.

Figures 3-5, 3-6, 3-7, illustrate changes in redox values for each treatment over time. Systems were fertilized in batch mode (completely mixed) on day 0 and again on day 20; however on day 20 the fertilization was performed by injecting a concentrated solution of MRS near the inlet of the system. Graphs have been grouped to facilitate comparison of canary grass and parrot feather under common fertility /density treatments. Figures 3-4, 3-5, 3-7, and 3-7 illustrate



Means are based on 12 observations over a 30 day period (September-October, 1995). Blue bars represent values in cell A and brown bars represent values in cell D (for wetland systems) and cell B for lagoon systems.

Figure 3-4

Average redox values as a function of treatment, location, and system (wetland versus lagoon).

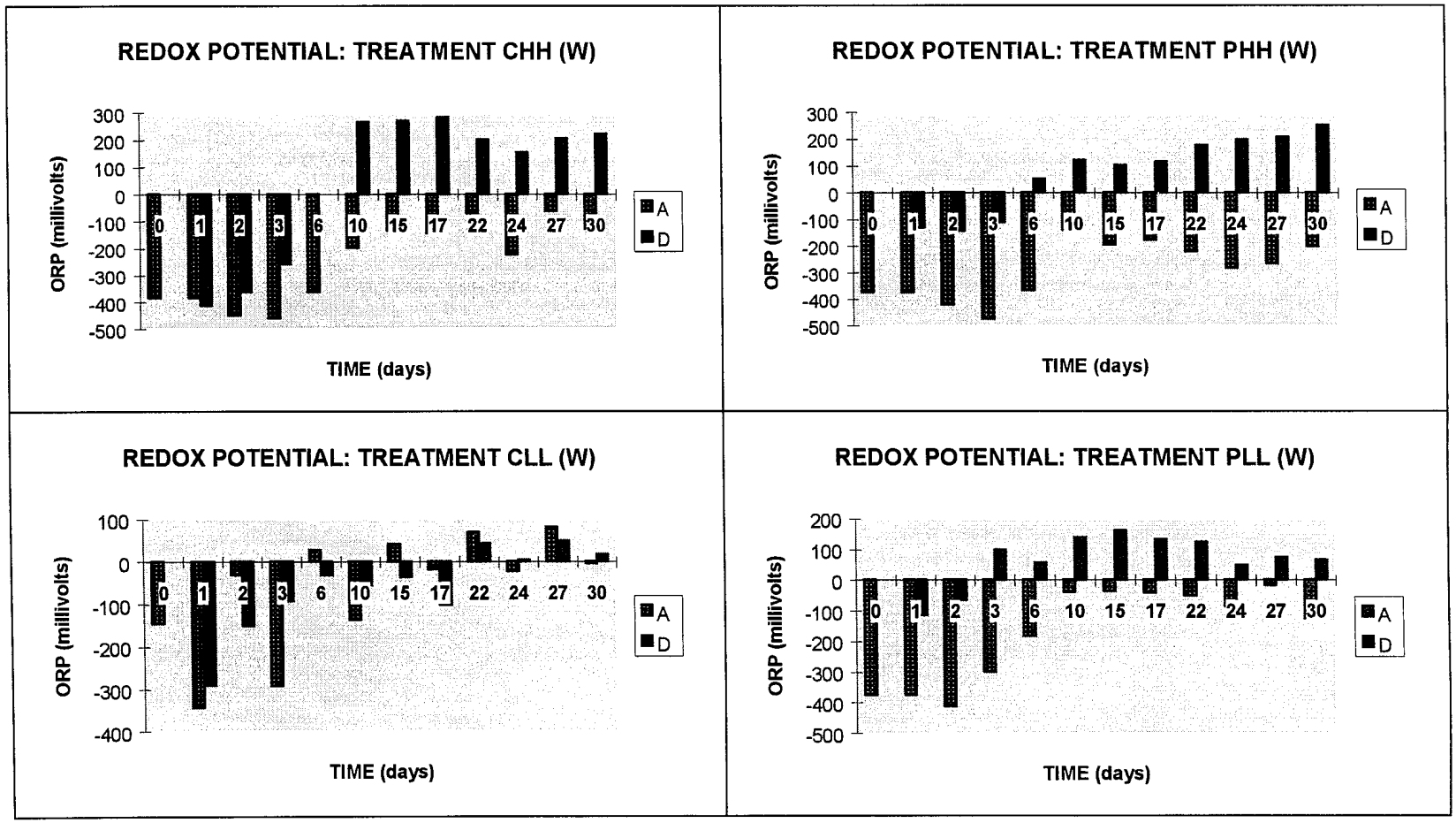


Figure 3-5

Redox potential as a function of wetland treatments and time for: CHH(W), CLL(W), PHH(W), and PLL(W)

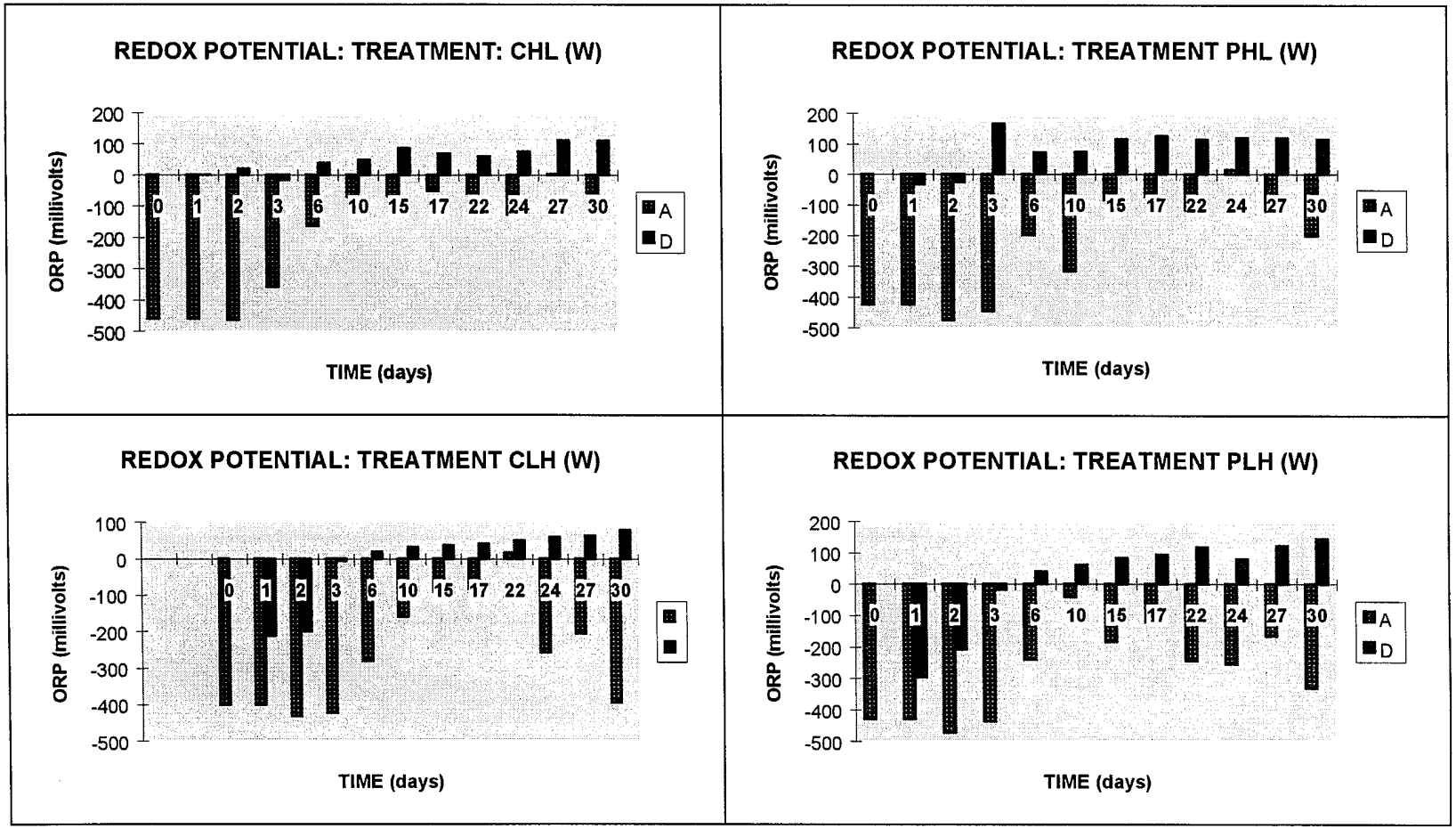


Figure 3-6

Redox potential as a function of wetland treatment and time for: CHL(W), CLH(W), PHL(W), and PLH(W).

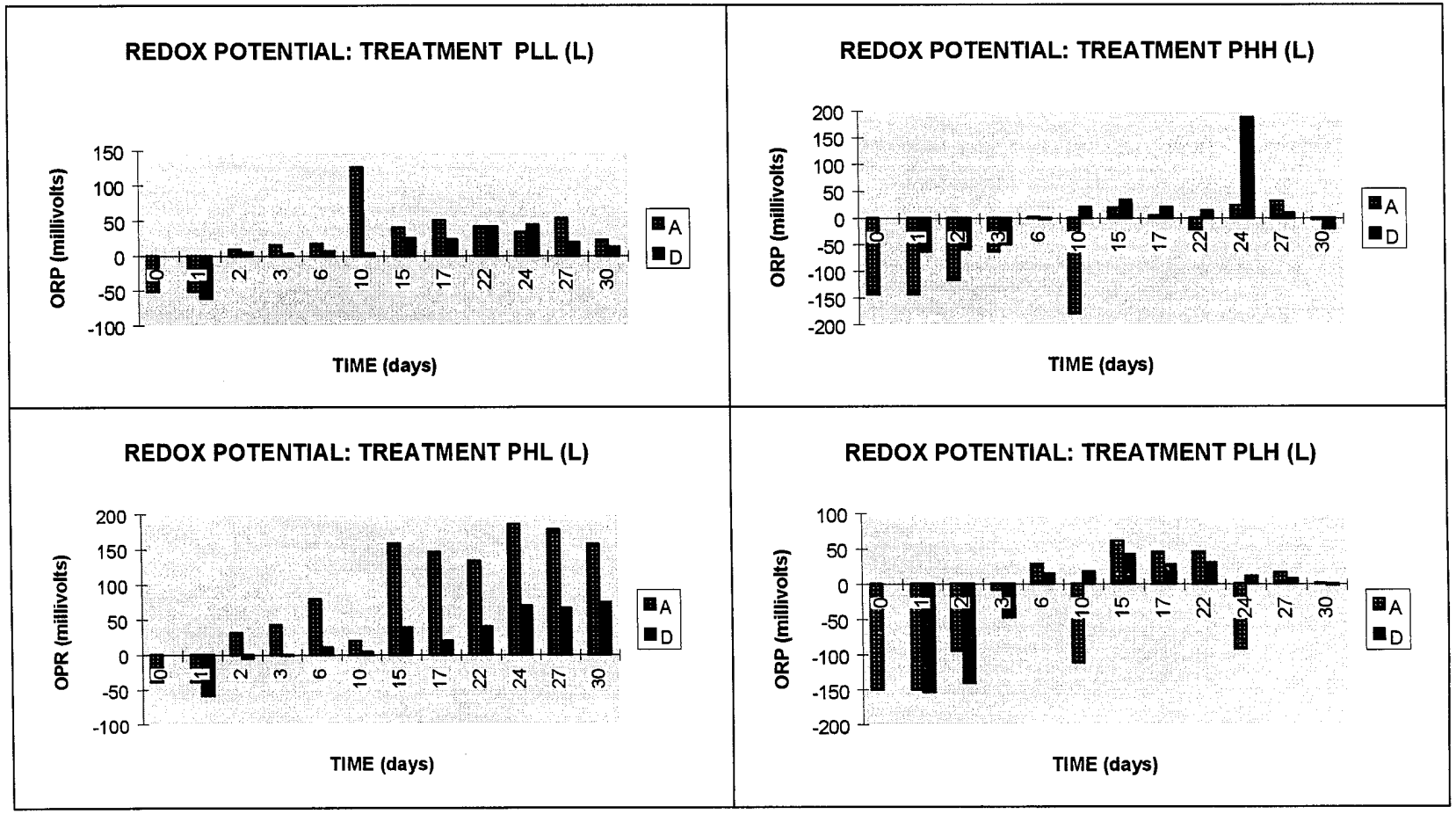


Figure 3-7

Redox potential as a function of lagoon treatments and time for: PLL(L), PHL(L), PLH(L), and PHH(L).

several important points:

- High fertility treatments (700 mg/l MRS), in wetland treatments resulted in lower redox conditions (-400 to -500) for a longer period of time than low fertility treatment (350 mg/l MRS). As will be seen later, low redox conditions are required for removal of several types of munitions and their by-products.

- Both species and plant density affected redox potential. Various organic compounds are known to be released by the roots into the rhizosphere and thus contribute carbon to the system. The carbon is subsequently oxidized and helps to maintain low redox conditions. This aspect of the systems ecology helps to sustain low redox values and the treatments efficacy. In the lagoon system there is also input of plant-based carbon, however there is adequate oxygen from surface diffusion and photosynthesis and thus the system stays aerobic.

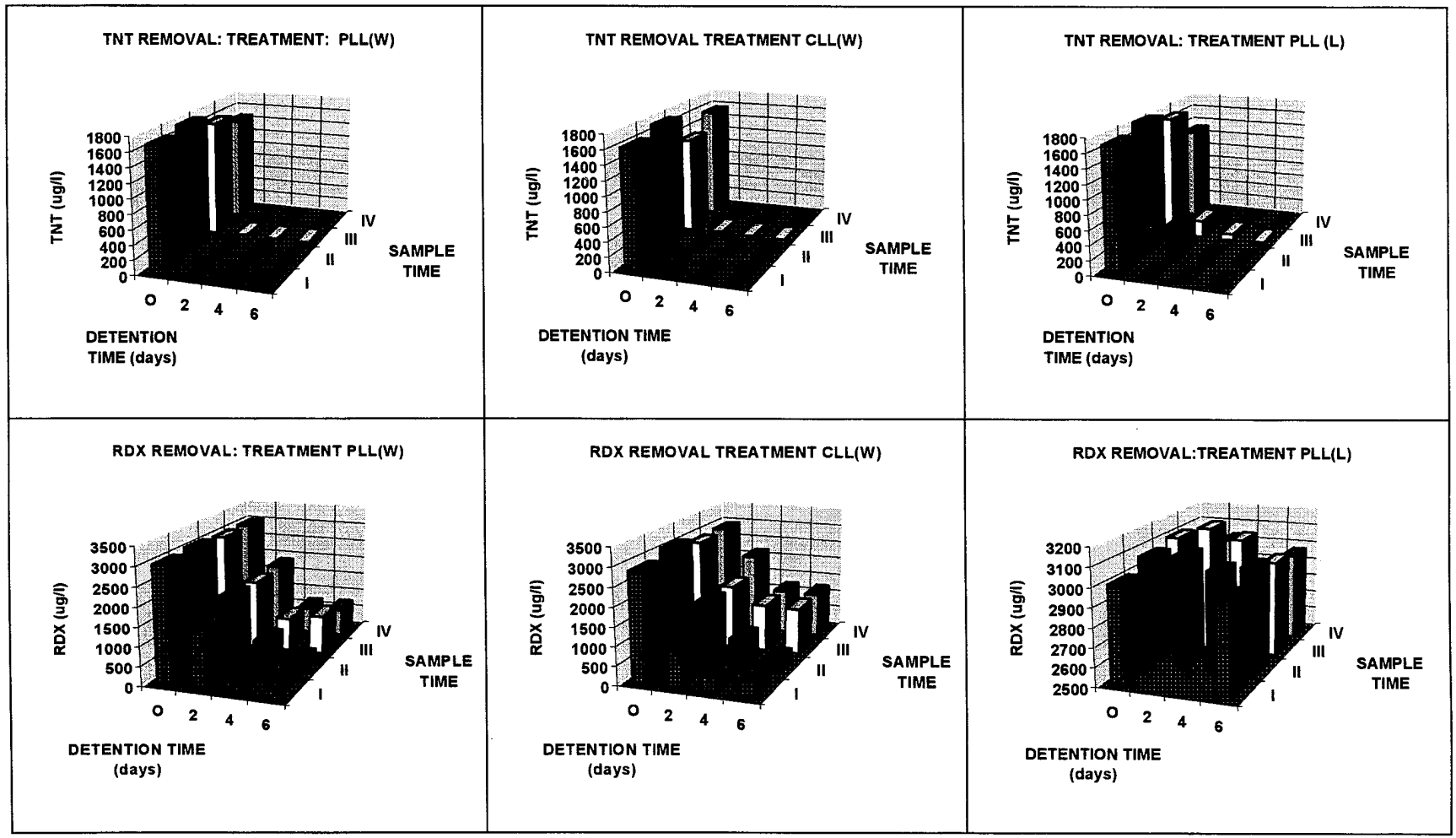
- The reciprocating action (cells C and D), infused oxygen into the system, thus facilitating development of aerobic biofilms and subsequent aerobic removal of excess carbon, nutrients and explosives by-products.

3.3 Explosives and Byproduct Removal

3.3.1 TNT and RDX

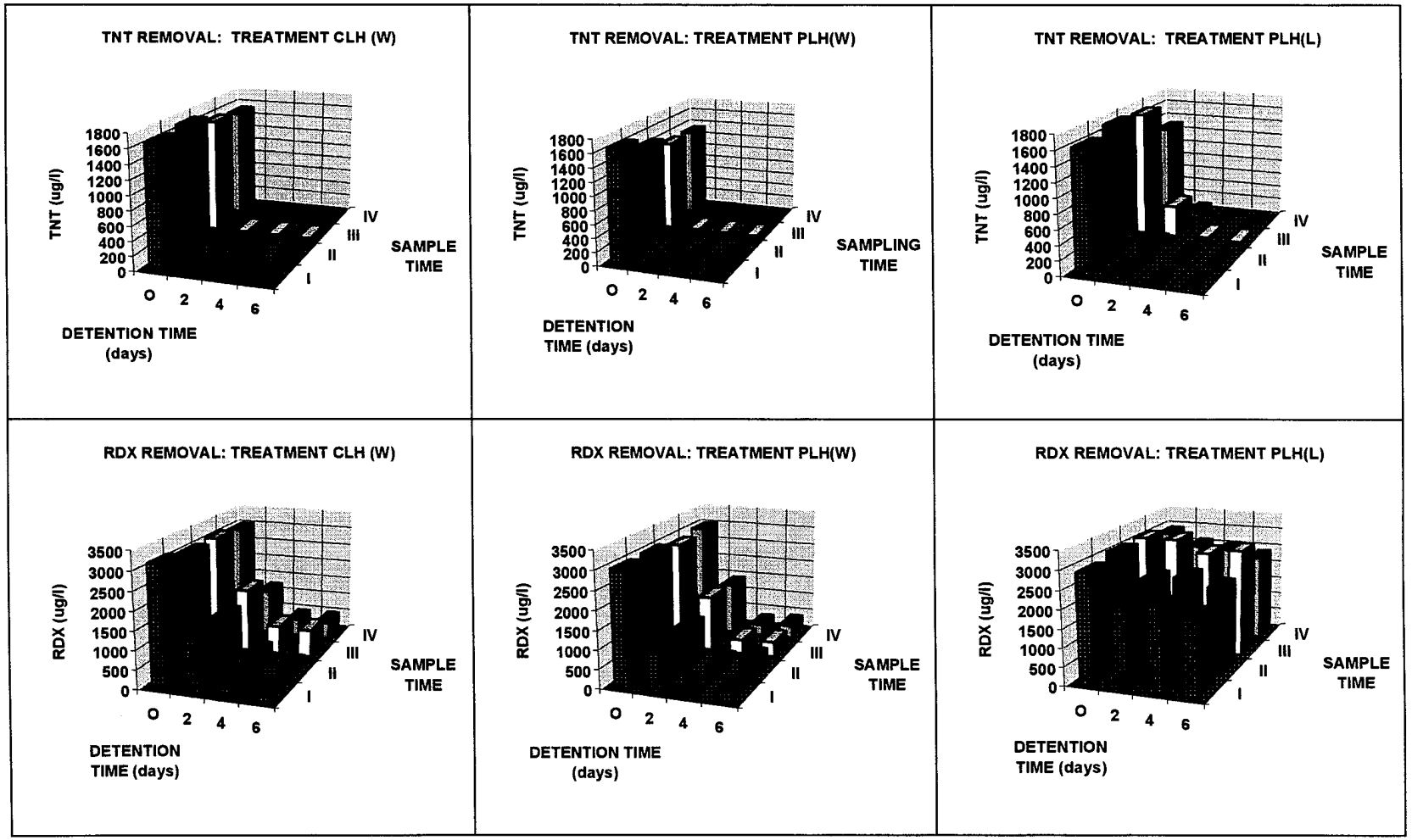
As in the previous microcosm (batch) study, TNT was rapidly removed from microcosms, irrespective of the treatment (Figures 3-8, 3-9, 3-10, and 3-11). Influent concentrations averaged 1600 ug/l, and were removed to below detection limits within 2 days in wetland microcosms; and within 4 days in lagoon treatments. However, there was a tendency for low concentrations of TNT to persist in some of the lagoon treatments beyond six days post fertilization (Figure 3-10).

RDX removal was rapid during the first six days post-fertilization, especially in the high fertility treatments. Examination of Figures 3-8 through 3-11 reveals rapid removal of RDX in all wetland treatments after initial fertilization, with a progressive lessening of efficacy with time, especially in the low fertility treatments (sample times I, II, III, and IV representing days 6, 10, 20, and 30).



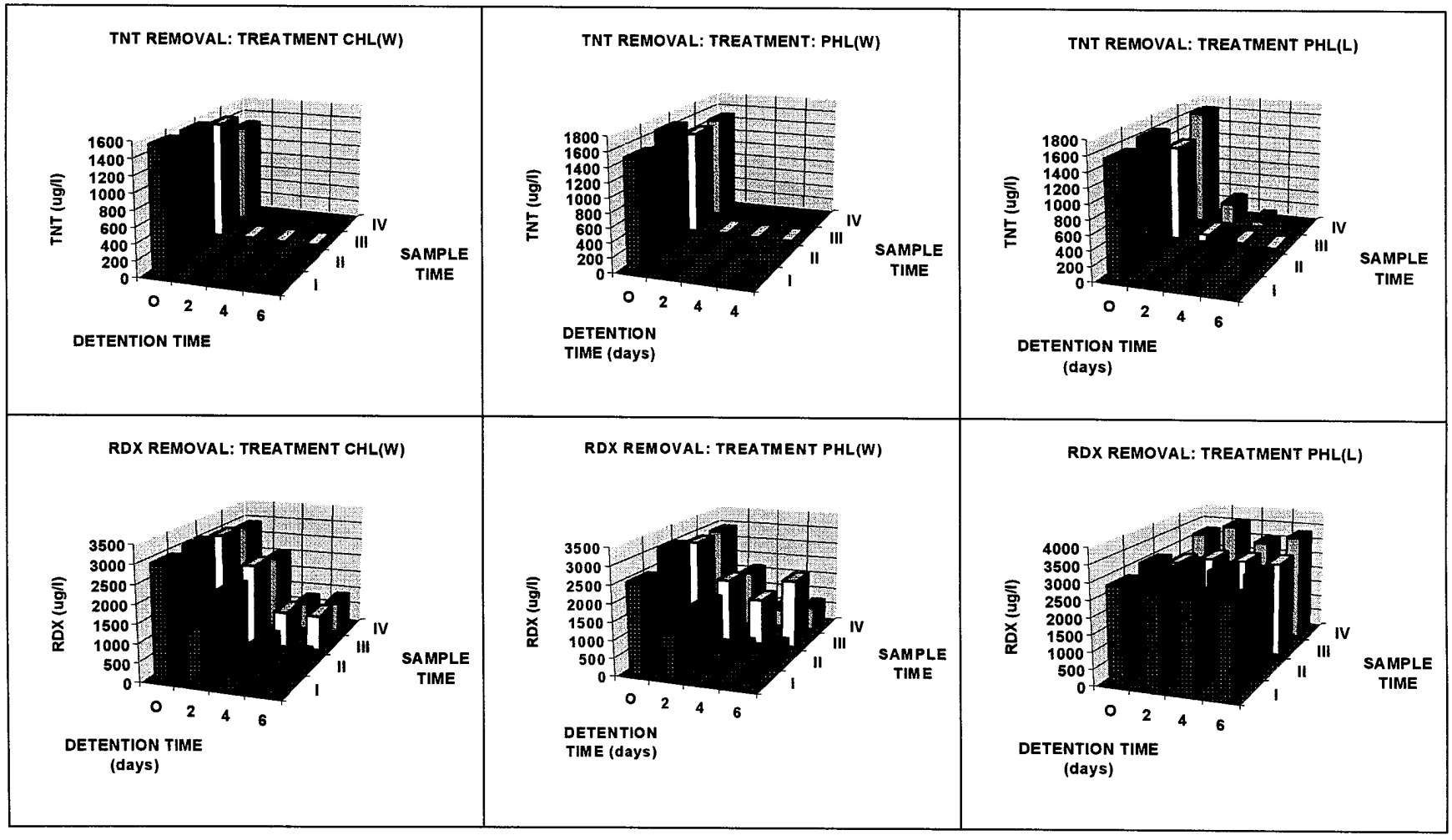
Notes: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).
2). Missing data for two cells in RDX graphic, treatment PLL(L)

Figure 3-8
Removal of TNT and RDX as a Function of Treatment for: CLL(W), PLL (W), and PLL(L).



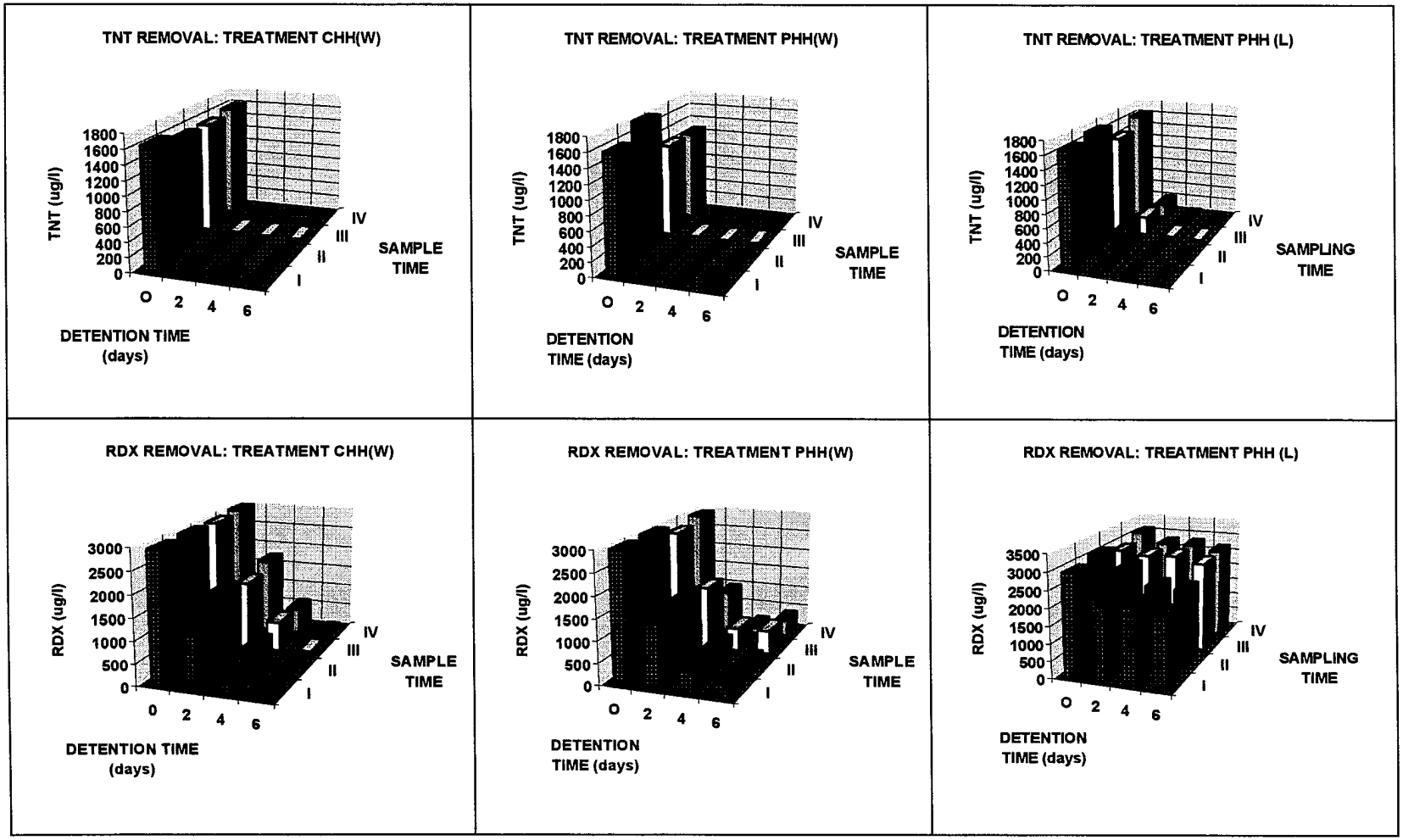
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-9
Removal of TNT and RDX as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-10
Removal of TNT and RDX as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-11
Removal of TNT and RDX as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

Figure 3-12 illustrates treatment efficiencies over time, as measured by K-values.

RDX influent concentrations averaged near (3000 ug/l), and were reduced to approximately 82 ppb in treatment CHH (W) after 4 to 6 days of retention (Figure 3-11). Treatment PHH (W) also reduced RDX substantially, to levels approaching 68 ppb. However, removal rates slowed progressively from day six to day twenty (Figures 3-8 to 3-11). Subsequent fertilization on day twenty did not result in a significant decrease in RDX concentrations, and may have been due to an inappropriate fertilization method. It is felt that better results will be obtained by step-feeding the fertilizer into the treatment train at different locations along its length, rather than inputting all of the concentrated fertilizer solution at the influent end of the system.

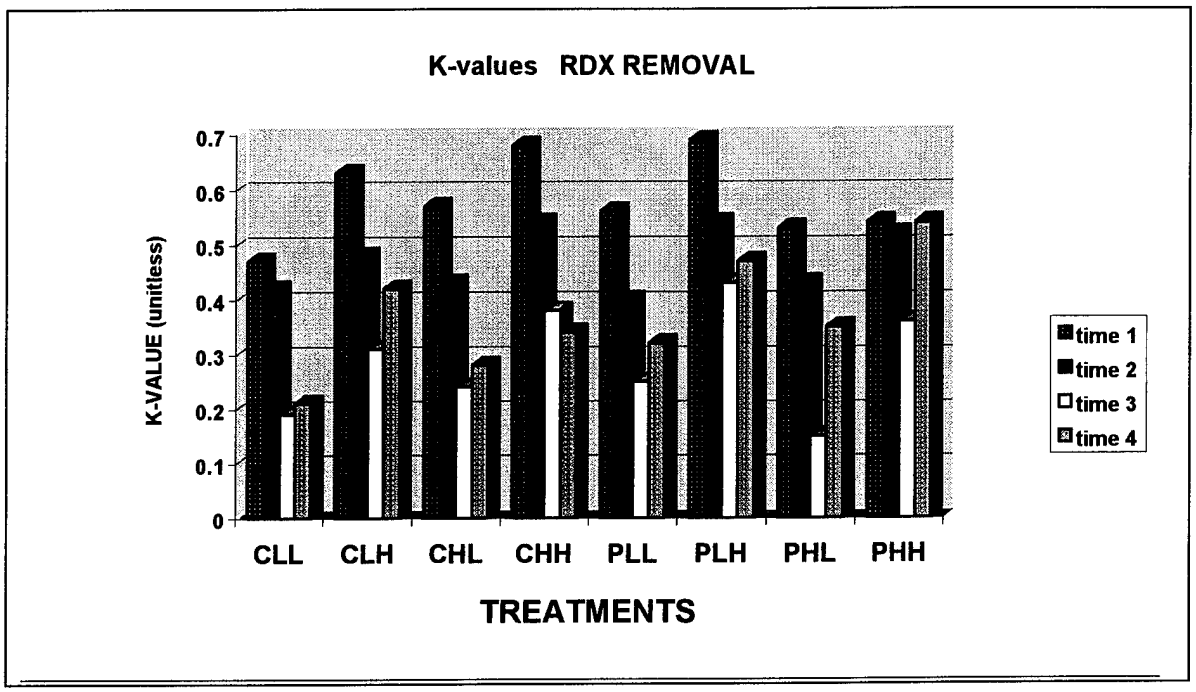
The lagoon treatments (L), were ineffective at removing RDX, irrespective of fertilization and planting regime. Even at high fertility and high planting density, RDX concentrations only decreased from 2900 ug/l to 2700 ug/l after six days of retention.

RDX removal was significantly influenced by redox level, with best removal rates achieved at low levels of redox (ORP< -250). High correlation was achieved between average redox levels and average RDX removal rates (r= 0.89), indicating that approximately 80 percent of the variation in RDX removal could be accounted for by variation in redox potential ($R^2 = 0.79$).

3.3.2 TNB and HMX

Influent TNB concentrations ranged from 20 to 50 ppb (ug/l). Wetlands, irrespective of treatment, effectively removed TNB to below detection limits within the first two days of retention, while lagoons often required 4 days (Figures 3-13, 3-14, 3-15, and 3-16). On one occasion there was a small spike subsequent to TNB being removed below detection limits (Figure 3-15).

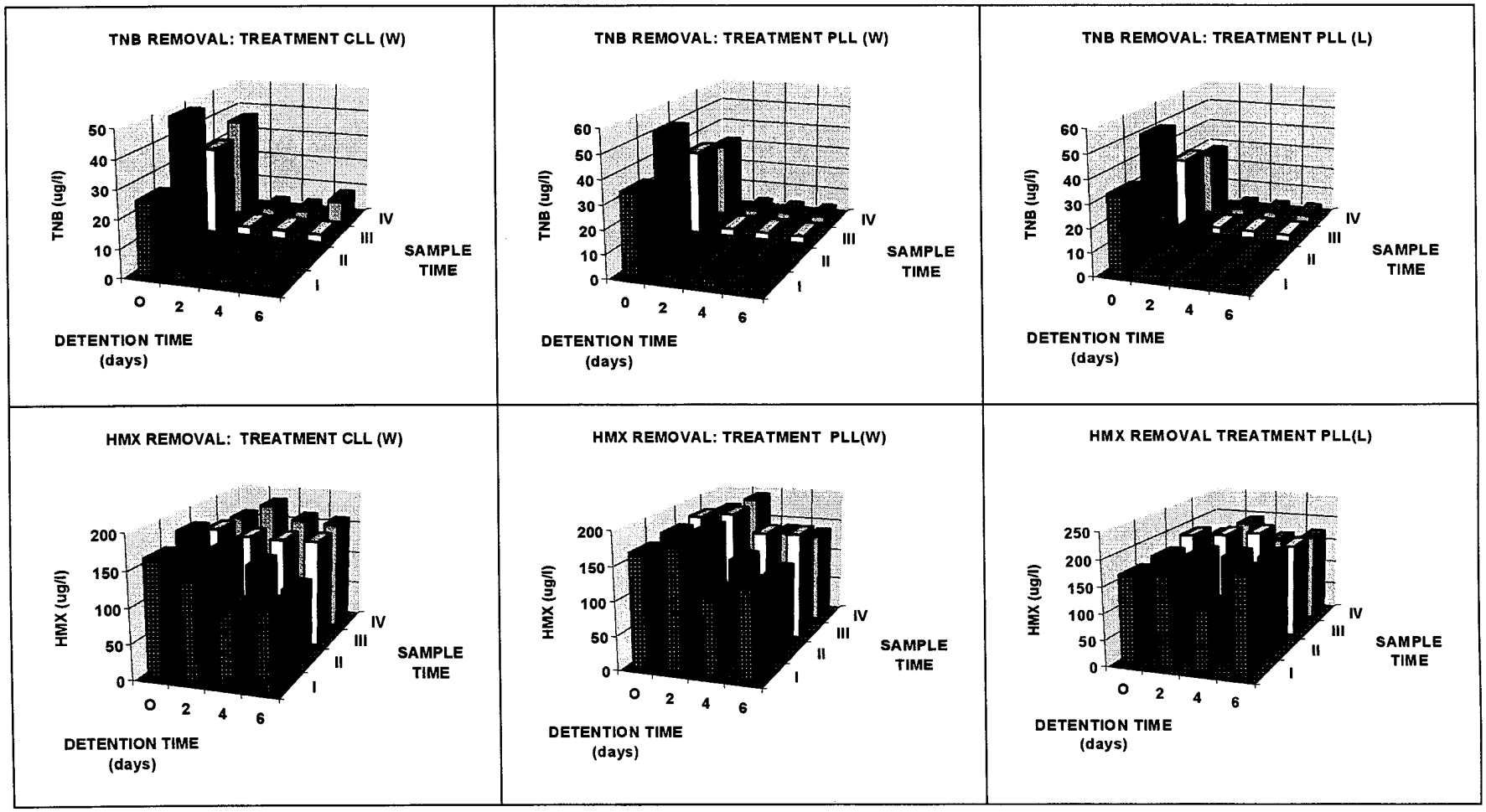
Influent concentration of HMX ranged from 150 to 160 ppb. No treatment effectively removed HMX to less than 50 ppb. There was a tendency for removal to be more effective soon after fertilization, but the efficacy dropped off with time. Additional studies should be undertaken to



Note: Notice marginal to moderate improvement in removal rates following fertilization on day 20 (time = 3).

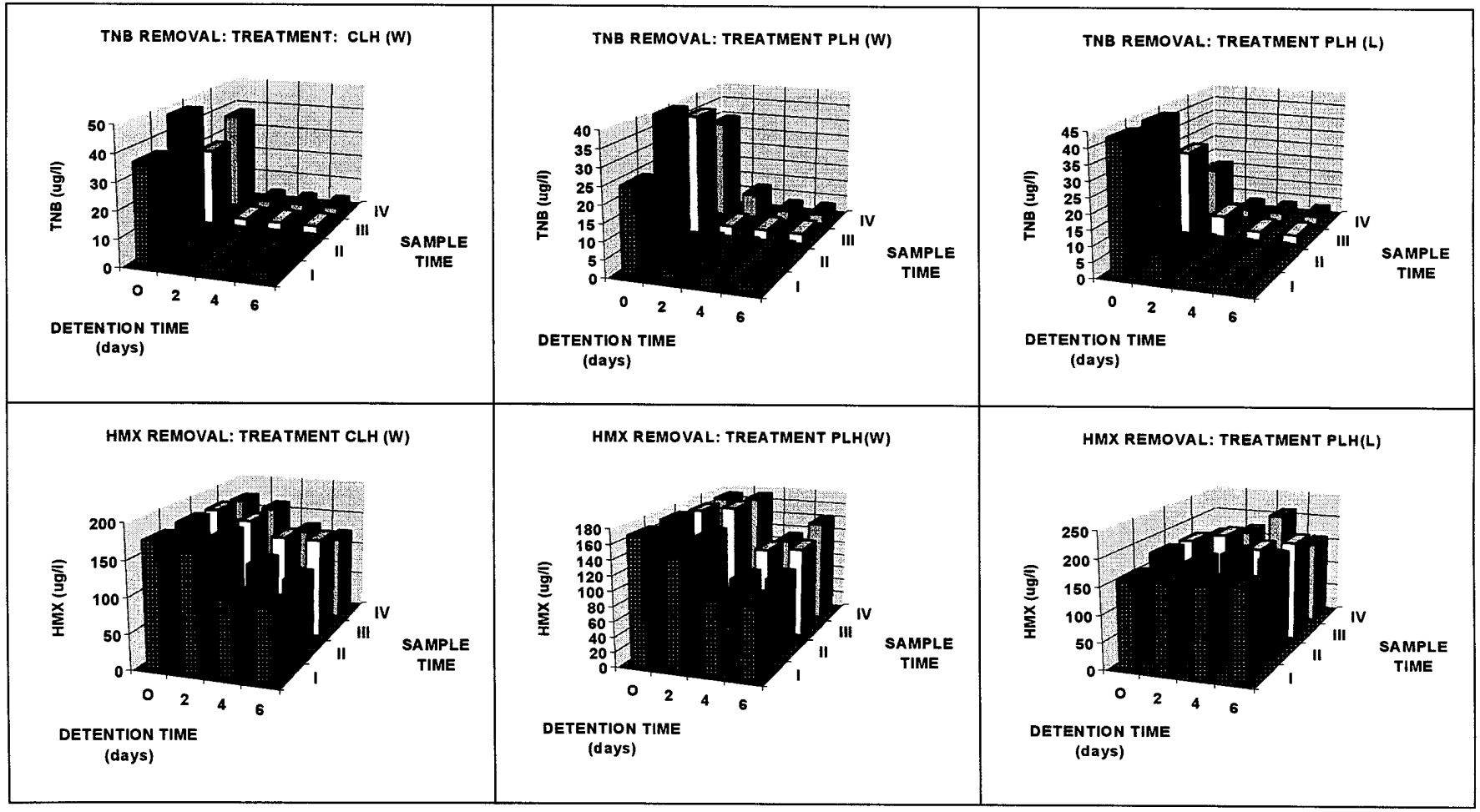
Figure 3-12

Relationship between K-value and treatments as a function of time.



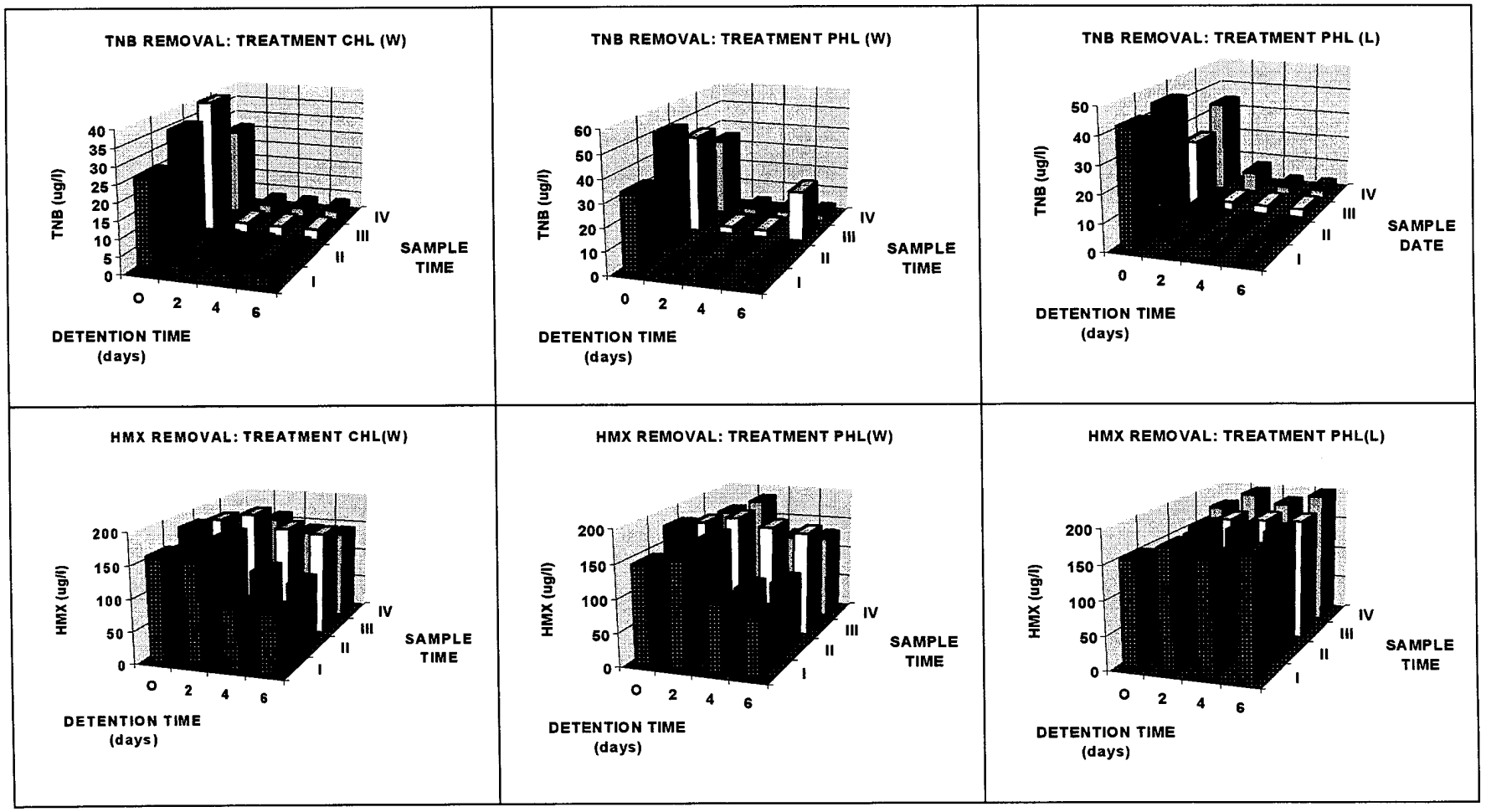
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-13
Removal of TNB and HMX as a Function of Treatment for: CLL(W), PLL (W), and PLL(L).



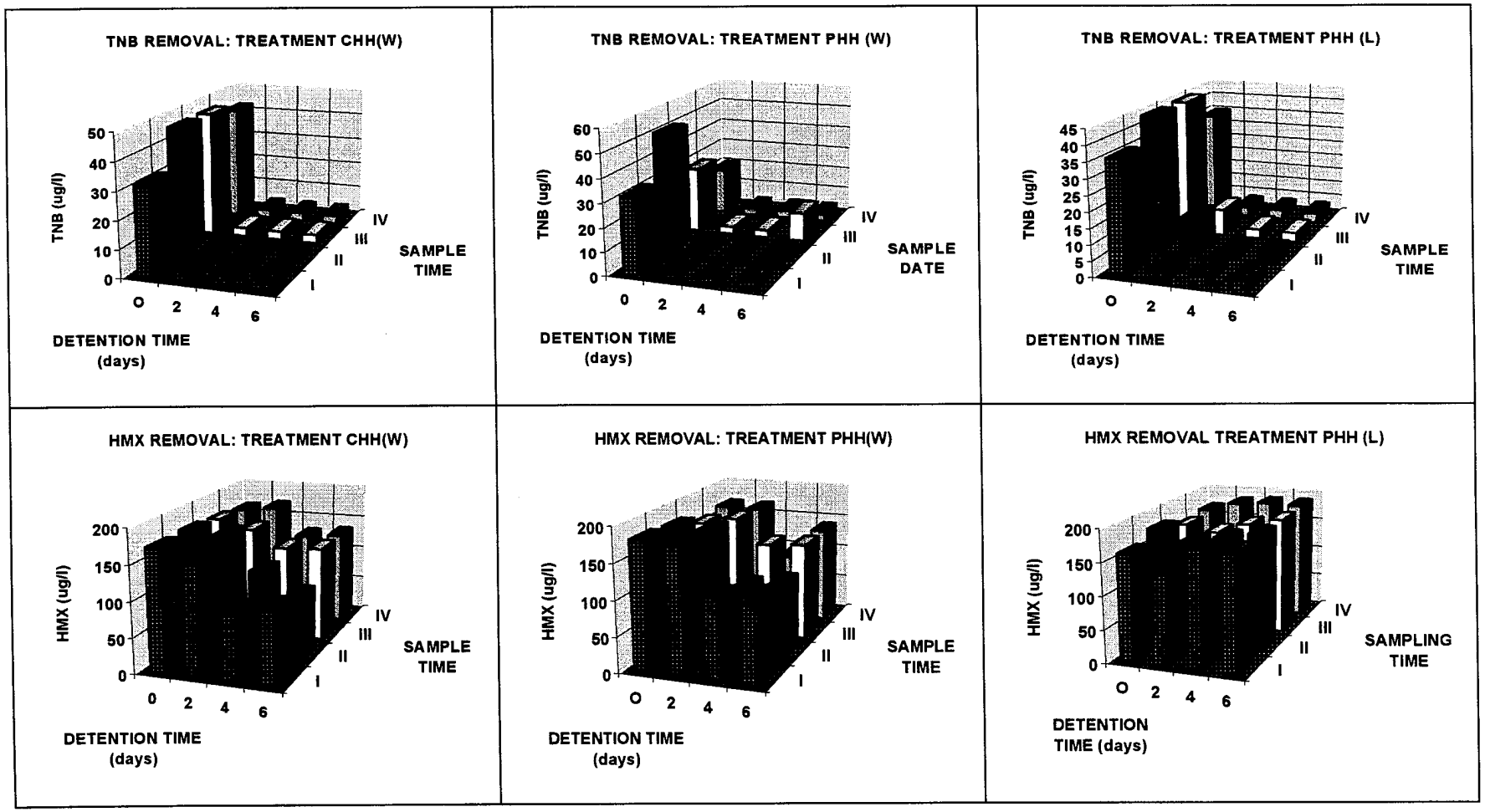
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-14
Removal of TNB and HMX as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-15
Removal of TNB and HMX as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

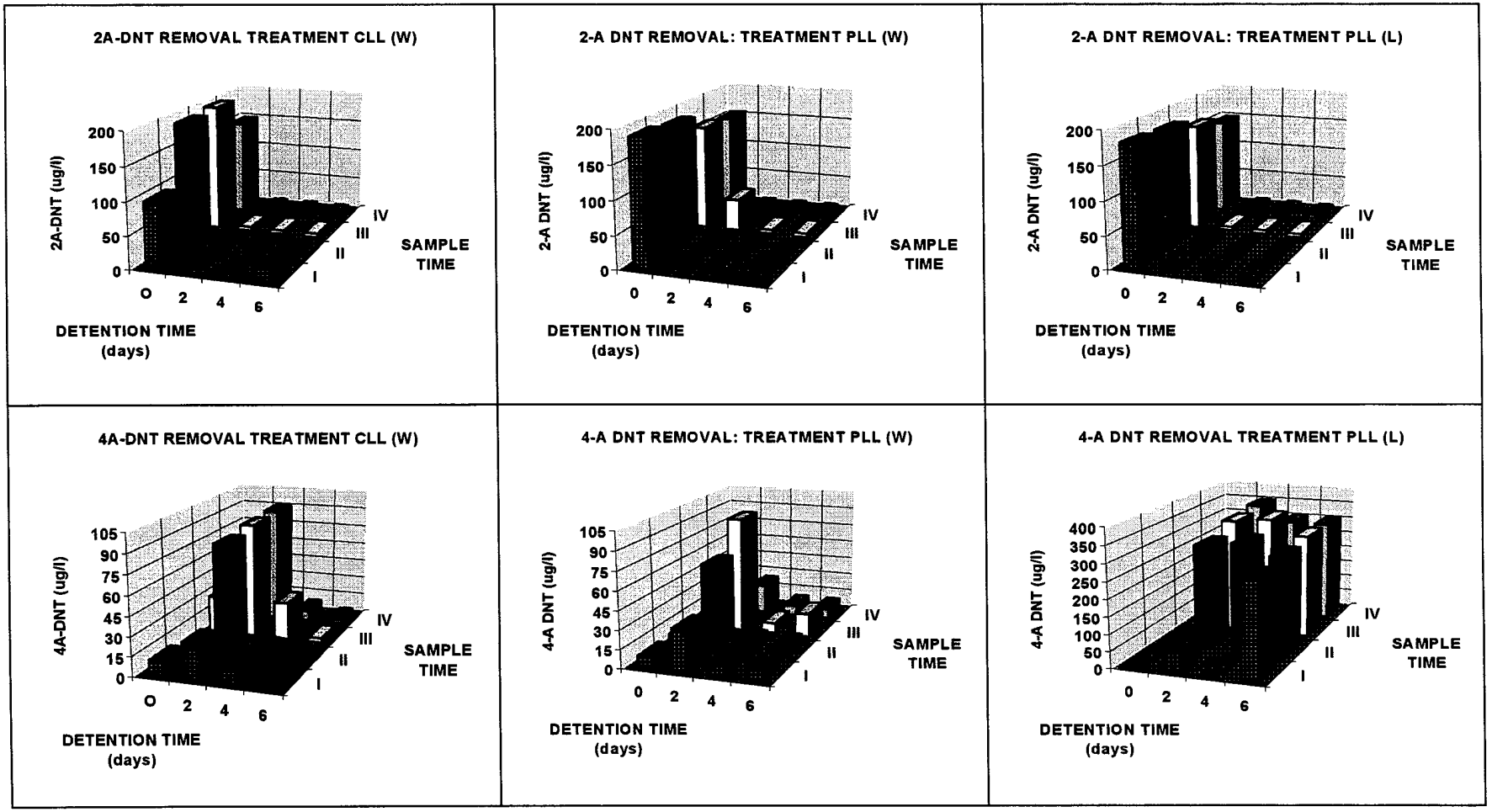
Figure 3-16
Removal of TNB and HMX as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

determine if HMX removal could be improved at even lower redox levels. HMX concentrations actually increased in some of the lagoon treatments probably as a result of very low removal rates and high evapotranspiration rates.

3.3 2-A DNT and 4-A DNT

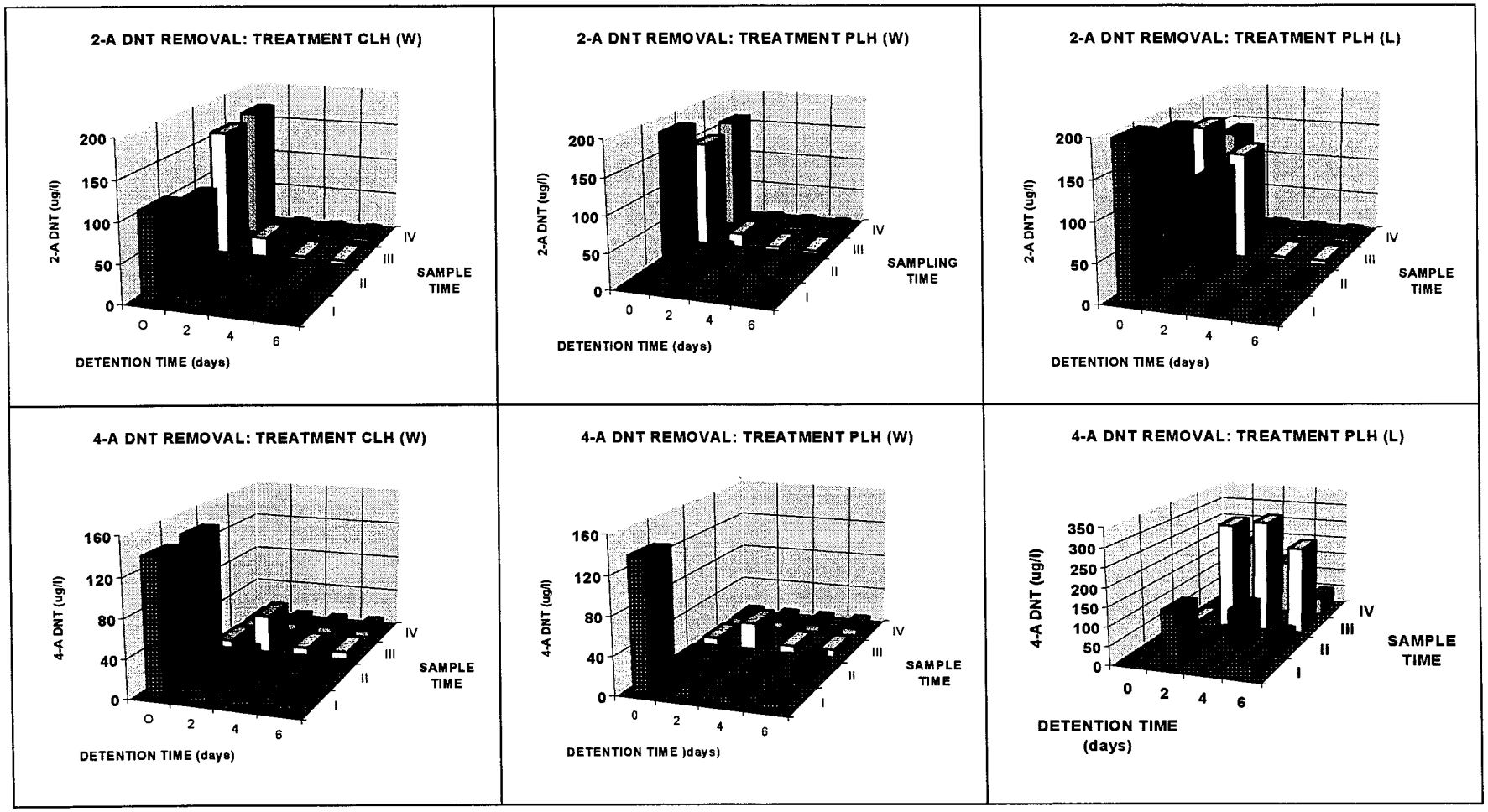
2-A DNT influent concentrations ranged from 100 to near 200 ppb. All treatments, with few exceptions, removed this by-product to below detection limits within 2 to 4 days (Figures 3-17, 3-18, 3-19, and 3-20). There was an occasional spike (Figure 3-19), which occurred on day 20, indicating that carbon limitation may be a factor (low carbon and elevated redox conditions may not be conducive to biological removal). Again, there was a tendency for the lagoon systems to remove 2-A DNT at a slower rate than their counterpart wetland system.

Concentrations of 4A-DNT ranged widely during the 30 day study, and seemed to be most effectively removed in wetland systems at high fertility rates. Lagoon systems at the low fertility rate had effluent concentration in excess of 250 ppb (Figures 3-17 and 3-19). 4A-DNT is a by-product of TNT degradation and 4A-DNT concentrations increased to high levels in the lagoon systems as TNT was removed. However, net removal of 4A-DNT in the lagoon systems was slow; thus leading to high discharge concentrations. In wetland systems, TNT was also rapidly degraded, but 4A-DNT concentrations never rose to levels experienced in the lagoons. We surmise this occurred because 4A-DNT removal rates were nearly as rapid as the rates of formation.



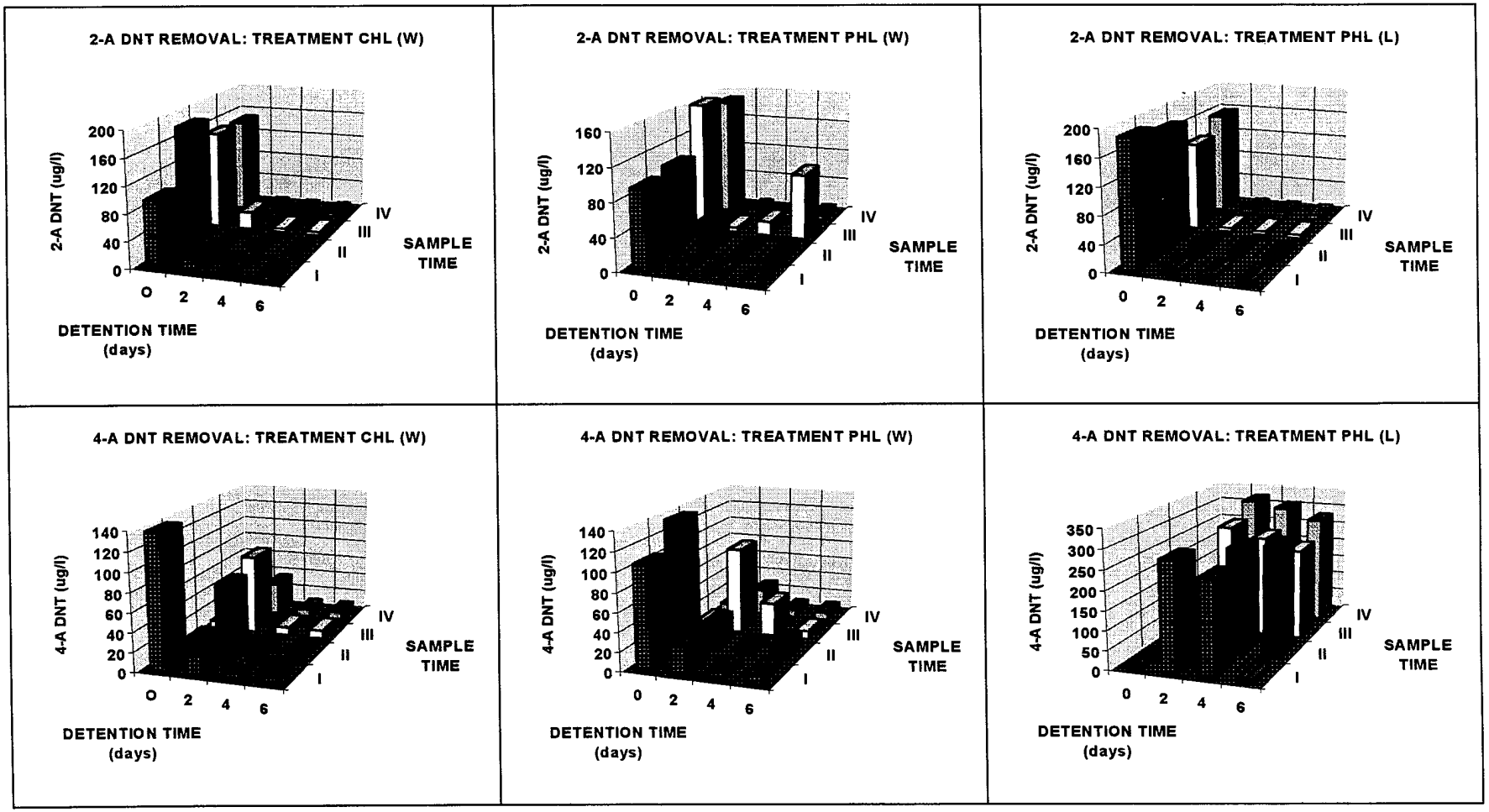
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-17
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for : CLL(W), PLL (W), and PLL(L).



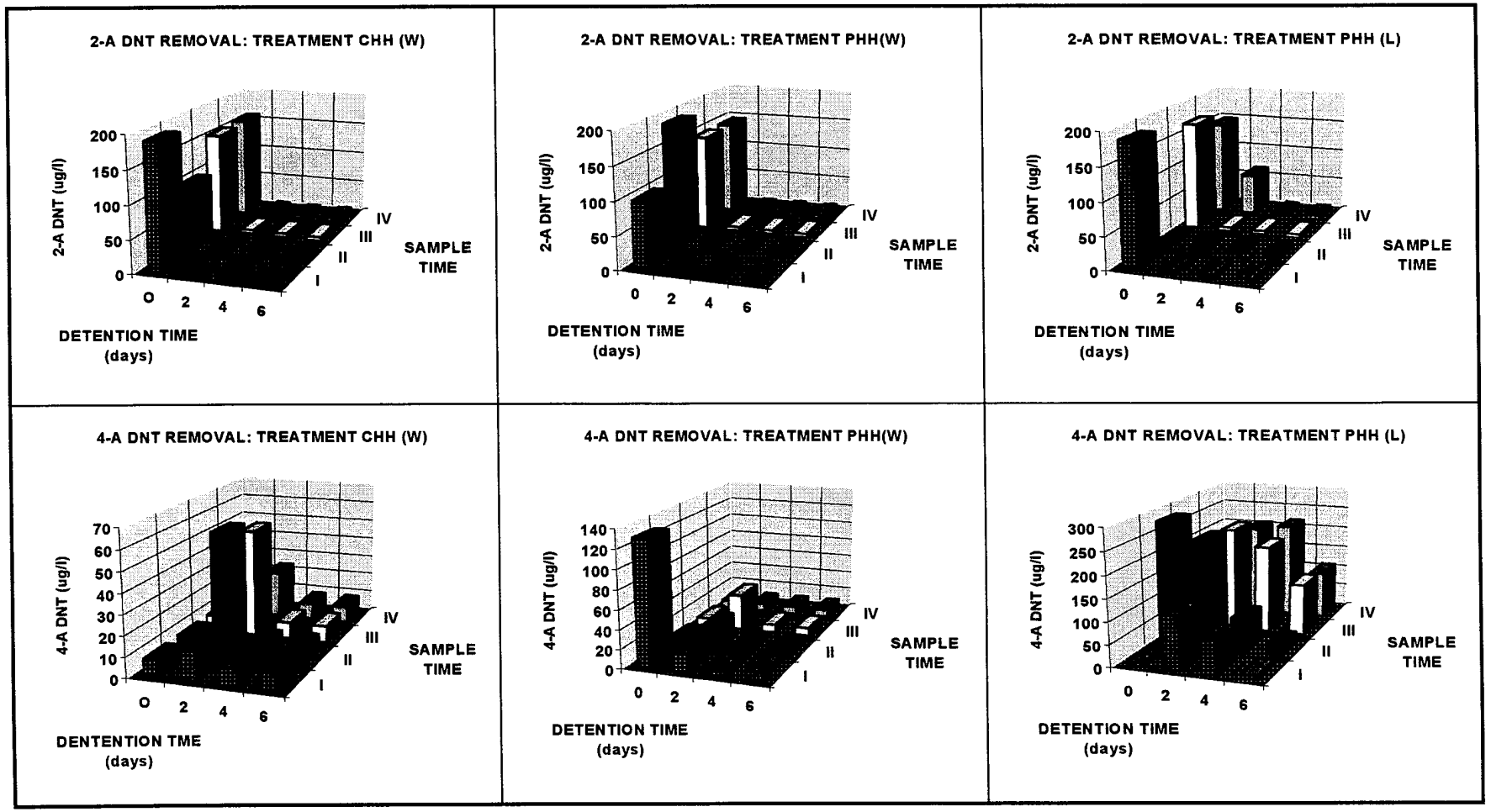
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-18
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-19
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-20
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

SECTION 4.0

CONCLUSIONS

This study further validates the findings of Study I, in which it was found that TNT, TNB, RDX, 2A-DNT and 4A-DNT could be effectively removed in wetland systems in which redox conditions were maintained below -250. This study also demonstrated that lagoons, irrespective of fertility level or plant density, were not able to remove RDX or 4A-DNT to levels required for discharge. The major factor impacting shallow lagoon systems is the import of dissolved oxygen from diffusion and photosynthesis, which precludes development of anaerobic zones.

Detailed analysis of plant production data, fertilization rates and redox potential indicates that fertilization, plant biomass and planting strategy (species selection and planting location), may play an important role in the sustainability of wetlands for treating munitions-contaminated groundwater.

Tracking redox potential internal to the system and over time may be an excellent management technique to monitor when and how best to fertilize the system to maintain low redox conditions and treatment efficacy.

Reciprocation was an effective strategy for removing COD, stabilizing pH, enhancing root to shoot ratios, and elevating dissolved oxygen levels to concentrations adequate for discharge.

SECTION 5.0

ACKNOWLEDGMENTS

Thanks is expressed to Jerry Clayton, Michael Bulls, Jerry Berry, Danny Williams, Eddie White, and Johnny Matlock for their diligent efforts in maintaining the experimental cells and making the study a success.

Thanks is also expressed to Richard Almond, the project manager, and Joseph Hoagland for their contributed ideas and direction to the project.