



DEPARTMENT OF THE NAVY

CRANE DIVISION
NAVAL SURFACE WARFARE CENTER
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CRANE INDIANA 47522-5001

IN REPLY REFER TO:

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Ser RP3/3420

16 DEC 2003

U.S. Environmental Protection Agency, Region V
Waste, Pesticides, & Toxics Division
Waste Management Branch
Illinois, Indiana, and Michigan Section
ATTN: Mr. Peter Ramanauskas (DW-8J)
77 West Jackson Blvd.
Chicago, IL 60604

Dear Mr. Ramanauskas:

Crane Division, Naval Surface Warfare Center (NSWC Crane) submits the Hydrogeologic Feasibility of Using Natural Attenuation and Phytoremediation as Remedial Alternatives for Explosives and TCE Contaminated Groundwater at the Ammunition Burning Grounds (ABG). Two copies of this draft report are supplied as enclosure (1). The permit required Certification Statement is provided as enclosure (2).

NSWC Crane point of contact is Mr. Thomas J. Brent, Code RP3-TB, telephone 812-854-6160.

Sincerely,

A handwritten signature in dark ink, appearing to read "James M. Hunsicker".

JAMES M. HUNSICKER
Manager, Environmental Protection
By direction of the Commanding Officer

Encl:

- (1) Draft ABG Natural Attenuation Report
- (2) Certification Statement

Copy to:

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SIGNATURE

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12/16/03
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ERDC/GSL TR-00-XX

Geotechnical and Structures Laboratory



**US Army Corps
of Engineers**
Engineer Research and
Development Center

Hydrogeologic Feasibility of Using Natural Attenuation and Phytoremediation as Remedial Alternatives for Explosives and TCE Contaminated Groundwater at the Ammunition Burning Grounds, Naval Surface Warfare Center, Crane, Indiana

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
feet	0.3048	meters
feet per mile	0.1893935	meters per kilometer
inches	2.54	centimeters
miles (U.S. statute)	1.609347	kilometers

Preface

The purpose of this report is to determine whether natural attenuation of explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and chlorinated solvent trichloroethene (TCE) contaminants in soil and ground water is occurring at the Ammunition Burning Ground located at Naval Surface Warfare Center Crane in Crane, Indiana.

At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL James R. Rowan, EN, was Commander and Executive Director.

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Executive Summary

The Naval Surface Warfare Center, Crane Division (NSWC Crane) is located in southwestern Indiana 75 miles southwest of Indianapolis. The Ammunition Burning Grounds (ABG) was established at the NSWC in the 1940s for the primary purpose of destroying munitions ranging from small arms cartridges to large bombs. The explosives to be ignited were spread on burning pads or placed in unlined pits and flashed allowing explosives and other contaminants to infiltrate the near-surface groundwater. The ABG is still being used to burn explosive materials but the burning is restricted to clay-lined pans.

Because of the potential for the release of contaminants at the ABG, a groundwater monitoring program was initiated in 1981 by the U.S. Army Corps of Engineers Waterways Experiment Station (WES) (now the Engineering Research and Development Center). An Initial Assessment Study conducted in 1983 by the Naval Energy and Environmental Support Agency and WES identified the ABG as a site needing further study. Hydrogeological investigation conducted by WES from 1986 to 1994 provided additional data that indicated the groundwater contamination at the site required remediation. Contaminants of concern were RDX, TNT, and TCE.

Research conducted at the U.S. Army Engineering Research and Development Waterways Experiment Station (ERDC-WES) confirmed the feasibility of monitored natural attenuation as a viable alternative to more expensive remediation at explosive contaminated sites that have favorable hydrogeologic conditions and satisfy specific regulatory concerns.

Another significant precedent for the use of monitored natural attenuation occurred in 1997 when the U.S. Environmental Protection Agency (EPA) released a policy statement titled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites. The EPA directive required the following three lines of evidence:

- a. Historical groundwater and /or soil chemistry data that demonstrate a clear meaningful trend of declining contaminant mass and/or concentrations at appropriate monitoring or sampling points.
- b. Hydrogeologic or geochemical data that can be used to indirectly demonstrate the type(s) of natural attenuation processes active at the site and the rate at which such processes will reduce contaminant concentrations to required levels.

- c. Data from field or microcosm studies (conducted in or with actual contaminated site media) that directly demonstrated the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern.

Based on past and ongoing investigations, the hydrogeologic conditions at the ABG appear to meet the needed criteria for making monitored natural attenuation a potential remedial action or component of a remedial action for groundwater. The aquifers of concern at the ABG are the Big Clifty Sandstone and the Beech Creek Limestone. Based on groundwater investigations conducted by WES and Indiana University, near-surface groundwater in the Little Sulfur Creek Valley where the ABG is located is controlled by solution cavities in the Beech Creek Limestone. Quantitative dye tracer tests showed that the contaminated groundwater below the ABG moves down the Little Sulfur Creek Valley by route of the solution cavities and exits at Spring A near the boundary of the NSWC. Chemical data indicates that the Beaver Bend Aquifer located below the Big Clifty/Beech Creek was not contaminated. RDX, TNT, and TCE were the only contaminants with concentrations above regulatory requirements. Monitoring of wells, springs, and Little Sulfur Creek indicated that concentrations of TNT and TCE were not detectable and that RDX was near the detection limit at the NSWC boundary.

Concurrent with the field investigations, soil samples from the ABG were taken to the EPA Research Laboratory at Athens, Georgia, for phytoremediation studies. These studies showed that Eastern Cottonwoods and Tall Fescue were ideally suited for removing TNT and RDX from the soils and near surface groundwater down gradient of the ABG near the installation boundary.

A split of the soil sample that was taken from the ABG for phytoremediation study was sent to WES for microbial mineralization testing. The native microflora demonstrated healthy viability by releasing more than half of the radioactivity from the acetate test as carbon dioxide within 6 days. When site soil is presented with carbon-14 labeled RDX or TNT, one of the possible mineralization products is radiolabeled carbon dioxide, which is an indicator that indigenous microbes are completely breaking down the compounds. The test for RDX showed a very good mineralization potential. TNT tests showed less mineralization potential than RDX but the TNT transformation products TNB, 4A-DNT and 2A-DNT were present. This supports groundwater analyses that indicate these same transformation products show up in the quarterly groundwater samples.

A groundwater model was developed using the data from the various field studies at the ABG. The flow model confirmed the ground flow paths in Little Sulfur Creek Valley as being controlled by the solution cavities in the Beech Creek Limestone. The transport model showed that the contaminants of concern would be expected to decrease with time if the upgradient residual sources were removed.

The conclusion based on the combined results of all the ABG research efforts indicates that the three lines of evidence required by the EPA have not been fully met. The unique groundwater conditions prohibit the ABG site from being analyzed as a traditional monitored natural attenuation site. However, an expectation

that remedial options are limited in such a complex hydrogeologic system suggest that MNA is worthy of serious consideration as a corrective measure or component of remedial action.

The attenuation processes in the groundwater at individual wells were not defined because of the unique hydrogeologic conditions where the groundwater becomes surface water before exiting the installation. However, the groundwater data indicates that the groundwater has reached a state of equilibrium where low concentrations have stabilized at or near the detection limits for the contaminants of concern.

The chemical data, the phytoremediation research, the microbial mineralization research, and the numerical modeling all indicate that natural attenuation is occurring with dilution being the primary attenuation mechanism and that MNA should be considered as a remedial alternative or component of remedial action after up-gradient residual sources have been removed.

List of Acronyms

Abbreviation	Term
2A-DNT	2-amino-4,6-dinitrotoluene
4A-DNT	4-amino-2,6-dinitrotoluene
ABG	Ammunition Burning Ground
ADNT	
BPLC Analysis	
BTEXq	Benzene, toluene, ethyl benzene and xylenes
CFR	Code of Federal Regulations
DOD	Department of Defense
EL	Environmental Laboratory
EPA	Environmental Protection Agency
ERDCVBG	Engineering Research and Development Center Vicksburg
ERDC-WES	Engineering Research and Development Center Waterways Experiment Station
FSP	Field Sampling Plan
GMS	Groundwater Modeling System
HAIEK	
HPLC	
IAAP	Iowa Army Ammunition Plant
IDEM	
IDW	Investigation-derived wastes
IN KOH	
JAAP	Joliet Army Ammunition Plant
KOH	Potassium hydroxide
LSC	Liquid scintillation counting
MODFLOW	
MT3D	
MvX	
NAD	North American Datum
Navy	U.S. Department of the Navy
NGVD	National Geodetic Vertical Datum
NSWC	Naval Surface Warfare Center
NSWC Crane	Naval Surface Warfare Center, Crane Division
NSWCC	Naval Surface Warfare Center Crane
OB/OD	Open Burning Open Detonation
ORP	Oxidation-reduction potential
PAHs	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PJDX	
PPE	Personal protective equipment
PVC	Polyvinyl chloride
QA/QC	Quality Assurance Quality Control
QAPP	
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RFI	RCRA Facility Investigation
SOUTHNAVFACENCOM	Southern Division, Naval Facilities Engineering Command

Abbreviation	Term
TCE	Trichloroethylene
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TINUS	Tetra Tech NUS, Inc.
U.S. EPA	United States Environmental Protection Agency
VOCs	
WES	Waterways Experiment Station

1 Introduction

Background

1.1 Natural attenuation

Research conducted at the U.S. Army Engineering Research and Development Center Waterways Experiment Station (ERDC-WES) confirmed the feasibility of monitored natural attenuation as a viable alternative to more expensive remediation at sites that have favorable hydrogeologic conditions and satisfy specific regulatory concerns (Pennington 1998). A report by Arthur D. Little (Balasco et al. 1996) concluded that regulators were increasingly more likely to accept monitored natural attenuation as a remediation for explosives-contaminated sites. The Balasco study indicated that most regulatory agencies would approve monitored natural attenuation at a site if the hydrogeologic conditions were favorable and detailed engineering and risk assessment data were provided.

More than 60 sites have been remedied using a protocol developed by the Air Force for monitored natural attenuation of fuels (Weidemeir et al. 1995b). The Air Force protocol was a significant precedent, which was based on the development of three lines of evidence showing natural attenuation. The Air Force protocol: (a) documented loss of contaminants in the field, (b) the use of chemical analytical data in mass balance calculations, and (c) laboratory microcosm studies using aquifer samples from the site.

Another significant precedent for the use of monitored natural attenuation occurred in 1997 when the U.S. Environmental Protection Agency (EPA) released a policy statement titled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites" (EPA 1997). Natural attenuation is described as "naturally occurring processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater." The EPA directive was similar to the Air Force protocol in that it required the following three lines of evidence:

- a.* Historical groundwater and/or soil chemistry data that demonstrate a clear meaningful trend of declining contaminant mass and/or concentrations at appropriate monitoring or sampling points.
- b.* Hydrogeologic or geochemical data that can be used to indirectly demonstrate the type(s) of natural attenuation processes active at the site and the

rate at which such processes will reduce contaminant concentrations to required levels.

- c. Data from field or microcosm studies (conducted in or with actual contaminated site media) that directly demonstrated the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern.

The Army also has a policy statement on natural attenuation in the Federal Register (1990) that states that natural attenuation has to be considered for remediation of all contaminated Army sites.

The Army protocol for determining feasibility of using monitored natural attenuation at explosives contaminated sites was developed at WES (Pennington et al. 1999b). The Army protocol was used successfully at the Joliet Army Ammunition Plant (JAAP) at Joliet, Illinois. The JAAP was used extensively during World War II for production and load-assemble-package of explosives. The explosives manufacturing area was re-activated for the Korean Conflict and the Vietnam War. The JAAP is underlain by fine-grained glacial silts and clays that contain scattered deposits of cobbles and boulders. The glacial materials lie unconformably on thinly bedded Silurian age dolomitic sandstone. The results of trend analyses of historical data and groundwater monitoring data showed a slowly diminishing plume for TNT, RDX, and TNB. The trend analyses and numerical simulation confirmed that the contaminant concentration was declining over time. Results of biomarker studies in microcosms and in situ provided additional evidence that natural attenuation was occurring at the Joliet site (Pennington et al. 1998).

The natural attenuation protocol developed by the Army has also been successfully demonstrated at the Louisiana Army Ammunition Plant near Monroe, Louisiana. At LAAP monitored natural attenuation relies upon continued mass reduction over time and demonstrated microbial degradation potential in microcosms (Pennington et al. 1999a).

1.2 Phytoremediation

Phytoremediation is a form of natural attenuation that is occurring at the ABG. Enhanced phytoremediation would be considered if concentrations of contaminants in the ground and surface water were not significantly reduced by microbial action, adsorption, and dilution before reaching the installation boundary. Phytoremediation describes the process by which aquatic or terrestrial plants and the microbial communities associated with their rhizospheres degrade contaminants in both soil and water (Sustainable Strategies 1997). The term phytoremediation was first used to describe the use of plants to accumulate metals from soil and water. In 1995 the definition of phytoremediation was changed to include the breakdown of organic chemicals (Lyman 1995). Chang and Coraciogla (1998) conducted research on several plant processes involved in the removal of contaminants from soils and groundwater including the modification of the physical and chemical properties of soil, increase of organic carbon by the release of

root exudates, and increased aeration and porosity of the soil. Plants can also be used to reverse hydraulic gradients and reduce vertical and lateral migration of contaminants in groundwater.

McCutcheon (1998) discussed several ways plants degrade contaminants. Phytoaccumulation is the process that uses cation pumps and sorption to remove metals and BTEX compounds. Rhizofiltration removes heavy metals, radionuclides, and organic compounds by absorption by plant roots. Phytostabilization is a process where plants control soil properties such as pH, gas exchange, and redoximorphic conditions. Phytovolatilization is a process where volatile metals such as mercury, selenium, and chlorinated solvents are taken up and transpired. Rhizosphere bioremediation is a process plants use to breakdown polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), benzene, toluene, ethyl benzene, and xylene (BTEX). Rhizosphere bioremediation uses enzymatic activity on mycorrhizal fungi and microorganisms to degrade contaminants. Phytotransformation is the process that involves the degradation of organic compounds to harmless compounds.

The first successful characterization of TNT uptake by a plant from solution was conducted by Palazzo and Leggett (1986) using yellow nutsedge (*Cyperus esculentus*). It was determined that the two transformation products 4-ADNT and 2-ADNT found in the leaves, roots, rhizomes, and tubers of the plant resulted from the uptake and transformation of TNT. Thompson (1998) demonstrated that hybrid poplar trees (*Populus deltoides X nigra*) absorbed TNT. Approximately 10 percent of the TNT absorbed by the poplars was translocated to the leaves while approximately 75 percent remained in the roots. Uptake to the poplars was fairly rapid in hydroponic solutions but was much slower in soil systems high in humic materials and clay. Peterson (1995) studied use of tall fescue (*Festuca arundinacea Schreb*) to reduce concentrations of TNT and 4-ADNT. Germination and growth of the fescue was inhibited by TNT concentrations exceeding 30 mg/L. Growth in the fescue was reduced by concentrations of 15 mg/L of 4-ADNT. Schneider (1994) conducted field studies at the Iowa Army Ammunition Plant (IAAP) and the JAAP to observe the uptake of TNT by terrestrial plants.

1.3 Characteristics of munitions

The activities being conducted at the ABG are typical of activities that are occurring or have occurred at many Department of Defense (DOD) facilities around the world where munitions are destroyed. These disposal activities have led to soil and ground water contamination by munitions and their transformation products (McCutcheon et al. 1995). The disposal of these munitions is treated as a hazardous waste management operation and requires compliance with Subtitle C of the Resource Conservation and Recovery Act (RCRA). TNT (2,4,6-trinitrotoluene) and RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) are the explosives that are the primary contaminants at the ABG and at most military installations that have explosives contamination. Contamination of groundwater, surface water, and soil by TNT and RDX poses a threat to humans. TNT is toxic to humans when ingested and is also mutagenic and carcinogenic in test animals (McLellan

et al. 1988). According to Budavari (1989), the ingestion of TNT can cause headaches, weakness, anemia, and liver damage. TNT is also toxic to marine copepods, oysters, and freshwater unicellular green algae. Two common transformation products of TNT (4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene) are formed by the interaction of TNT with the plant enzyme nitroreductase (Wolfe et al. 1995; McCutcheon and Wolfe 1998). These transformation products are often found at sites contaminated with TNT. The transformation by-products of TNT may not be an acceptable endpoint of remediation if they are harmful to the environment.

1.4 Objectives

The objectives of the study were to:

- a.* Use representative chemical compounds, simulations, and environmental monitoring data, to determine whether natural attenuation of explosives and volatile organic compounds (VOCs) is a potentially viable remedial option for explosives and VOC contamination at the ABG.
- b.* Represent graphically the monitoring data generated for the ABG.
- c.* Estimate and correlate contaminant attenuation rate(s) with the hydrogeologic conditions.
- d.* Develop a three-dimensional conceptual hydrogeologic model and numerically simulate long-term attenuation of contaminants at the ABG.
- e.* Demonstrate in microcosm studies that microbial activity is of a type and of sufficient activity to support natural attenuation.

2 Site Description and Historical Perspective

2.1 Location and Physiography

The Naval Surface Warfare Center (NSWC) is located in southwestern Indiana in the northern portion of Martin County and small portions of Greene, Daviess, and Lawrence counties. The 62,463-acre facility is approximately 75 miles southwest of Indianapolis. The ABG is approximately 2000 ft long and 1000 ft wide and is located in the upper part of the Little Sulphur Creek Valley in the eastern part of NSWC in the northwest quarter of Section 28 and the southwest quarter of Section 21, Township 5 North, and Range 3 West (Figure 1). The area included in this study includes not only the ABG, but the entire Little Sulphur Creek Valley down to the point where Little Sulfur Creek crosses the NSWC boundary. The topography in the study area is rugged with steep-sided ridges and valleys that range in elevation from around 480 ft to 845 ft above mean sea level. The land surface generally slopes downward toward the NSWC boundary.

2.2 Historical Activities

The Ammunition Burning Grounds was established at the Naval Surface Warfare Center, Crane in the 1940s for the primary purpose of destroying munitions ranging from small arms cartridges to large bombs. Materials burned at the ABG include bare explosives, explosives contaminated material, rocket motors, flares, solvents, red phosphorus, fuse materials, and detonators. Over 10,000 major weapons were destroyed from 1970 to 1981. The most extensive use of the ABG occurred between 1956 and 1960 when 63,000 combined pounds of smokeless powder and high explosives such as H-6 and Composition B were burned. The explosives to be ignited were spread on burning pads or placed in unlined pits and flashed allowing explosives and other contaminants to infiltrate into the near surface groundwater. The ABG is still being used to burn explosive materials but the burning is restricted to clay-lined steel pans. Figure 2 shows operational features at the ABG.

Because of the potential for the release of contaminants at the ABG site, a groundwater-monitoring program was initiated in 1981. The U.S. Army Corps of Engineers Waterways Experiment Station (WES) began installing a series of

monitoring wells, which showed that groundwater in the ABG was being contaminated by explosives and solvents. An "Initial Assessment Study" conducted in 1983 by the Naval Energy and Environmental Support Agency, the Ordnance and Environmental Support Agency, and WES identified the ABG as a site requiring further environmental studies. In 1986 to 1987 WES conducted a hydrogeological investigation of the ABG and Little Sulphur Creek Area. It was determined from the WES effort (Hunt 1988) that groundwater flow in the area of the ABG was moving primarily through rock joints in the Big Clifty and Beech Creek Aquifer. The Beech Creek Aquifer is composed of limestone and the rock joints have been enlarged by solution in the study area. The solution cavities controlled groundwater flow and are the main pathway of groundwater in the ABG area.

Hunt (1988) recommended that dye trace tests be conducted to determine pathways in the Beech Creek Aquifer. The dye trace tests were conducted by WES and documented in a WES technical report (Murphy and Ciocco 1990). The results of the dye trace tests proved that there was a direct hydrologic connection between the ABG and the karst conduits in the Beech Creek Aquifer.

The Indiana Geological Survey completed detailed surface and subsurface geological maps for several areas at Crane including ABG during 1992 to 1994. The Indiana University Hydrogeology Laboratory (Department of Geological Sciences) was funded through WES to conduct studies to more fully characterize the groundwater flow from the ABG and down the Little Sulfur Creek Valley and assess the potential for contaminant movement. The Indiana University research was initiated in 1993 and continues to the present. Additional dye tests were conducted by Indiana University (Krothe 1994, 1996) Subpart X permit work by TtNUS include GWMP, FSP, CCCRA, air emissions human health risk assessment, and post permit quarterly groundwater monitoring. TtNUS also assessed groundwater surface water contamination in Little Sulfur Creek and the ABG Jeep Trail area.

3 Hydrogeology

3.1 General Geology

The NSWC is located in the southeastern part of the geologic structural feature known as the Illinois Basin. Other structural geologic features include the Cincinnati Arch to the east, the Kankakee Arch and Michigan Basin to the north, and the Ozark Uplift to the west (Figure 3). The geology of the ABG site had not been mapped until 1988 when Hunt (1988) conducted a comprehensive field-mapping program in the area. Hunt's efforts were expanded by Murphy (1994), Barnhill and Ambers (1994) and Kvale (1995).

At the ABG the near surface rocks are lower Pennsylvanian and upper Mississippian in age. The Pennsylvanian marine sandstones and shales cap the hills in the study area but have been removed by erosion in the valley of Little Sulfur Creek. A geologic disconformity separates the Pennsylvanian and Mississippian strata at the site. The strata underlying the ABG from youngest to oldest (Hunt 1988) include the Indian Springs Shale (20 ft thick), the Big Clifty Sandstone (40 ft thick), the Beech Creek Limestone (18 to 22 ft thick) and the Elwren Shale (20 ft thick). Figure 4 is a stratigraphic section for the area showing the position of the geologic units and the disconformity at the base of the Pennsylvanian strata.

During drilling activities at the ABG voids or subterranean cavities were encountered in the Beech Creek limestone. The creek valleys in this area of the NSWC may be present because they are following zones of fracturing and weakness in the subsurface strata. The fractures in the Beech Creek limestone have been enlarged due to calcium carbonate being dissolved and forming cavities. The overlying fractured Big Clifty sandstone collapses into the solution cavities in the Beech Creek forming areas of collapse features unique to this area. The solution cavities appear to be restricted to certain sections of the Little Sulfur Creek Valley and are not found beneath the topographic divides on either side of the valley. This is very important because the solution cavities are controlling the groundwater flow and moving water down the valley, but not allowing the groundwater to move under the valley walls and contaminate the adjacent creek valleys.

Figure 5 is a plan view of the ABG showing the location of cross-sections M-M' and AA-AA'. Figure 6 is a geologic cross section (M-M') from the ABG down the axis of Little Sulfur Creek Valley. The areas where the limestone has been removed due to solution can be seen. Figure 7 is a geologic cross

section (AA-AA') perpendicular to the longitudinal profile of Little Sulfur Creek and extending into the valley walls. It should be noted that the boring data beneath the valley walls does not show any solution features.

3.2 Groundwater Aquifers

The two aquifers of concern are the Big Clifty/Beech Creek and the Beaver Bend. The Big Clifty and Beech Creek formations are considered as one aquifer in this study because of the interconnectivity caused by the fractures and solution cavities, especially in the areas where blocks of the Big Clifty have collapsed into the voids in the underlying Beech Creek. For natural attenuation to be a viable remedial option at the site, it is critical to demonstrate that contaminated water from the Big Clifty/Beech Creek aquifer is not moving downward and carrying contaminants into the Beaver Bend. In order to determine if the two aquifers were hydraulically isolated, Steven Baedke (1988) looked at the chemistry of the groundwater in both aquifers. By using the Piper diagram method (Piper 1944), Baedke was able to characterize the prevalent chemical character of each aquifer. By plotting the concentrations of calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride and dissolved SiO_2 on Piper diagrams the prevalent chemical character of groundwater can be analyzed to gain an understanding of the origin and movement of water and the potential reactions taking place in or between aquifers. Piper diagrams of water chemistry analysis from wells in the Big Clifty/Beech Creek aquifer and the Beaver Bend aquifer show that the naturally occurring chemicals are significantly different in the two aquifers. The Piper diagram in Figure 8 shows that the groundwater in the Beech Creek is rich in calcium sulfate and chloride whereas the Piper diagram for groundwater from the Beaver Bend aquifer (Figure 9) shows that the water is higher in sodium bicarbonate. Additional evidence showing that the Beaver Bend is not connected to the Big Clifty/Beech Creek Aquifer in the study area is presented in the graph comparing the hydraulic heads in the Beech Creek and Beaver Bend aquifers (Figure 10). The heads in the Big Clifty/Beech Creek Aquifer are about 46 ft higher than heads in the Beaver Bend Aquifer during the same time frames.

3.3 Hydraulic Parameters

Hydraulic parameters in karst terrains generally range from those associated with the flow in the rock matrix to those associated with the flow through the open solution cavities. At the ABG three distinguishable flow systems predominate. The three flow systems are the conduit, mixed, and diffuse systems and can be distinguished easily by constructing rain event hydrographs. The hydrographs are prepared by plotting discharge from a spring versus time. Figure 11 is a typical recession hydrograph from springs in the study area. It can be seen from the hydrograph that the peak flow is representative of the spring discharge from flow through the solution cavities or conduits, followed by a gradual reduction in flow as water flows through the mixed flow part of the system, and finally the lowest or base line flow representing flow through the diffuse (rock matrix) system. Two-month recession hydrographs are shown for Springs A and C in Figure 12.

By analyzing the slopes of the various segments of the recession curves, ratios of transmissivity (T) and specific storage (Sy) can be calculated using the following equation where Q equals the discharge at time t_1 and Q_2 equals the discharge at time t_2 .

$$T/Sy = \log (Q_1/Q_2)/(t_2-t_1) \times L^2 /1.071$$

The value for L is measured from the discharge point (the spring sampled) to the topographically defined drainage divide (Shevenell 1996; Teutsch and Sauter 1991; Atkinson 1977). The value used for L by Baedke (1998) was 220 m for Spring A and 840 m for Spring C.

Krothe and Baedke (1994) also looked at the variability through time of the saturation indices of aragonite, calcite, dolomite, and halite in the Big Clifty/Beech Creek Aquifer. The areas that showed very little variability were interpreted as being in the diffuse flow system as opposed to areas with high fluctuation in the saturation indices, which were thought to be in the conduit flow system.

Groundwater flow through the rock matrix has been determined using pump tests from wells screened in the Beech Creek Aquifer. Analysis of the pump test data using the Jacob method (Jacob 1950) provided transmissivities for the unfractured Beech Creek Limestone that ranged from 0.28 m²/d to 5.79 m²/d and storativities that range from 4×10^{-4} to 2.5×10^{-5} (Murphy 1995). Pump tests analysis plots are shown in Figures 13 and 14. The hydrogeology at the ABG appears to be well suited for natural attenuation to be occurring.

3.4 Dye Tracer Tests

Groundwater flow through the solution cavities was first looked at by Murphy and Ciocco (1990). Using fluoresceine dye they determined that hydraulic connection between the Beech Creek aquifer and springs in Little Sulphur Creek Valley could be confirmed. Springs A and A' were found to be the primary outlets for the Big Clifty/Beech Creek Aquifer at the ABG. Baedke (1998) conducted a quantitative dye tracer test of the karst system at ABG. During this test 1.6 kg of rhodamine WT (20 percent) and 18.3 kg of bromide ionic tracer were injected in well 03-C02P2. The four springs that were believed to be the most likely to be hydraulically connected to well 03-C02P2 were continuously monitored for discharge and continuously sampled for dye. Another 10 springs in the general area were monitored with passive dye detectors. Rhodamine and bromide were detected at Spring A and Spring A' and at several diffuse seeps about 2000 m from the injection well. None of the other springs that were monitored contained the tracer dyes. Approximately 80 percent of the bromide was recovered from Spring A and A' and an additional 10 to 15 percent of bromide is believed to have issued from the diffuse seeps. Approximately 90 to 95 percent of the injected bromide was accounted for. The calculated recovery for the rhodamine dye was over 100 percent indicating that practically all the injected tracers were recovered from Spring A and A'. Using the time of arrival for the bromide

tracer, the effective conductivity for the karst system is 286 m/hr (Figure 15, Baedke 1998).

4 Groundwater, Surface Water and Spring Water Monitoring

4.1 Background

The groundwater, surface water, and spring water sampling for the natural attenuation study was incorporated into the existing environmental sampling program at Crane. The Field Sampling Plan (FSP) for the Naval Surface Warfare Center Crane (NSWC Crane), Indiana, was prepared for the U.S. Department of the Navy (Navy) by Tetra Tech NUS, Inc. (TtNUS) under the Southern Division, Naval Facilities Engineering Command (SOUTHNAVFACENGCOM). A copy of the FSP is maintained at the NSWC Crane Environmental Division offices. The FSP describes the standard sampling procedures to be used for the long-term groundwater monitoring program for the Ammunition Burning Grounds (ABG). All monitoring complied with applicable Indiana and EPA regulations. All field-sampling activities were conducted in accordance with the site security and health and safety plan developed for the field sampling activities described in the FSP.

4.2 Monitoring Wells

A total of 98 monitoring wells were installed in the ABG as a part of the field investigation for the RCRA Facility Investigation (RFI) (Murphy 1994). Eighteen of the monitoring wells were selected for sampling as a part of the approved long-term Ground Water Monitoring Plan, which includes the natural attenuation sampling. Each of these wells was constructed of 2-in.-diam polyvinyl chloride (PVC) riser above the water table and polytetrafluoroethylene (i.e., Teflon) riser and screen below the water table. Each of the wells was installed with 10-ft-long well screens. Table 1 summarizes the construction details for the 18 wells included in the RCRA monitoring program. Figure 16 shows the locations of the ABG monitoring wells, including surface water monitoring points. Figure 17 shows a typical well installation at the ABG. The wells were designed to prevent contamination from moving between aquifers. The EPA has approved this design, which does not incorporate concrete well pads. IDEM requires that wells have pads. Therefore, the wells at the ABG used for closure monitoring have pads.

4.3 Monitoring Approach

This section describes the details concerning the monitoring wells, surface water, and spring waters to be sampled, frequency of sampling, sampling procedures, and target constituents for the NSWC Crane facility, as outlined by the Resource Conservation and Recovery Act (RCRA) Ground Water Monitoring Requirements as described in 40 CFR 264 Subpart F and the approved Ground Water Monitoring Plan. A total of 18 monitoring wells, two surface water locations, and two ground water springs from the ABG were included in the monitoring efforts. The approved QAPP also contains the detailed field and laboratory Quality Assurance and Quality Control (QA/QC) requirements. Table 1 also lists each of the ABG ground water, spring water, and surface water monitoring points and, for each monitoring well, the associated screened formation. Quarterly analysis will take place for a minimum of three years or one year after contaminated soil is removed and cleaned up, whichever is later. Semi-annual monitoring shall continue after that point for the same parameters. Monitoring for natural attenuation occurred during the first eight quarters. Table 2 describes the monitoring points and sample analyses that were conducted on each monitoring point every quarter for the first eight quarters. The Appendix IX analyses are in addition to the quarterly and semi-annual monitoring. Field measurements, including specific conductance, pH, temperature, turbidity, oxidation-reduction potential (ORP), and dissolved oxygen, were obtained by a meter at each sampling location. Water-level measurements were made for all wells during all sampling events using a water-level meter at each sampling location. Alkalinity (carbonate, bicarbonate, and hydroxide) was analyzed in the field for each monitoring point using a field test kit. Additional field analyses were conducted for ground water, spring water, and surface water included in the natural attenuation-monitoring program. These additional field analyses include carbon dioxide, dissolved oxygen, ferrous iron, hydrogen sulfide, nitrate, and nitrite.

All existing ground water monitoring wells were surveyed prior to this investigation. The horizontal locations were surveyed to the nearest 0.10 ft and the vertical locations or elevations were surveyed to the nearest 0.01 ft. The elevations at the ground surface, where the uncapped well riser is notched, and at the top of the protective casing were surveyed. All horizontal survey measurements were tied into the Indiana State Plane Coordinates and the 1983 North American Datum (NAD83). All vertical survey measurements were referenced to the 1988 National Geodetic Vertical Datum (NGVD88) and mean sea level (msl). All elevations were adjusted, as necessary, from the 1929 NGVD (NGVD29) to NGVD88 per National Geodetic Survey Data Sheets north central district, October 1995.

4.4 Field and Laboratory Parameters

4.4.1 Field parameters

Measurements of dissolved oxygen, pH, specific conductivity, temperature, turbidity, oxidation-reduction potential (ORP), alkalinity (carbonate, bicarbonate,

and hydroxide), carbon dioxide, ferrous iron, hydrogen sulfide, nitrate, nitrite, and water level were performed during each sampling event at the ABG. Flow rate and direction were determined annually.

4.4.2 Laboratory parameters

The list of laboratory parameters (and likely chemicals of concern) for the ABG was developed based on RCRA ground water monitoring requirements in 40 CFR Subpart F and site-specific information (i.e., known waste composition and treatment residues, results of previous ground water monitoring, etc.) and general knowledge of open burning/open detonation at NSWC Crane. Additional guidance regarding the parameter list for the evaluation of natural attenuation of chlorinated solvents was obtained from the EPA document entitled “Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water” (EPA September 1998). The general list of laboratory parameters to be analyzed is provided in Table 3.

4.5 Field Sampling and Analysis Procedures

This section describes the field sampling and analysis procedures for ground water, surface water, and spring water monitoring at the ABG. For a detailed description of the procedures used during sampling efforts in the ABG please refer to Appendix B in the Field Sampling Plan (Tetrattech 1999). Before each monitoring well was sampled, a brief inspection was conducted. Water-level measurements were obtained for each well unit during every sampling event before purging and sampling activities were conducted and water-level measurements were obtained within a 24-hr period. Dedicated 1.66-in.-diam, low-flow, bladder pumps (Teflon-lined PVC) were installed in all the monitoring wells prior to ground water sampling. Each pump was placed at the midpoint of the saturated well screen and, if possible, no less than 2 ft above the bottom of the well in order not to disturb any sediment that was located at the bottom of the well. Prior to pump installation, all the wells were developed using a surge block and a submersible purge pump capable of reaching depths of 60 ft. In cases where well depths exceeded 60 ft, a bailer was used instead of the submersible pump. The pumps were certified contaminant free; this certification, as well as lot numbers, was provided in an appendix of the initial ground water monitoring report.

Purging was accomplished by using low-flow techniques. Low-flow purging and sampling were implemented because this method provided the least disturbance to the surrounding formation (i.e., less turbulence in sampling and hence less turbidity) and allowed for a more representative sample to be collected.

Low-flow sampling procedures were used in accordance with procedures described in the EPA ground water flow paper, Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures (EPA/540/S-95/504). Table 4 contains a summary of sample analyses and associated container types and volumes, preservation requirements, and holding times.

4.6 Sampling of Springs and Little Sulphur Creek at the ABG

Springs A and C were sampled by extracting a sample from the first surface water pool into which each spring discharges. Two samples were obtained from Little Sulphur Creek. One sample was collected below Spring A and the second was collected at the boundary of NSW Crane for each sampling round. All surface water samples were extracted by using a dip sampler.

4.7 Field Analysis

Test kits were used for the analyses of several parameters in the field. These parameters are listed as follows:

- a. Alkalinity (carbonate, bicarbonate, and hydroxide).
- b. Carbon dioxide.
- c. Dissolved oxygen.
- d. Ferrous iron.
- e. Hydrogen sulfide.
- f. Nitrite.
- g. Nitrate.

In addition, water-quality parameters (i.e., dissolved oxygen, pH, specific conductance, temperature, turbidity, and ORP) were measured using a meter for all ground water, surface water, and spring water monitoring points. Water-level measurements were performed for all monitoring wells.

4.8 Decontamination and Handling of Investigation-Derived Waste

Dedicated sampling equipment such as pumps and tubing was used at each well location. The dedicated sampling equipment did not require decontamination. If any non-dedicated equipment was required for field sampling activities, it was decontaminated prior to and during sampling activities. Any decontamination water that was generated was handled in the same manner as purge water. These procedures can be found in Tetrtech FSP (1999).

Four types of investigation-derived wastes (IDW) [personal protective equipment (PPE), purge water, decontamination solutions, and spent test kit reagents] were generated during the ground water monitoring program. Based on the

activities and types of contaminants present, none of these residues are expected to represent a significant risk to human health or the environment if properly managed.

4.9 Handling and Quality Control of Samples

Each sample collected at NSWC Crane was assigned a unique sample tracking number. Certain preservatives were added as required by the FSP and stringent chain-of-custody procedures were followed to document sample possession. All samples taken at the ABG were properly labeled with a sample label affixed to the sample container and a sample tag secured by a wire tied around the neck of the sample container.

Field duplicates were obtained during the sampling and used to assess the overall precision of the sampling and analysis methods used. The duplicates were collected at a minimum of 1 per every ten samples. Trip blanks for VOCs were used to assess the potential for contamination resulting from contamination getting into sample bottles or jars during sample shipment and storage. Ambient blanks were collected in the field and analyzed to check for interfering contaminants that could potentially be present in ambient air at the sampling site. Matrix spikes are investigative samples analyzed to provide information about the effect of the sample matrix on the digestion and measurement methodology and were collected as required.

4.10 Results

The results of the natural attenuation surface water and groundwater monitoring were plotted as time versus concentration plots. By analyzing these plots the long-term contamination trends at individual locations can be determined. The quarterly results for FY1999 and FY2000 for RDX, TNT, and TCE are shown in Table 5. Trend analyses for RDX and TNT are shown in Appendices A and B. Only contaminants with concentrations above regulatory requirements were plotted on the same graph for easier comparison. These plots are shown on Figures 18 through 23. The chemical data indicates that the highest concentrations of TNT, RDX, and TCE are found in wells in the area of the currently active burning grounds. The lowest levels of explosives and TCE were found in the area where Little Sulfur Creek exits the Crane facility. Many wells show a general decrease in contamination throughout the monitoring period with some wells showing seasonal variations in concentrations. Wells B02, B04, C03, C15, C17, C25, and C30 had non-detectable concentrations of TNT, RDX, and TCE for the entire two-year monitoring period. Well C04 had only one detection of TCE during the two-year study. Well C20 had the highest concentration of TCE with most of the values being over 3500 ppb. Well C09P2 contained the highest levels of RDX. TNT was not detected in 19 of the 22 sampling sites and where it was detected, concentrations were close to the detection limit. The wells closest to the boundary had concentrations below detection for all three contaminants of concern during all monitoring periods. Low concentrations of RDX remained in

samples from Spring A and C and in creek samples throughout the sampling period.

5 Preliminary EPA Phytoremediation TNT Studies

5.1 Approach

Two primary studies, a batch-scale kinetic study, and a vegetated column study were conducted to demonstrate the plants in the Little Sulfur Creek Valley are capable of significantly reducing contamination. The studies were conducted by personnel from the Ecosystems Research Division of the U.S. Environmental Protection Agency (EPA) in Athens, GA. If the results of the phytoremediation research were favorable and the monitoring data indicated that contaminants in Little Sulfur Creek at the installation boundary posed a threat to the environment, enhanced phytoremediation could be considered as a potentially cost effective method to implement.

5.2 Soil Collection and Vegetation Classification

Soil collection occurred in an area adjacent to the ABG along Little Sulfur Creek. A soil sample was taken from the surface to a depth of 50 cm by personnel from the EPA Ecosystems Research Division. A split of this soil sample was sent to the Engineer Research and Development Center (ERDC) at Vicksburg, MS, for microbial mineralization analyses. The soil was sieved on site with a 1.27 cm wire mesh to remove large rocks and debris. A soil core sampler manufactured by Soil Moisture Equipment Corp. was used to obtain soil for bulk density measurements. Large blocks of soil were also collected for comparison bulk density measurements in the laboratory. Concurrent with the soil sampling a vegetation survey was conducted to determine dominant species. Samples of the dominant grass in the area, *Festuca arundinaceae*, were collected and stored in an ice chest to be used in the column study.

The soil was sieved a second time in the laboratory using a 64-cm wire mesh. Samples were then analyzed by the Cooperative Extension Service, U.S. Department of Agriculture, University of Georgia, College of Agricultural and Environmental Sciences, Soil, Plant and Water Laboratory (Table 6). The nutrient concentrations of calcium, potassium, phosphorus, magnesium, manganese,

sodium, and zinc were determined using the Maylick Double Acid Extraction Method. Percent organic matter was calculated using a titration method. Percent sand, silt, and clay was determined using the Biucas Hydrometer method. Cation Exchange Capacity was calculated based on the sodium and lime index. Soil samples were processed for TNT extraction and analyzed for initial TNT concentration using liquid chromatography.

5.3 Liquid Chromatography and Chemicals

For TNT and ADNT measurements a Hewlett-Packard 1100 HPLC was used with a Hamilton PRP1 column (10- μ m particle size, 250 mm \times 4.1 mm diam) and a 2- μ m in-line filter. A 12-min isocratic run and 1-min postrun was used with a 65:35, acetonitrile: deionized water pH 10 ratio, 1 mL/min flow rate, and UV detection at 238 nm. Acetonitrile (HPLC grade) was purchased from Fisher Scientific. All TNT dilutions were prepared using 2,4,6-trinitrotoluene (30 wt percent water, 99 percent purity) that was purchased from Chem Service.

5.4 Kinetics

The batch scale kinetics study was performed on a variety of terrestrial plant species. The native Indiana prairie grasses, Big Blue Stem (*Andropogon gerardii*), Little Blue Stem (*Schizachyrium scoparium*), Indian Grass (*Sorghastrum nutans*), and Switchl Grass (*Panicum virgatum*) were purchased from Spence Restoration Nursery, Muncie, IN. Tall fescue (*Festuca arundinaceae*) was collected at NSWCC. Yucca (*Yucca filamentosa*) was grown from seeds obtained from plants at NSWCC. Tulip Poplar (*Liriodendron tulipifera*) and Loblolly Pine (*Pinus taeda*) leaf samples were collected at the W. B. Warnell School of Forest Resources, Whitehall Experimental Forest, Athens, Georgia. American Sycamore (*Platanus occidentalis*) seedlings were purchased from Greenwood Nursery, McMinnville, TN. The selected species were chosen based on native habitat, potential water usage, and abundance at the ABG. The replications were designed to compare TNT degradation rates between species and obtain species specific degradation constants. Leaf tissue samples from each species were collected, washed, using deionized water, blotted dry with clean paper towels, and cut into small pieces less than 1 cm. Samples of each species were placed in individual 118 mL Qorpak Bottle Beakers with screw caps. Three replications were used for each species. Each replication was covered with aluminum foil to block light penetration and thereby reduce the probability of photodegradation. Samples were submerged using a constant density of 0.10 g/mL plant:10 mg/L TNT solution. After the plant material was added, samples were extracted on a schedule of increasing time intervals for up to 30 hr, at which time 2 mL of the aqueous solution was withdrawn with a micropipette and transferred to HPLC vials and capped with aluminum seals. Sampling of the solutions occurred until non-detect levels were reached. All samples were characterized using liquid chromatography. Half-lives and degradation constants were calculated for first-order reactions with each plant species (Table 7).

5.5 Sorption Analysis

A sorption study was performed to determine TNT partition coefficients for the soil used. The data was fit using the Freundlich equation (Table 8). Soil samples were ground in a mortar and sieved using a Dual Mfg. Co. mesh number 20, Market Grade Sieve. In order to reduce microbial activity and the formation of metabolites in solution, the soil was autoclaved for two 30-min periods at 120 deg C. Soil samples were then placed in 20 ml scintillation vials at a constant density of 0.5 g/ml soil: solution. TNT solutions ranged from 50 mg/l to 0.05 mg/l. Each replicate was shaken at 2500 rpm on a Vortex-Genie Mixer for 1 min and allowed to sit for 24 hr at room temperature. Then each sample was shaken again for 1 min and centrifuged at 3300 rpm for 10 min. Afterwards, 2 ml of the supernate was withdrawn with a micropipette, transferred to HPLC vials, capped with aluminum seals, and characterized using liquid chromatography.

5.6 Column Study

In order to study TNT degradation in a plant-soil system, soil columns were constructed and monitored in a greenhouse at Russell Research Center. Fifteen columns were constructed using 10.2-cm-diam PVC pipe cut to a length of 75 cm. Female adapters were attached to the bottom of each column using PVC primer and cement. PVC screw caps had holes drilled in them and fitted with T-connectors using silicone caulk. Two racks were constructed to hold the columns.

A layer of washed gravel was placed inside the bottom of the columns overlying a thin layer of polyester fiber. An additional layer of fiber was placed on top of the gravel. This layering acted as a filter allowing only leachate, not soil to exit the column. The total depth of the filtration system was 5 cm, making the total length 70 cm.

The sieved soil collected at NSWCC was packed in the columns at the field density previously measured (1.33 g/cm^3). After all columns were packed, 6.4-mm-diam vinyl tubing was attached to the connectors exiting the bottom of the columns. An Ismatec Digital Drive pump was used to back saturate the columns at a flow rate 10 ml/min. This allowed the soil to settle and reduced the probability of preferential flow through the column.

Four species used in the kinetic study were selected to plant in the columns. *P. occidentalis*, *Y. filamentosa*, *F. arundinaceae*, and *S. scoparium* were selected based on the degradation rates obtained during the kinetic study as well as their overall health at the time of planting. Supplemental lighting was provided by eight "GE Grow Lights" with 120-watt intensity. Each species occupied three replicate columns in addition to three replicate control columns containing only the sieved soil and gravel filtration system. After all columns were back saturated and planted, 118 ml Qorpak Bottle Beakers covered with aluminum foil were prepared for leachate containers. Each beaker's screw cap was drilled with a hole and inserted with a piece of vinyl tubing, which was then attached to the

connector exiting the columns. All columns were allowed one week for plants to root before TNT application. After this one-week period, a 1 mg/l TNT solution was applied to the tops of the columns. Each column containing a plant was supplied with 200 ml of the solution and each control was supplied with 50 ml of the solution. This application rate, based on expected evapotranspiration occurred twice weekly for seven weeks. Each day following an application, the beakers were monitored for leachate. If any leachate was present, the volumes were recorded and placed in 20 ml scintillation vials for transport to the laboratory for analysis using liquid chromatography.

After determining that no TNT was present in the leachate during the seven weeks of pulse inputs, the total amount of TNT applied to the column thus far was calculated. The maximum amount of TNT that can adsorb to the soil in each column was calculated using the partition coefficients obtained during the sorption study. In order to verify TNT was being taken up by the plants or being degraded by microbes, a continuous input of 10 mg/l TNT was applied to all columns using an Ismatec Digital Drive pump at a flow rate of 1 ml/min. This application rate was continued until the amount of TNT applied to the columns surpassed the adsorptive capacity of the soil column. Leachate volumes were recorded daily, and collected for analysis.

5.7 Extractions

When application of TNT was concluded, all columns were dismantled. Soil and plant tissue samples were obtained for TNT extractions. Soil samples were obtained at three depths: 0-10 cm, 25-35 cm, and 45-55 cm. Plant samples consisted of leaf, stem, root, and tuber tissue.

Soil extractions were conducted following EPA Method 8330 (EPA 1998). Three replications were obtained for each soil sample at each depth collected. Wet weights were recorded and each sample was allowed to air dry for 48 hr. Each sample was ground with a mortar and pestle and passed through a 20-mesh sieve. Two grams of soil were placed in 20 ml scintillation vials and covered with 10 ml acetonitrile. Samples were vortex swirled for 1 min and placed in a cooled ultrasonic bath for 1 hr then placed on a shaker table at 150 rpm for 24 hr. Afterwards, the samples were centrifuged at 2500 rpm for 5 min. Five milliliters of supernatant was removed and combined with 5 ml of 5-g/l calcium chloride in a scintillation vial. Each vial was vortex swirled for a second time for 1 min and allowed to settle for 15 min. The supernatant was removed, placed in a disposable syringe, and filtered through 0.45 μm Teflon filter. The first milliliter was discarded, retaining the remainder to analyze using liquid chromatography.

Plant extractions were conducted following the method outlined by Larson et al. (1998). Three replications of leaf, root, stem (*P. occidentalis*, and *Y. filamentosa*) and tuber (*Y. filamentosa*) tissues were collected from each plant. Plants were harvested, washed using deionized water, blotted dry with paper towels, and weighed. All samples were cut into small pieces (less than 1 cm) and weighed. Samples were then freeze-dried using a Labonco Freeze Dryer 4. After the drying

process, the plant material was ground in an electric laboratory mill using a size 20 mesh. Dry weights were obtained for each replicate. In a scintillation vial, 25 g of the dried material was covered with 10 ml acetonitrile, vortex swirled for 1 min, and placed in a cooled ultrasonic bath for 1 hr then allowed to settle overnight. Each replicate was centrifuged for 5 min at 2500 rpm. Five milliliters of the supernatant was removed and filtered. Filters were prepared by placing a small amount of glass wool in a disposable syringe. The glass wool was covered with 0.5-g florisil, which was then topped with 0.5- μ m alumina. Five milliliters acetonitrile was passed through the filter and discarded. Five milliliters of the supernatant was passed through the filter and collected in a scintillation vial. Next, 5 ml of acetonitrile was passed through the filter and collected in the same vial. The vials were vortex swirled for 1 min. Two milliliters of the supernatant was removed and placed in a clean vial with 2 ml deionized water, which was vortex swirled for another minute. The supernatant was removed and placed in a disposable syringe and filtered through a 0.45 μ m Teflon filter. The first milliliter was discarded and the rest was retained to analyze using liquid chromatography.

5.8 Results

5.8.1 Kinetics

After completing the batch-scale kinetics study, differences in nitroreductase activity among species tested were apparent (Figure 24). *Festuca* was found to degrade TNT at a more rapid rate than the other species. However, most species tested showed similar degradation potential. The only exception proves to be *Pinus taeda*, which had a degradation rate much slower than the other species. This seems to confirm the work done by Fitter and Hay (1987), which showed that plants adapted to acidic soils have little or no nitroreductase activity. The species-specific degradation constants and half-lives for first-order reactions with TNT (Table 9) quantify the difference in nitroreductase activity between species.

5.8.2 Sorption

The TNT adsorption isotherm (Figure 25) is linear. Most adsorption is thought to be linear at low concentrations and non-linear as concentration increases. However, in the case of TNT, tested with the soil obtained at NSWCC, the isotherm result was linear even at the highest concentration tested (50 mg/L). Apparently, the saturation concentration had not been reached in this test. Price et al. have observed a similar effect and refer to similar results obtained by others when surface coverage of the substrate is low (Price, 2000). This produced a partition coefficient of 0.00274 l/mg. This means that TNT is moderately adsorbed to the soil collected from NSWCC. The experimental design of the column study called for the continuous input of 10 mg/L TNT.

When this concentration was input into the Freundlich equation along with the partition coefficient obtained from the adsorption isotherm and then multiplied by the 7.0 kg soil contained in each column, the result was that the maximum amount of TNT that could adsorb in each column was 191.9 mg.

Because the data plotted as $C_w = K_f C_w$ were linear as shown by the regression coefficient ($R^2 = 0.9722$) at concentrations up to 20 mg/L (actually up to 50 mg/L), it was concluded that $n = 1$ which gave a partition coefficient of 0.00274 mg/L. Thus, the empirical value of $n = 1$ was used to calculate the concentration of 191.9 mg.

5.8.3 Column Study

In order to ensure that TNT was being taken up by the plant and degraded or being degraded microbially, it was necessary to monitor the leachate exiting each column. During both application methods, all leachate was analyzed for TNT and the formation of ADNT. At no time did any of the aqueous leachate collected show signs of either of the munitions. The fact that no TNT or ADNT was found in the solution exiting the columns could not prove that TNT was being taken up by plants or degraded. There was the possibility that all the TNT applied was adsorbing to the soil. So, the experimental design of the column study called for the continuous application of 10 mg/L TNT, until enough volume had been applied to exceed the calculated maximum adsorptive capacity of each column found during the sorption study. A total of 220 mg TNT was applied to each column. This exceeded the computed maximum TNT adsorptive capacity of each column by 28.1 mg. If TNT were not being degraded in the column or plant, breakthrough of TNT in the leachate should have occurred at less than 200 mg. In order to totally ensure the accuracy of the test, the total amount of TNT applied well exceeded the computed adsorptive capacity of each column. When breakthrough of the munition did not occur, it was concluded that indeed, TNT was either being degraded by microbes in the soil or being absorbed by the plants.

The only way to know for sure if the TNT was being degraded or absorbed was to eventually dismantle the columns and analyze the soil and plant tissues for TNT and its by-products. After all extractions were complete, it was determined that three of the four plants tested; Little Blue Stem, Yucca, and Sycamore; contained a small amount of TNT in their root tissue. However, there was no significant difference in the amount of TNT found in each species.

TNT was also found in the top ten centimeters of all nine columns. The fact that no TNT was found in any column at a depth greater than 10 cm reiterates the conclusions drawn from the sorption study that TNT is strongly adsorbed to the soil tested. Although all columns showed TNT in the top 10 cm, it was expected that the control column, containing only soil would prove to contain the highest concentration of TNT, but this was not the case. Although the differences in concentration between the columns are not truly significant, the column containing Sycamore contained the highest mean TNT concentration in the top 10 cm.

ADNT formation was identified in almost all plant tissues. The root tissues of all species showed the highest concentrations of the metabolite. Once again, there are no significant differences between the concentrations found in each species. Note that included in the table of ADNT concentrations in the roots is also the ADNT concentration found in the woody stem of Sycamore. Only the two grasses tested, Fescue, and Little Blue Stem contained ADNT in the leaf tissue. This

coupled with the fact that these two species had faster first-order degradation rates than the other species used in the column study, means that the degradation of TNT is more complete in these species than in the Yucca and Sycamore. The large amount of error shown in the concentration of ADNT found in the leaf tissue of Little Blue-Stem can be explained by the fact that only one plant of the three replicates contained ADNT. This fact along with the smaller error margin in the Fescue replicates makes it more obvious that Fescue is truly capable of degrading TNT at a faster rate than the other species tested. This is also shown when comparing the first-order degradation rate constants of each species.

ADNT was formed in all columns at 0 to 10 cm depth. Although there was no significant difference between concentrations, Fescue was found to have the highest ADNT concentration in the soil. This could be explained by the increased microbial activity found surrounding the dense roots of the grass. The fact that the control column contained similar ADNT concentrations as the planted columns is interesting because it would be expected that the planted columns would have lower concentrations. Once TNT is metabolized microbially in the soil, the plant has the ability to absorb the ADNT. Hence, the planted columns should have lower ADNT concentrations than the control. Although the concentrations found in all columns at 25 to 35 cm are very similar, as expected, both the columns planted with Sycamore and Yucca had the highest concentrations. This can be explained by the low root surface area at this depth. Both the grasses were found to have a rooting depth that spanned the entire depth of the columns. However, both Sycamore and Yucca had a rooting depth of approximately half the depth of the column. The smaller root zone of these two plants explains the increased ADNT concentrations. In the case of Fescue and Little Blue Stem, ADNT was easily absorbed by their deep roots, explaining the lower soil concentrations.

The concentrations of ADNT found at 45 to 55 cm depth produced a trend that was expected. The control column had the highest concentration due to the lack of plant roots at this depth. The planted columns were able to absorb ADNT formed at this depth resulting in lower concentrations. The Sycamore has the highest concentration at this depth due to the lack of roots. The large amount of error found in all columns at this depth can be explained by the fact that of three planted columns of each species, only one of the replicates had detectable concentrations of ADNT at this depth. Although there is ADNT at this depth, the concentrations are drastically lower than those found higher in the column. In summary, ADNT concentrations were reduced with depth. At 45 to 55 cm depth, the amount of ADNT was almost undetectable in the columns containing roots in that depth interval. This suggests that the possibility of ADNT leaking to a water table in a field irrigation system is limited when the soil TNT concentrations are equal to or less than those of this column study. Nearly all of the applied munitions were degraded at the time of take down.

5.9 Conclusions

Over 95 percent of TNT applied to the planted and unplanted columns was metabolized to its by-product ADNT. Of the ADNT formed, over 90 percent of it was degraded as well. An important point to realize is that the TNT concentrations used in this experiment (10 mg/L) were an order of magnitude greater than those actually found at the site of contamination (0.01 mg/L). Because of this, the probability of contamination leakage throughout the soil to ground water is limited at the site. The rate of TNT and ADNT degradation is so rapid, that food chain contamination is not a problem to consider. Over 90 percent of ADNT formed, stayed in either the soil itself or the root tissue of the plants.

Although the species tested showed only small differences in TNT degradation, the grasses had higher degradation potential. The root zone depths of both Tall Fescue and Little Blue Stem extend deep into the soil. The fact that the field adjacent to the contaminated stream is already planted with Tall Fescue indicates that attenuation is occurring if site conditions mimic the laboratory conditions of these studies. The most interesting conclusion of this experiment is that the control columns, containing only soil, degraded the contaminants almost as well as the planted columns. Applying TNT contaminated water to the bare ground at NSWCC should produce the same results as applying to vegetation. However, the reduction of roots in the upper horizons of a bare soil would decrease infiltration rates and possibly cause overland flow of the contaminated water back to the stream before the munitions had a chance to be degraded. The rate of microbial degradation was faster than that of the plant assisted degradation. Once the metabolite ADNT has been formed in the soil, it is available to be absorbed by the plants. At this time, the reduction reaction becomes slower than that of microbial degradation. The analysis of plant tissues also produced two concentration peaks at retention times that were unidentifiable with the available analytical equipment. These peaks could be toxic metabolites of TNT or harmless by-products. More analysis is needed to truly understand the nature of these by-products. The first-order kinetic degradation of TNT by the microbes found in the soil at NSWCC is another study that is needed to truly understand the degradation of TNT in this system. In conclusion, the results of this study suggest that TNT in contaminated water that is present in vegetated areas during flood events would be attenuated by plants in the Little Sulfur Creek Valley.

6 Preliminary EPA Phytoremediation Eastern Cottonwoods Study

6.1 Approach

Column and hydroponic studies along with sorption analysis were conducted on the explosives contaminated soils of the ABG with emphasis on attenuation potential of the eastern cottonwood. The eastern cottonwood grows well in this area of the country. The studies were conducted by personnel from the Ecosystems Research Division of the U.S. Environmental Protection Agency in Athens, GA. If the final results of the phytoremediation research were favorable, this would be further evidence that plants are likely to be attenuating contaminants along the Little Sulfur Creek Valley.

6.2 Sorption Analysis

Soil collection occurred in an area adjacent to the ABG along side a small stream. The soil was obtained from the upper horizons to a depth of 50 cm. The soil was sieved on site with a 1.27 cm wire mesh to remove any large rocks or debris. Then, it was allowed to air dry to a constant weight. After grinding with a mortar and pestle, the soil was sieved with a Dual Mfg. Co., mesh number 35, Market Grade Sieve. Samples were prepared in duplicate by adding 3.0 g of soil to 20 mL scintillation vials. Various concentrations of TNT, RDX, and HMX were prepared by diluting saturated stock solutions. TCE was not studied because it is being attenuated primarily by dilution and volatilization in the solution cavities and as surface water (after it exits the springs). Various 2-ADNT and 4-ADNT concentrations were prepared in water by diluting a solution containing 500 mg/L of each compound. Since these two compounds co-elute during HPLC analysis, henceforth they will be referred to as ADN'T. Ten milliliters of each solution was added to the vials containing soil. The vials were shaken in darkness for 24hr at 20°C. After incubation, samples were centrifuged at 2500 rpm. Three-milliliter sample aliquots were filtered with a 0.22 micrometer (μm) syringe filter and retained for HPLC analysis.

6.3 Hydroponic Study

Eastern Cottonwood (*Populus deltoides*) cuttings were established for 60 days in a half-strength Hoagland's solution. After the period of establishment, the rooted cuttings were transplanted into foil wrapped 2 L Erlenmeyer flasks that contained the above-mentioned nutrient media spiked with RDX and TNT. One treatment consisted of approximately 2 mg/L TNT and 15 mg/L RDX. The second treatment consisted of approximately 5.5 mg/L TNT and 3 mg/L RDX. Each day, fresh water was added to the flasks to replace water that was removed due to transpiration. At this time, 2 mL aliquots were removed and centrifuged at 5000 rpm. Each sample was filtered with 0.22 um syringe filters and retained for analysis.

6.4 Column Study

Explosives contaminated soil was obtained from NSWCC, allowed to air-dry, then ground, sieved, and packed in to PVC columns. Columns were constructed using 10.2-cm-diam PVC pipe cut to a length of 15 cm. Female adapters were attached to the bottom of each column using PVC primer and cement. PVC screw caps had holes drilled in them and fitted with T-connectors using silicone caulk. A layer of washed gravel was placed inside the bottom of the columns overlying a thin layer of polyester fiber. Pre-rooted cottonwood cuttings were transplanted into the columns. Harvesting occurred every 7 days. The tree was removed and separated into leaf, roots, and stem. The column was cut in half and soil samples were collected at 3 depths. Soil and plant tissue extractions were conducted following EPA Method 8330.

6.5 Summary and Conclusions

In the hydroponic study TNT was taken up quickly by the Eastern Cottonwood (*populus deltoide*). Non-detect levels in the nutrient media were reached in approximately 48 hr. Root associated microbes are the suggested cause for the formation of ADNT in the nutrient media. RDX was taken up much more slowly than TNT. Most RDX was removed after 260 hr (Figures 26 and 27).

In the column study TNT was not identified within any of the plant tissues. RDX was found to bioaccumulate within the leaf tissue. RDX concentrations within the root and stem tissue seem to remain steady (Figures 28 through 30).

The sorption analysis data showed the relative affinity to the NSWCC soil to be TNT > ADNT > HMX > RDX. This finding is consistent with the work of others (Figures 31 through 34).

This research indicates that plants are contributing significantly to the attenuation of contaminants in the Little Sulfur Creek Valley.

7 ERDC Microbial Mineralization Study

7.1 Approach

A split of the soil sample that was taken from the ABG for phytoremediation study was sent to the ERDC, Environmental Laboratory (EL), for microbial mineralization testing. When site soil is presented with carbon-14 labeled RDX or TNT in the laboratory, one of the possible mineralization products is radio-labeled carbon dioxide. This will be produced only when the indigenous microbes completely breakdown the compounds. Therefore, this simple test indicates the potential for degradation that is present at the site. However, positive results do not prove that the degradation process is occurring at the site; only that the potential is there.

7.2 Methods

Soil subsamples were mixed with a solution containing the radiolabeled contaminant of interest. Some samples receive radiolabeled RDX, others receive radiolabeled TNT, and others receive radiolabeled acetate. The acetate is included to indicate the general viability of the native microflora. If no carbon dioxide is produced from acetate, the native microflora is limited in numbers and/or activity (vigor). The acetate soil slurries were incubated for 6 days; explosives soil slurries for 30 days at room temperature. Carbon dioxide was trapped by 1%¹⁴C potassium hydroxide (KOH) placed in a sidearm of the flask. The KOH was assayed by liquid scintillation counting (LSC) (Pennington et al. 1998). The soil and solutions phases of the tests were also assayed by LSC. The untested soil was also assayed for explosives and explosives transformation products by high performance liquid chromatography (USEPA 1994).

7.3 Results

Acetate (Figure 35). The native microflora demonstrated healthy viability by releasing more than half of the radioactivity from the acetate as carbon dioxide within 6 days. Most of the remainder was in the soil.

RDX (Figure 35). The native microflora released 75 percent of the radioactivity from RDX as carbon dioxide in 30 days. This is very good mineralization potential.

TNT (Figure 35). The native microflora released only 3.7 percent of the radioactivity from TNT as carbon dioxide in 30 days. This is typical for TNT, which is not readily mineralized in the environment. About 83 percent of the radioactivity was associated with the soil phase.

HPLC Analysis (Table 10): Results of HPLC analysis indicated that the soil was high in RDX (1490 ppm), and exhibited a very small amount of one of its transformation products, TNX. Although TNT concentrations were not high (24.1 ppm), the following TNT transformation products were present: TNB, 4A-DNT, and 2A-DNT. These suggest the potential for transformation of TNT at the site. HMX was detected, but not tetryl. (See attached laboratory data sheets for meaning of acronyms, quality control values and detection limits).

7.4 Conclusions/Microbial Mineralization

Mineralization potential for RDX in the Crane ABG site soils is high. Past exposure of the native microflora may have enhanced the development of a community capable of degrading RDX. Mineralization of TNT in the radioassay was not much above background suggesting limited potential for complete degradation at the site. However, detections of transformation products of TNT by HPLC analysis indicate that transformation is occurring at the site. Transformation products in groundwater samples also strengthen the interpretation that transformation is occurring.

8 Numerical Modeling

8.1 Introduction

Numerical modeling is a cost-effective means for the quantitative evaluation of multiple natural processes represented as a set of mathematical expressions, consistent with site-specific conceptualizations. The complex and incompletely understood processes involved in the natural attenuation of explosives require the computational power and flexibility of an appropriate numerical model. Selection or consideration of natural attenuation as a feasible remediation alternative requires the prediction capabilities afforded by numeric modeling (Pennington et al. 1998).

The main objective of the modeling of the ABG is to complement the field monitoring and data collection for better evaluation and graphic representation of natural attenuation of explosives. The modeling effort focuses on conceptualization of the site hydrogeology and reduction of explosives by processes such as immobilization, degradation, and first-order decay.

The Department of Defense Groundwater Modeling System (GMS) (1966) with its subsurface model MODFLOW was selected for the modeling element of this study. GMS is a comprehensive computer graphical system. The GMS includes numerical tools to facilitate site characterization, site conceptualization, mesh and grid generation, geostatistical computations, and visualizations.

8.2 Conceptual Model

A conceptual model based on the site hydrogeological and chemical data was developed before the numerical modeling was conducted. It is described here. Explosives and VOC contaminants released from the 1940s to 1980s were released to the ground surface through combustion of explosives and solvents in pits, and through combustion, surface impoundments, and waste piles of explosives- and VOC-contaminated materials.

The contaminants, with explosives being by far the greatest mass of released chemicals, would have migrated from soils into the ground water and perhaps even into bedrock (Figures 36 and 37). Ground water under the ABG exits the ground at various springs such as Spring A located in the Little Sulphur Creek

valley and carries the contaminants with it. The ground water also flows via porous flow through the rock matrix and through fractures in the bedrock.

Based on hydrogeological data and physical site characteristics and associated watershed characteristics, the near-surface groundwater moves from the OB/OD area, downgradient in the Little Sulfur Creek valley, where the groundwater returns to the surface at Spring A (Figure 38). The available hydrogeologic data indicates that contaminated groundwater from the ABG is not moving laterally across drainage divides into adjacent creek valleys or moving downward through the Elwren shale. Groundwater contours representing the top of the water table show that groundwater moves toward solution features in the Beech Creek limestone and then downgradient where it exits at Spring A. In this conceptual model dilution is a major factor as the groundwater is diluted when it enters the solution cavities and further diluted as it comes out at Spring A and enters Little Sulfur Creek.

Based on the relative magnitudes of adsorption coefficients (K_d s) for TNT and RDX (K_d s are presented below), RDX migration is faster than TNT migration in the ground water that moves through the soils or rock matrix. For water moving through karst conduits and rock fractures, the migration rates for RDX and TNT should be essentially identical.

Phytoremediation and microbial studies showed that processes other than dilution are actively attenuating the contaminants. The conceptual model is composed of the alluvial material, the Big Clifty/Beech Creek aquifer system, and is bounded on the bottom by the Elwren Shale and laterally by the drainage divides of Little Sulfur Creek.

Biochemical and/or chemical degradation of these chemicals takes place, as evident from the detection of their degradation products in various ABG environmental media. It is logical to expect that the degree of degradation increases with residence time of the explosives in the ground water, whereupon they have more exposure to microbes and chemical reactants. Therefore, the degree of degradation would be much greater for the slower moving porous flow ground water than for the karst conduit flow ground water.

Based on what is known and expected of contaminant release patterns and the persistence of contaminants in ground water, soil is expected to be the ultimate source of ground water, surface water, and sediment contamination. Little is known about contaminant concentrations in the bedrock matrix. Soil sampling at the ABG did not extend deeper than approximately 7.5 ft below ground surface, thus the total mass of contamination in soil is unknown.

8.3 Groundwater Model Construction

A groundwater flow and solute transport model was created in the vicinity of the OB/OD area to evaluate the distribution of TCE, RDX, and TNT (for concentrations above regulatory requirements) in the groundwater (Figure 39 shows borehole locations for the model). The groundwater model extends along the

ridge tops as shown in Figure 39. The OB/OD area is in the center of the model. The model is created using the GMS software as a preprocessor for the MODFLOW flow model and the MT3D solute transport model. The model is approximately 10,000 ft long in the east/west direction, and 13,000 ft in the north/south direction. The model is 120 nodes east/west, and 120 nodes north/south and 3 layers deep.

Figure 39 shows outputs from a geologic model of the Elwren Formation that represents the bottom of the groundwater flow model and shows the locations of the boreholes that were used to create the solid model. Figure 40 shows the different layers of the model, which are from top to bottom: alluvium (overburden), the Big Clifty Formation, the Beech Creek Formation, and the Elwren Formation.

The groundwater model was constructed for both the MODFLOW flow model and the MT3D solute transport model. Final input parameters resulting from calibration for the models are summarized in Table 11. Horizontal hydraulic conductivity values for the different formations vary from 0.3 to 2.0 ft/day. Vertical hydraulic conductivity values vary from 0.2 to 0.3 ft/day. Drain conductance used was 100 ft²/day/ft.

For the MT3D solute transport model advection, dispersion, retardation, and decay of the compounds were included. The compounds simulated in the MT3D runs included the solvent trichloroethylene (TCE), and the explosives TNT and RDX. The longitudinal dispersivity value for all formations was 100 ft, with the transverse dispersivity value being 33 ft. Distribution coefficients (K_d) for adsorption of compounds onto the soil varied from 0.003 to 0.21 L/mg. Rate constants for decay of TCE, TNT, and RDX were 0.003, 1.0×10^{-5} , and 8.13×10^{-6} . The source of the rate and decay constants for TNT and RDX are Figure 25 and 34 of the report, as well as standard constants for TCE taken from another modeling study (HLA 1996).

8.4 Groundwater Model Results

Initial conditions of the groundwater model were derived from the local site data. Constant head boundaries were placed along the northern, western, and eastern boundaries of the groundwater model. These water levels on the boundaries were derived from wells along model boundaries, or extrapolated from well data. The hydraulic conductivity values, both vertical and horizontal, for the different formations were taken initially from another modeling study at Crane (Haitjema and Kelson 1994). Drain conductivities were empirically estimated from Haitjema and Kelson (1994), however, the model did not prove very sensitive to this parameter. The solver used for the model was the preconditioned conjugate gradient (PCG2) solver. Discussions of comparisons between simulated and actual data are included for hydraulic heads (Figure 42), which showed good agreement. Figures 43, 44, and 45 show a 57-year run, which simulates the period 1940s to 2002. These figures show that the model is capable of simulating the TCE, TNT, and RDX plumes. Calibration was performed to the 1999 to 2000

data, which would be expected to be representative of later periods (such as 2002), since the system likely had reached a steady state flow condition.

The results of the groundwater model flow directions are shown in Figure 41. Groundwater flow directions extend from the end of the model into the center under the streambed. They also extend north to south (Figure 42). Figure 42 shows the simulated versus hydraulic head map. A generally good agreement is shown between the simulated and actual heads.

Figures 43 through 45 show the distribution of TCE, TNT, and RDX simulated after 57 years. These runs assume that the first compounds were released in the mid 1940s through 2002. The runs assume that advection, dispersion, retardation, and decay impact the compounds and that the source is constant. Figures 46 through 48 show the distribution of TCE, TNT, and RDX, respectively, projected into the next 20 years with the source removed. Figures 43 through 48 show that the compounds naturally attenuate in the system, and compounds are discharged into the stream and karst topography under the stream. Natural attenuation results in the concentrations being reduced.

9 Conclusions and Recommendations

9.1 Site Conceptual Model

The hydrologic data indicates that the near-surface groundwater underneath the ABG moves down-gradient in the Little Sulfur Creek valley where it is controlled by solution features in the Beech Creek aquifer till it exits at its primary discharge point at Spring A as surface water. This ground water is contaminated by chemicals released at the ABG. The primary attenuation of contaminants in the solution cavities would be by dilution. The solution cavities are only a part of the aquifer system. Groundwater would be moving much slower through the fractured media and the alluvial material and would allow some biodegradation to occur. Studies conducted by Indiana University show that there is solution cavity flow, diffuse flow, and a mixture of these transport modes, in the Little Sulfur Creek Valley.

Dye tracer studies indicated that practically all the injected tracers were recovered from Spring A and A' which supports a conceptual model of flow being contained within the Little Sulfur Creek valley.

A groundwater model based on hydrogeologic site data supports the concept that groundwater flow is toward Little Sulfur Creek and down the Little Sulfur Creek valley. The model indicates that RDX, TNT, and TCE concentrations in ground water and surface water would decline through time if all up-gradient sources were removed.

The surface water moves into Little Sulfur Creek and then exits the Crane facility. The available data shows that contamination is not moving downward into the underlying Beaver Bend or laterally underneath the Little Sulfur Creek Valley walls. Surface water moves into Little Sulfur Creek and then exits the Crane facility.

Allocation of contaminant masses among soils, sandstone and limestone has not been done and is not possible without additional data collection.

9.2 Attainment of Principal Study Objective

The principal objective of this study, as presented in Section 1.4, was to determine whether natural attenuation is occurring at the ABG for chemicals that are representative of two classes of compounds – organic explosives and VOCs. Natural attenuation of these chemicals represents natural attenuation of similar chemicals.

The chemical data shows that RDX, TNT, and TCE are being naturally attenuated as they move down Little Sulfur Creek Valley. Break down products of RDX (MNX, DNX, TNX) and TNT (DNA, 2,4 DANT, 2,6 DANT) in ground-water samples are evidence of destructive degradation.

The ground water contaminant concentration data, which generally does not increase over time (Figures 18 through 22), shows that the groundwater contaminants have reached a steady state with residual amounts of contaminants at or near the detection limits (in the lower reaches of Little Sulfur Creek) being introduced to the system from up-gradient contaminant sources. Low concentrations of RDX remain in surface water samples from Spring A (less than 20 ug/L) and Spring C (less than 5 ug/L) and in surface water samples from the two sites in Little Sulfur Creek. Temporal concentration plots (Figure 23) spanning November, 1998 to September, 2000 showed that RDX concentrations may be increasing at Spring A, Creek A, and Creek B, and they are increasing at Spring C. The cause(s) of such increases is unknown. TNT concentrations are non-detectable in surface water and ground water for most sampling points. TCE is non-detectable in well, spring, and creek samples in the lower end of the study area near the installation boundary. The decrease in ground water concentrations with distance from the contaminant source(s) reflects the attenuation of contaminants in those media caused by dilution and degradation, especially in ground water. Increases of RDX concentrations in Spring and Creek samples near the facility boundary may reflect a flushing mechanism that occurs under periods of heavy precipitation, although data are not available to confirm this.

The dye tracer studies indicated that practically all the injected tracers were recovered from Spring A and A' which supports the conceptual model of flow being contained within the Little Sulfur Creek valley.

The groundwater flow model (Figure 39) confirms that the groundwater flow is toward Little Sulfur Creek and down the Little Sulfur Creek valley and that RDX, TNT, and TCE concentrations would decline through time if all up-gradient sources were removed.

The principal objective of this study was to demonstrate whether or not natural attenuation is occurring at ABG. Results of trend analyses of groundwater monitoring data that includes measurements of TCE, TNT, and RDX degradation products, plus the model prediction of slowly diminishing plumes for TNT, RDX, and TCE, indicate that natural attenuation is occurring. Temporal concentration plots show very slight concentration changes in the wells for which concentrations are decreasing. The primary mechanism for this attenuation is evidently dilution rather than destructive degradation.

Cyclical seasonal effects were not observed, although some apparently random differences from season to season were observed in the contaminant concentration data. Many of the data sets exhibit a large degree of variability which would yield little statistical power. Nevertheless, visual inspection of some of the trend plots leads to the conclusion that some concentration decrease is occurring in select wells. With the degree of data scatter observed, additional monitoring will be needed to definitively demonstrate the data trends.

9.3 Attainment of Secondary and Tertiary Study Objectives

The secondary and tertiary study objectives were to:

- a. Generate graphical representations of the ABG data.
- b. Estimate and correlate the attenuation rate of contaminants with the hydrogeologic conditions.

Numerous graphical representations of the ABG data were presented and discussed. The overall site conceptual model was corroborated by the ground water flow computer model, which shows that ground water flow in the ABG system is directed toward the Little Sulphur Creek. Solution cavity flow is a major contaminant transport pathway and dilution of contaminants in solution cavities is significant, although dilution rates or factors have not been quantified. Attenuation rates are qualitatively different for the conduit, mixed, and diffuse ground water and surface water flow systems comprising this site.

The ground water flow model was used to estimate the concentrations of ground water contaminant concentrations as much as 57 years into the future. The simulated outputs from this model indicate that contaminant concentrations in ground water would be less in 20 years when the contaminant source is removed than it would be in 57 years with a continuing contaminant source. This demonstrates the importance of source remediation to the future conditions of the ABG study area.

The unique groundwater conditions, and the fact that up-gradient residual contaminant sources are present, prohibit the ABG site from being analyzed as a traditional monitored natural attenuation site. At most sites the groundwater is not controlled by the geology in such a way that it becomes surface water before it exits the site boundary, although this is what occurs at the ABG.

9.4 Attainment of Final Project Objective

Results of biomarker studies both in microcosms and in situ support the second and third lines of evidence set forth by EPA concerning the evaluation of MNA as a remediation alternative (USEPA 1997). The potential for a slow

microbial mineralization mechanism for TNT and a faster RDX degradation was demonstrated in laboratory studies of ABG samples. All of these results indicate that natural attenuation, including destructive degradation, is occurring and is causing declining concentrations in explosives over time.

The phytoremediation studies showed indirectly that plants are likely to be contributing to the attenuation of contaminants in the Little Sulfur Creek Valley. Over 95 percent of TNT applied to the planted and unplanted columns was metabolized to its by-product ADNT. Over 90 percent of the ADNT was degraded as well. Tall Fescue was the best-suited grass for degrading TNT at the ABG. RDX was found to accumulate in the leaf tissue of the Eastern Cottonwood. An extrapolation of results from laboratory contaminant uptake studies suggests that Tall Fescue and Eastern Cottonwoods are probably reducing TNT and RDX concentrations in the soils and near-surface groundwater of the Little Sulfur Creek Valley.

9.5 Overall Conclusions

The combined results of all the studies conducted in the Little Sulfur Creek study area indicate that not all of the EPA “traditional” three lines of evidence for monitored natural attenuation have been met. Review of the historical groundwater contaminant data indicate downward trends for some wells and the concentrations in the wells that do not have downward trends are easily explained by the unique groundwater regime in which they occur. The hydrogeologic setting, the chemical data, the phytoremediation studies, the microbial mineralization study, and the numerical modeling together provide evidence that natural attenuation is occurring at the site. The fact that natural attenuation is occurring and an expectation that the array of potential remedial options is limited, largely because of the complex site hydrogeology, render monitored natural attenuation (MNA) an option for serious consideration as a component of a corrective measure.

9.6 Recommendations

Implementation of a Corrective Measure Study is understood to be in progress. No single remedial option is expected to reduce ABG contaminants to acceptable concentrations within a desirable time frame. For example, elimination or control of contaminant source terms coupled with chemical or biochemical treatments, phytoremediation, etc. is expected to yield the most rapid contaminant reductions. Because of the complex hydrogeology of the ABG, however, it is possible that no remedial strategy would be cost-effective and suitably protective of human health or the environment in a desirable time frame, hence the technical practicability of implementing corrective measures should be considered.

Additional data collection is indicated before corrective measures can be fully evaluated. In particular, continued monitoring of ground water and surface water is warranted to better define concentration trends in those media. This would be an important both in the absence and the presence of corrective measures

implementation. In the former case, it would serve as a means of alerting the facility operator should contaminant concentrations behave as predicted and continue to spread. In the latter case, it would serve as a monitoring tool to demonstrate if and when suitable contaminant concentration levels have been attained.

Additional delineation of contaminant sources is also warranted to establish the mass of contaminants in soils and the volumes or masses of soil that need to be remediated to achieve acceptable contaminant cleanup goals. Further investigation of the compartmentalization of contaminants among soils, limestone and sediment may be warranted, depending on corrective measures that are under consideration. Collection and analysis of on-site vegetation may be warranted to extend the phytoremediation studies described in this report, thus demonstrating whether or not the laboratory studies reflect actual site conditions with regard to plant uptake or degradation of contaminants. This latter investigation should only be considered if phytoremediation is considered as a component of remedial action.

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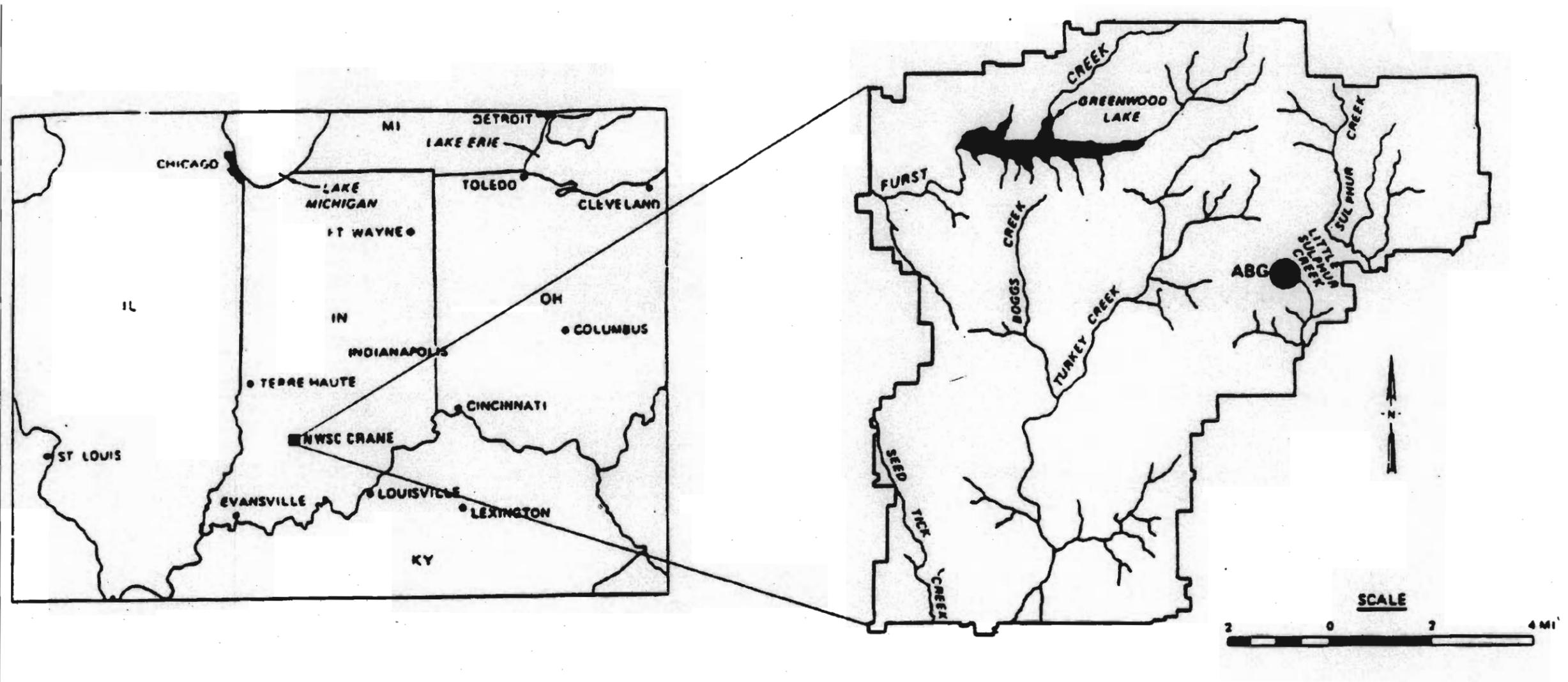


Figure 1. Location of NSWC in Indiana (left). Location of the ABG within the NSWC (right) (After Baedke 1998)

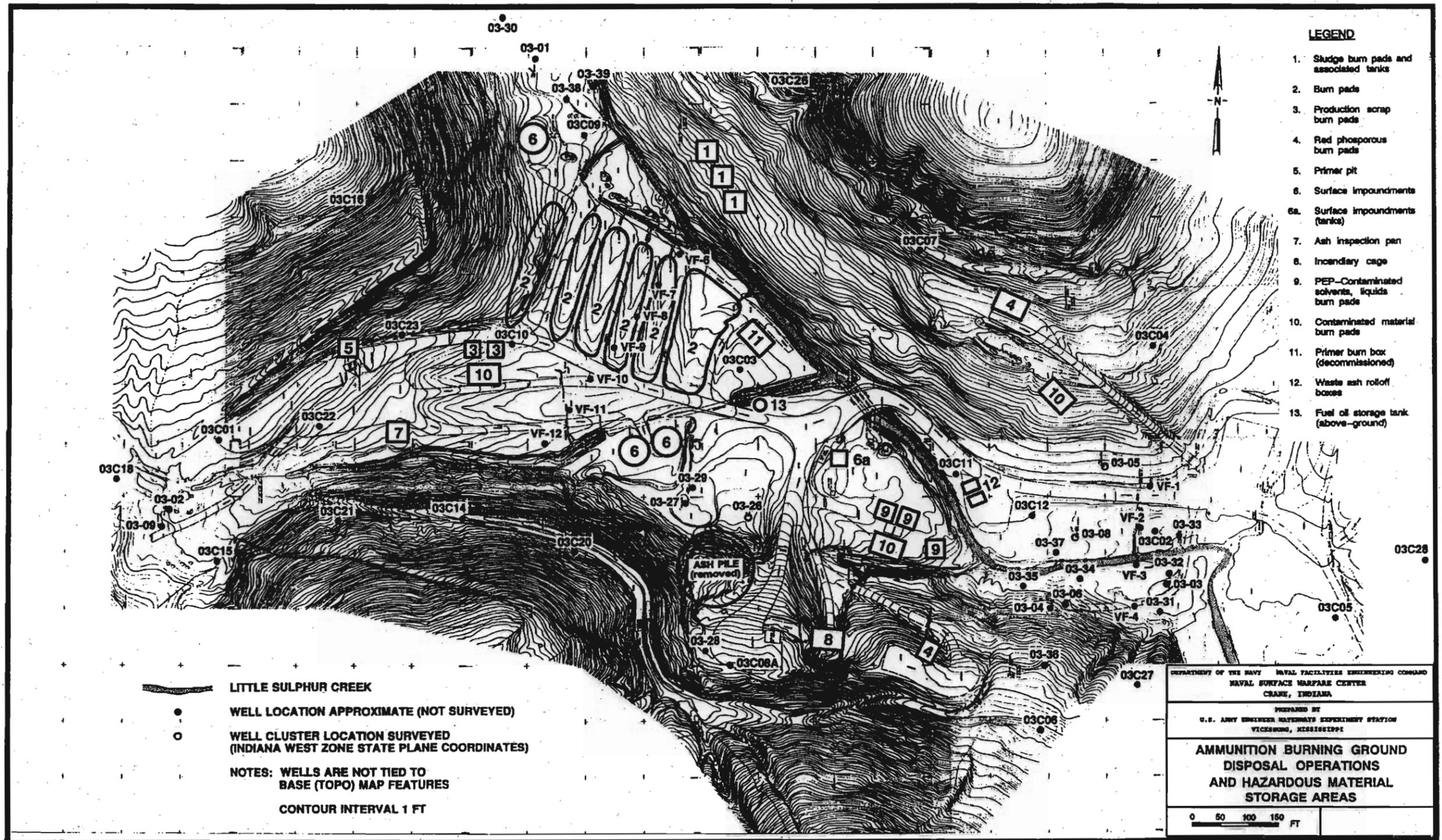


Figure 2 Operational features of ABG
(From Murphy 1994)

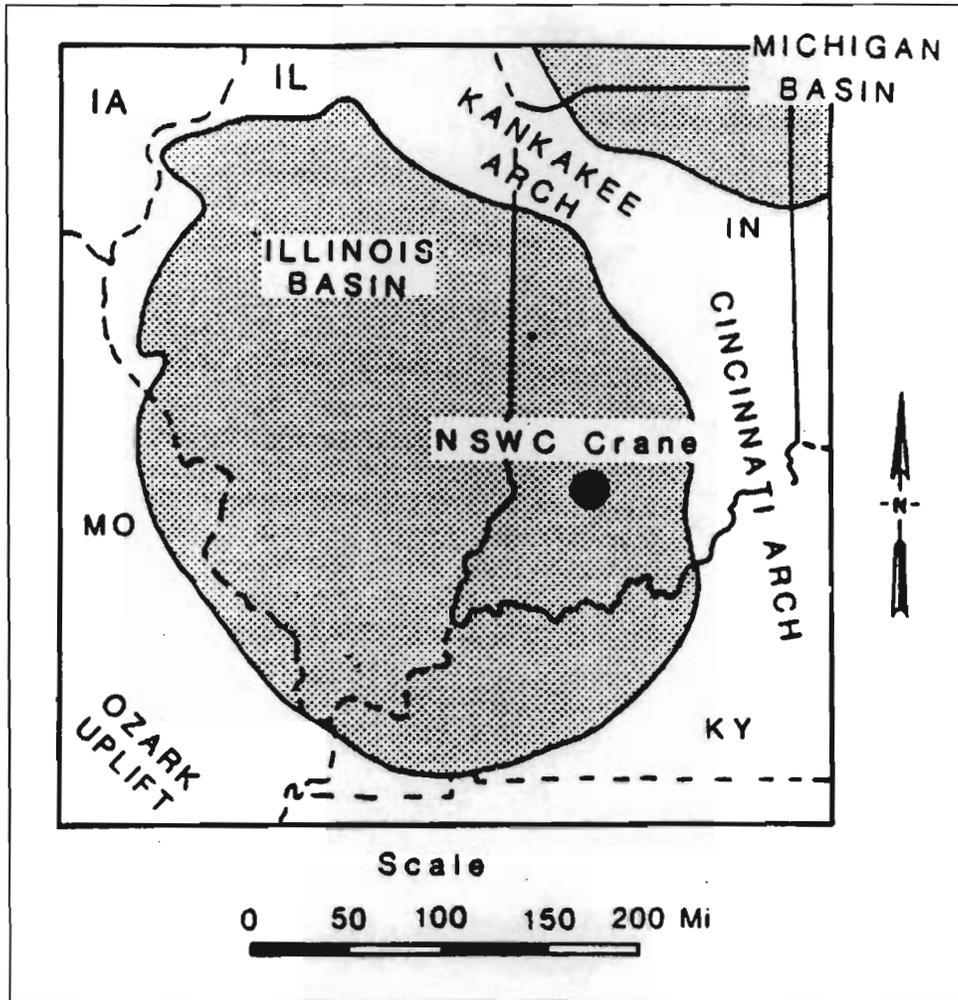


Figure 3. Location of Crane and some structural elements of the mid-continent. (From Barnhill and Ambers 1994)

TIME UNIT		ROCK UNIT		LITHOLOGY
Period	Epoch	Group	Formation	
MISSISSIPPIAN	PENN	Morrowan	Raccoon Creek	Mansfield Fm.
				Chesterian
	Hardinsburg Fm.			
	Golconda-Haney Ls.			
	Indian Springs			
	West Baden	Big Clifty Fm.		
		Beech Creek Ls.		
		Elwren Fm.		
		Reelsville Ls.		
	Sample Fm.			
Beaver Bend Ls.				

Figure 4. Stratigraphic section of the rocks in the study area

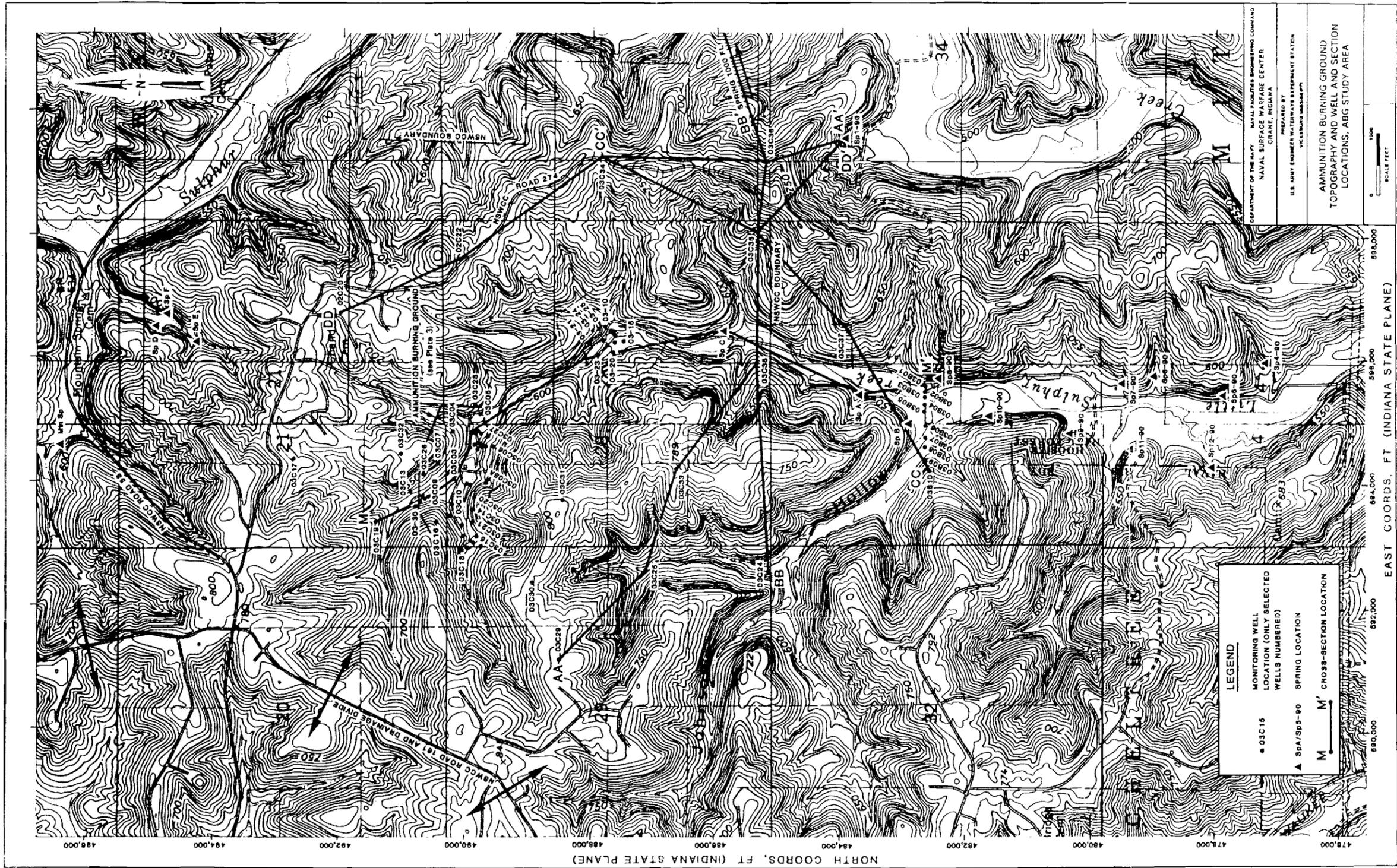


Figure 5 Topography of ABG showing locations of borings, wells and cross sections. (From Murphy 1994)

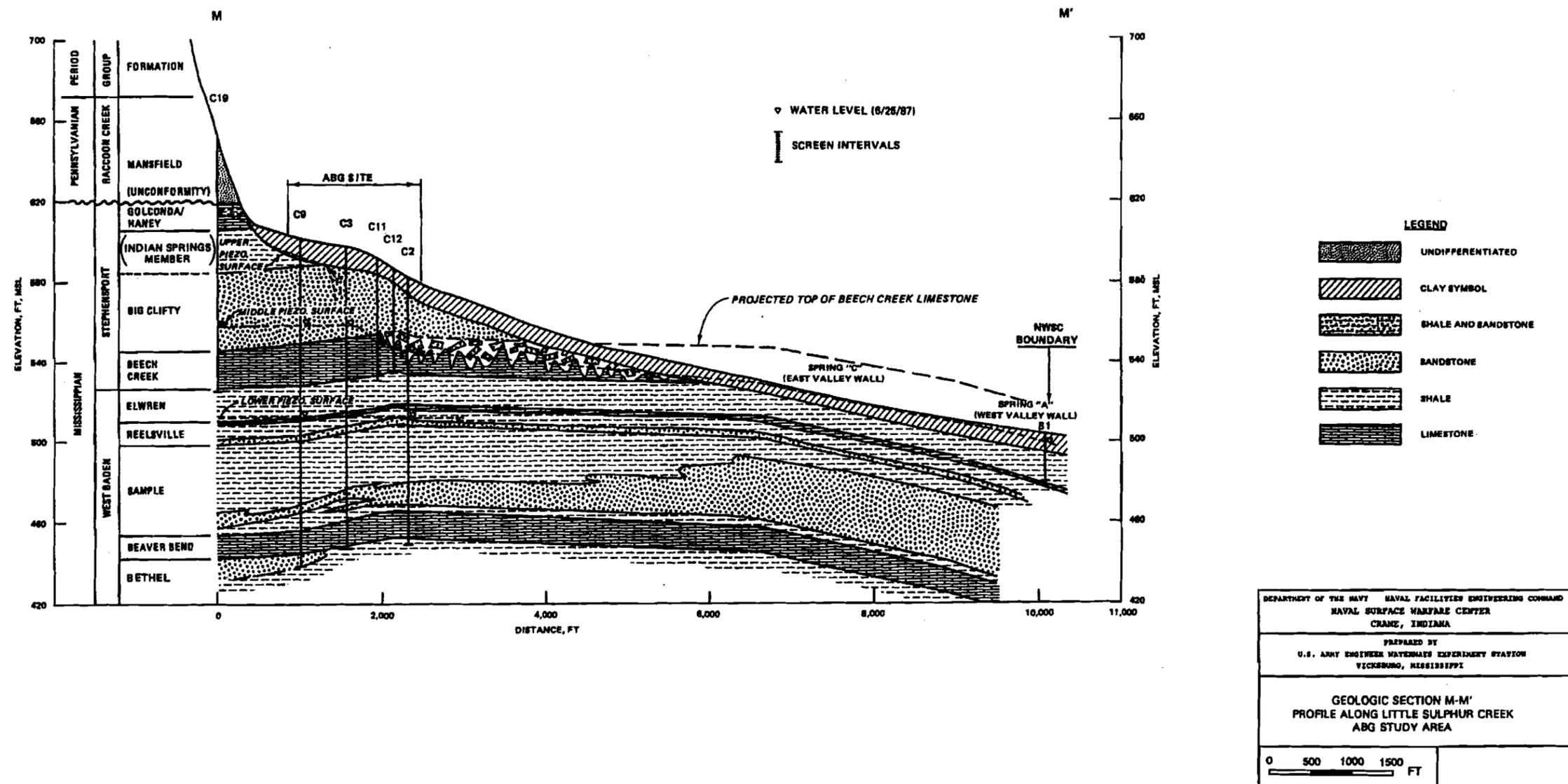


Figure 6. Geologic profile from the ABG to the NWSC boundary in the Little Sulphur Creek drainage basin showing the area of karst feature formation. (From Murphy and Ciocco 1990)

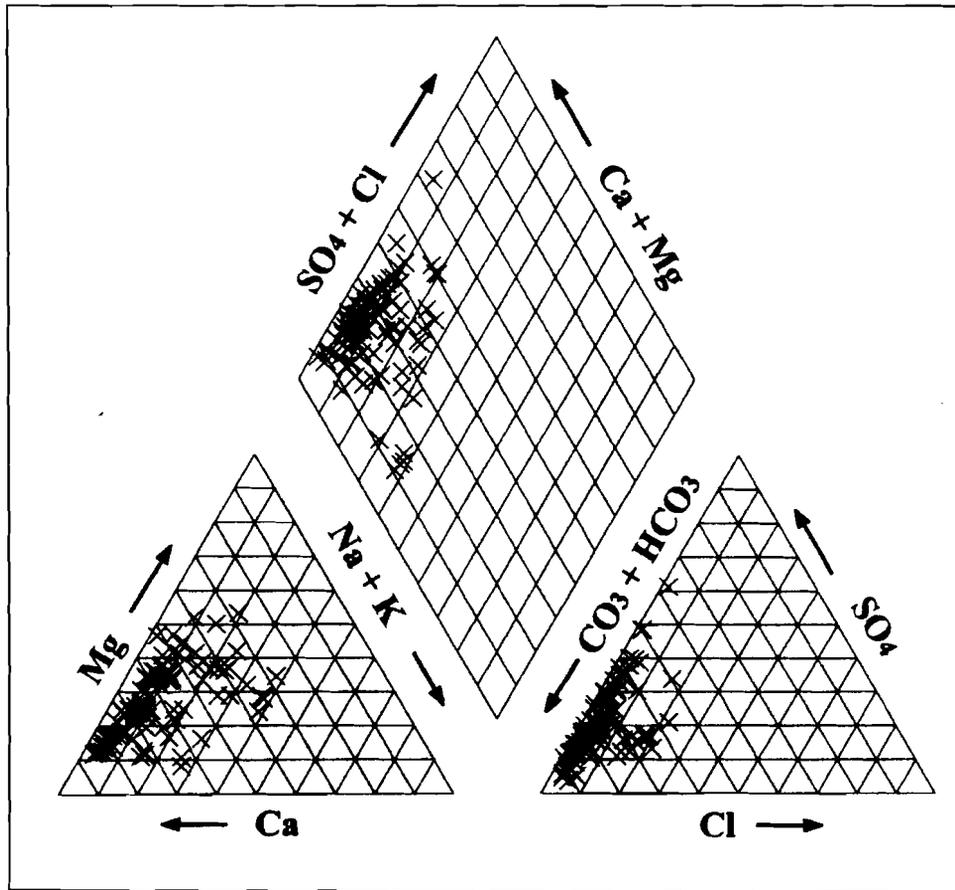


Figure 8. Piper diagram of water chemistry analyses taken from "uncontaminated" wells in the Beech Creek Aquifer (After Beadke 1998)

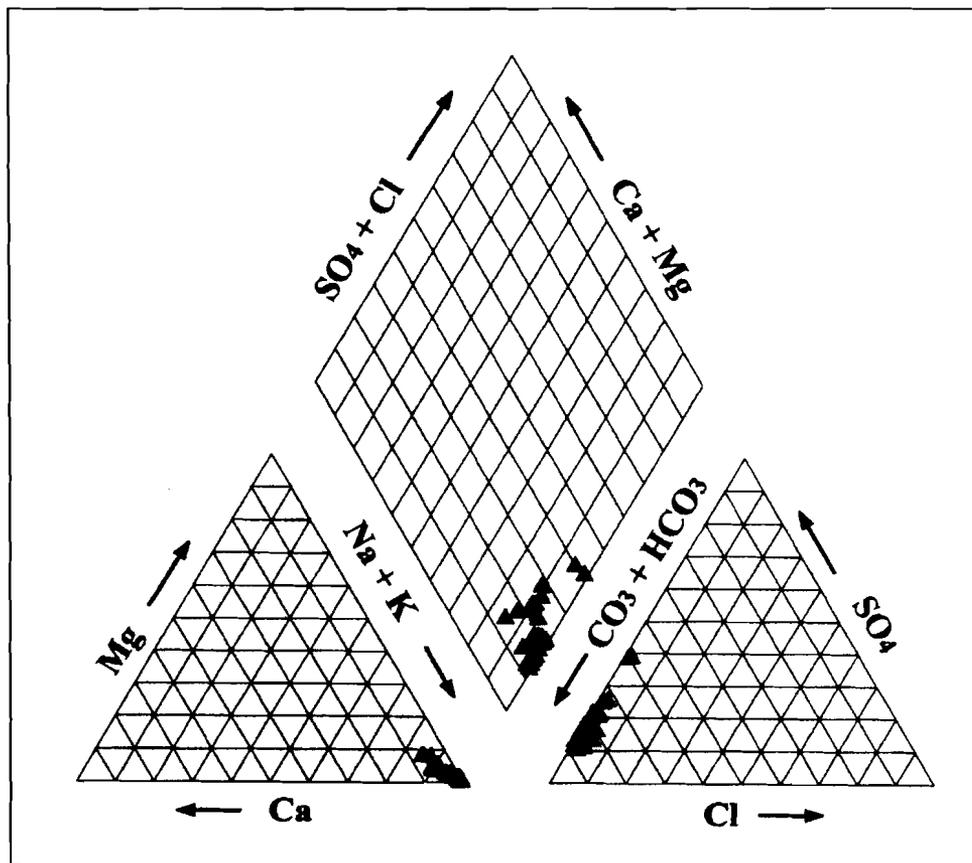


Figure 9. Piper diagram of water chemistry analysis from wells in the Beaver Bend Aquifer (After Baedke 1998)

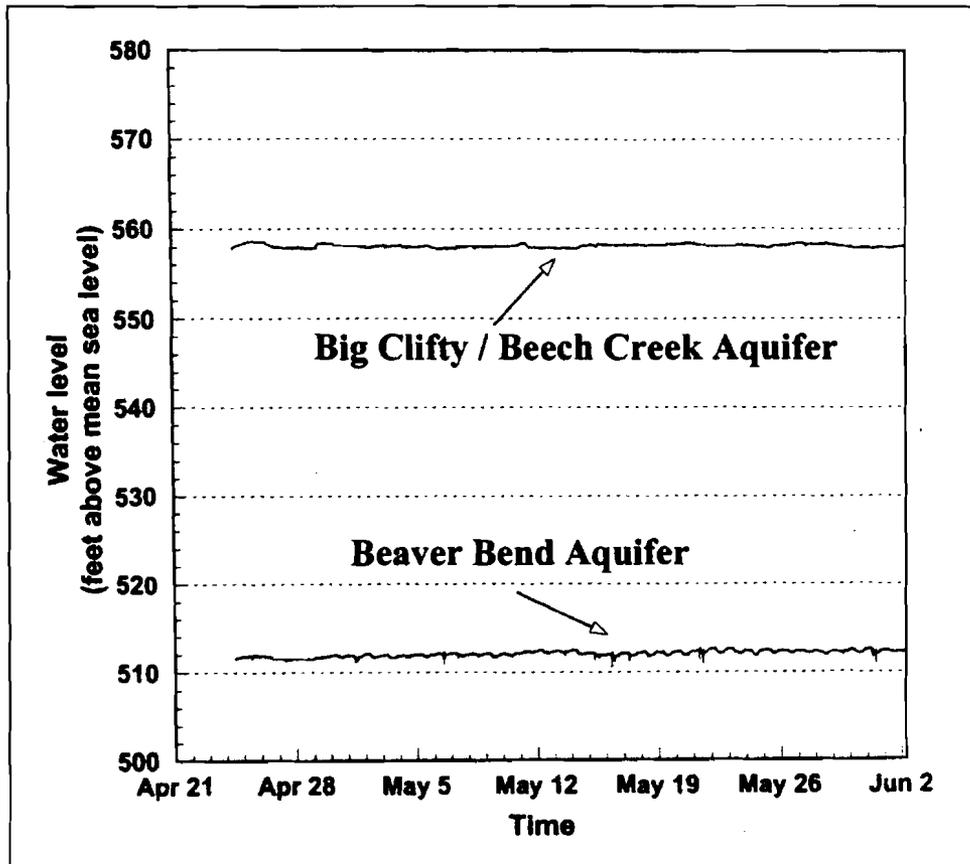


Figure 10. Graph comparing the hydraulic heads in the Beech Creek and Beaver Bend aquifers through time (After Baedke 1998)

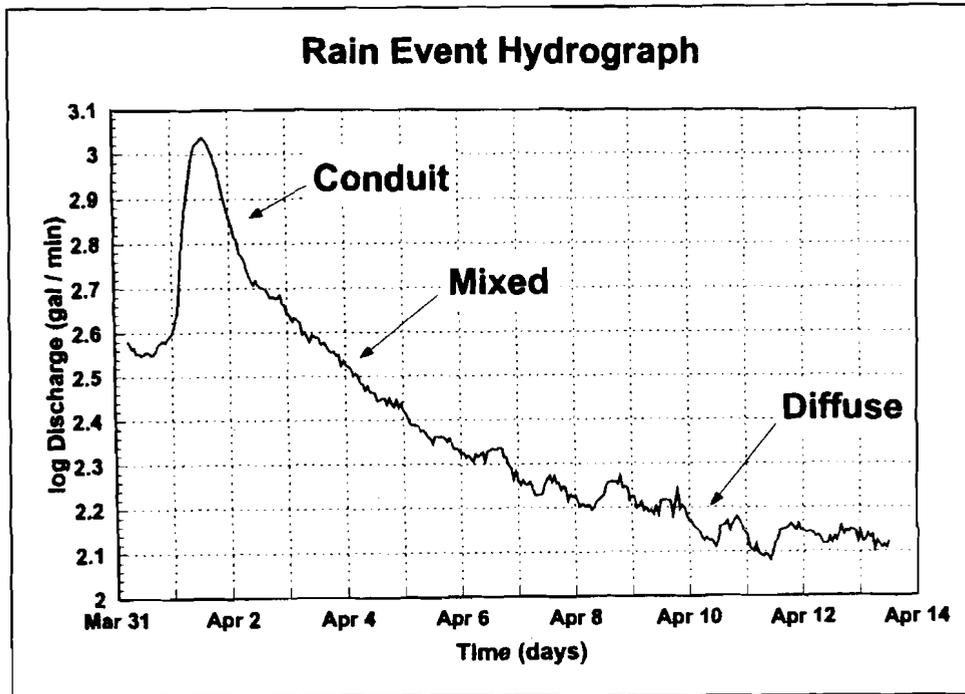


Figure 11. Typical recession hydrograph from springs in the study area. Hydrograph shows three segments related to the conduit, diffuse, and mixed-flow parts of the karst system (After Baedke 1998)

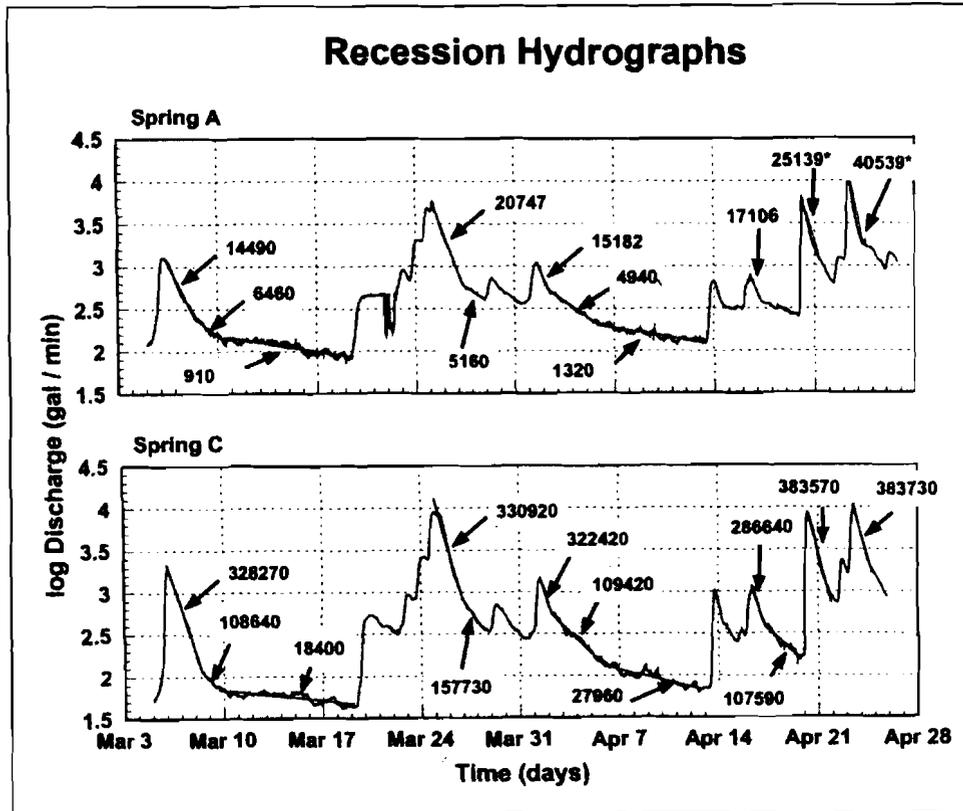
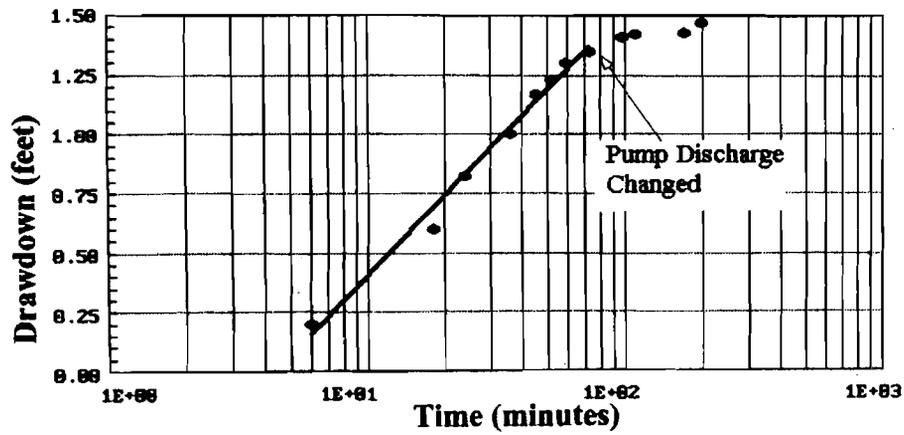


Figure 12. Two-month hydrographs for Springs A and C (thin lines) during March – April 1996. Heavy lines show the conduit-, mixed-, and diffuse-flow systems. Numbers correspond to the ratio of T/Sy calculated from the corresponding segment of the hydrograph. An * next to the values of T/Sy indicates that discharges exceeded the calibrated range of the weir and pressure transducers for the rain event (After Baedke 1998)

Pump Test Results: Well 03PMP08

Jacob Method



Transmissivity = $1.61E-04$ (ft²/s) or 1.29 (m²/day)
Storativity = $5.39E-05$

Figure 13. Pump test results of Well 03-PMP08 as analyzed by the Jacob method (after Baedke 1998)

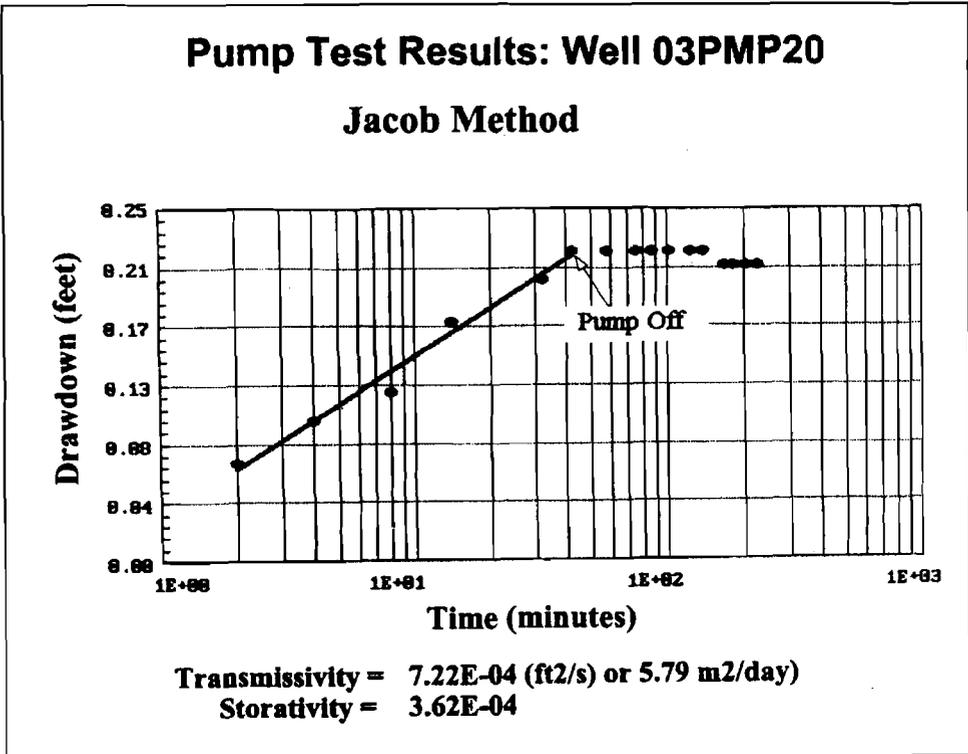


Figure 14. Pump test results of Well 03-PMP20 as analyzed by the Jacob method (after Baedke 1998)

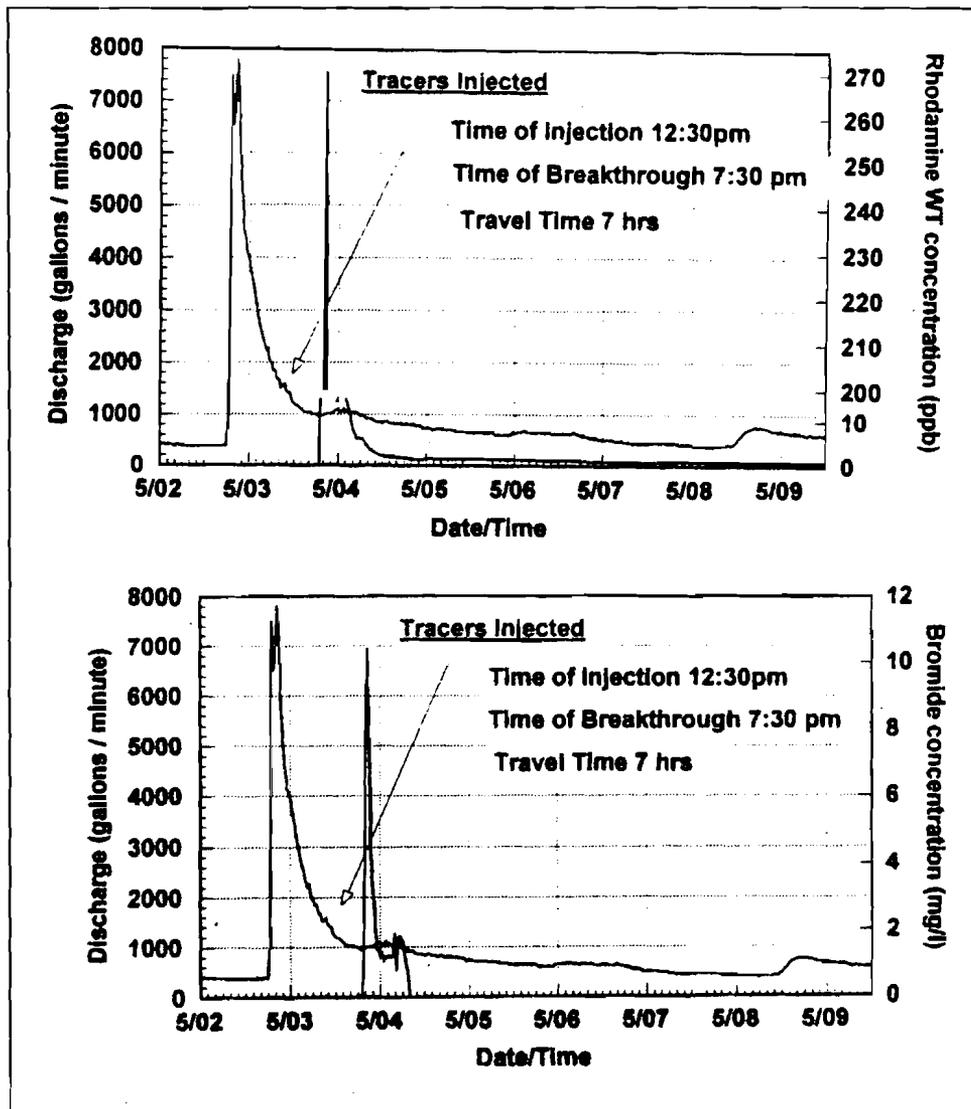


Figure 15. Breakthrough curves for Spring A: (a) Rhodamine WT, (b) Bromide (After Baedke 1998)



Figure 16. Sampling location

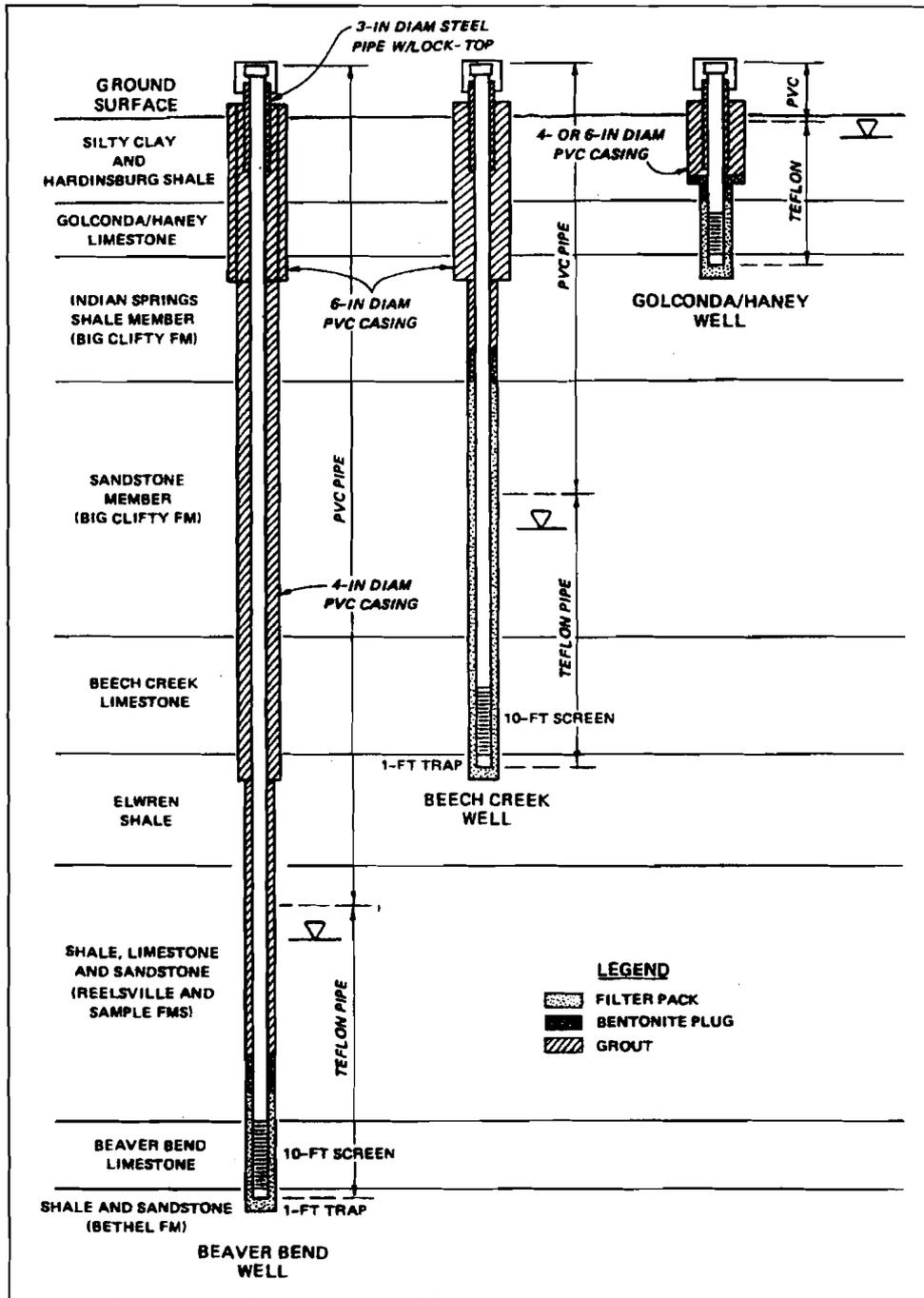


Figure 17. Typical well installation at Ammunition Burning Ground (After Murphy 1994)

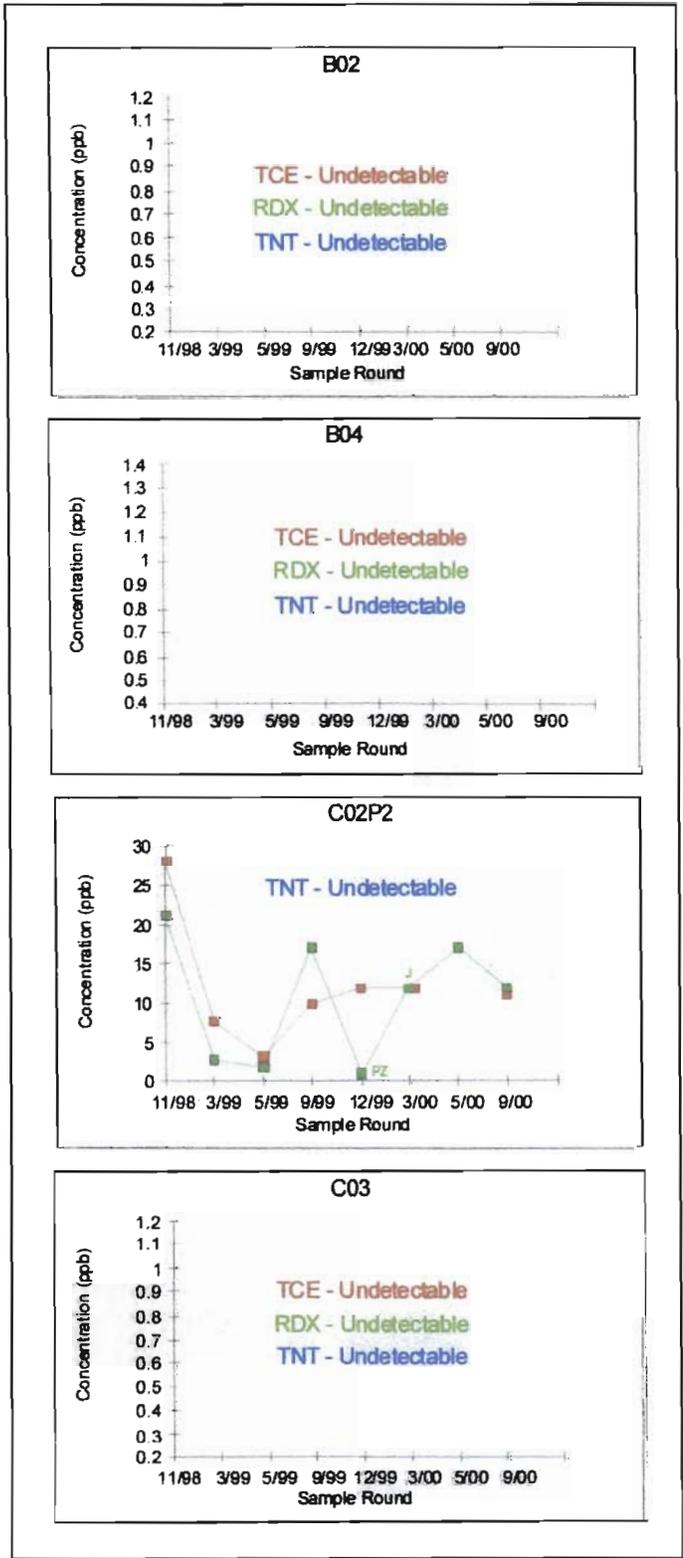


Figure 18. Concentration versus time plots for Wells B02, B04, C02P2, and C03

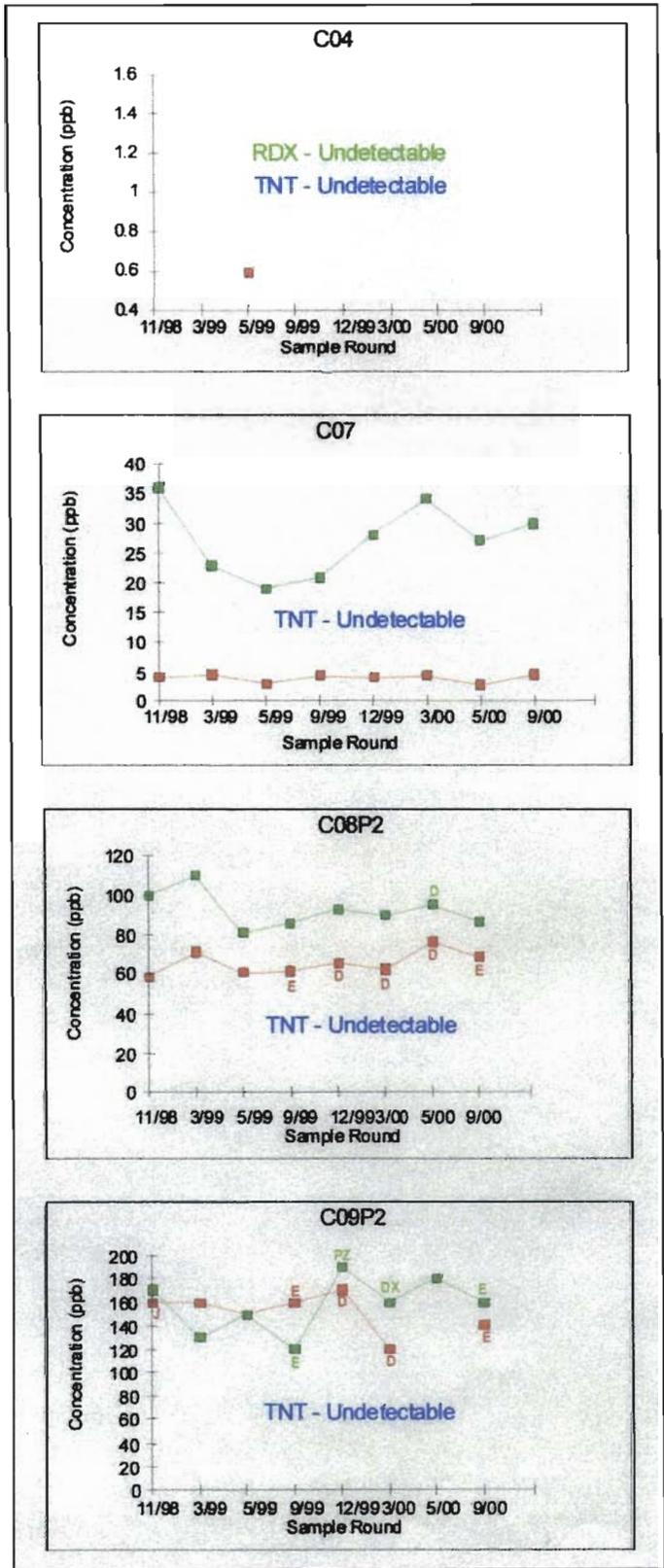


Figure 19. Concentration versus time plots for Wells C04, C07, C08P2, and C09P2

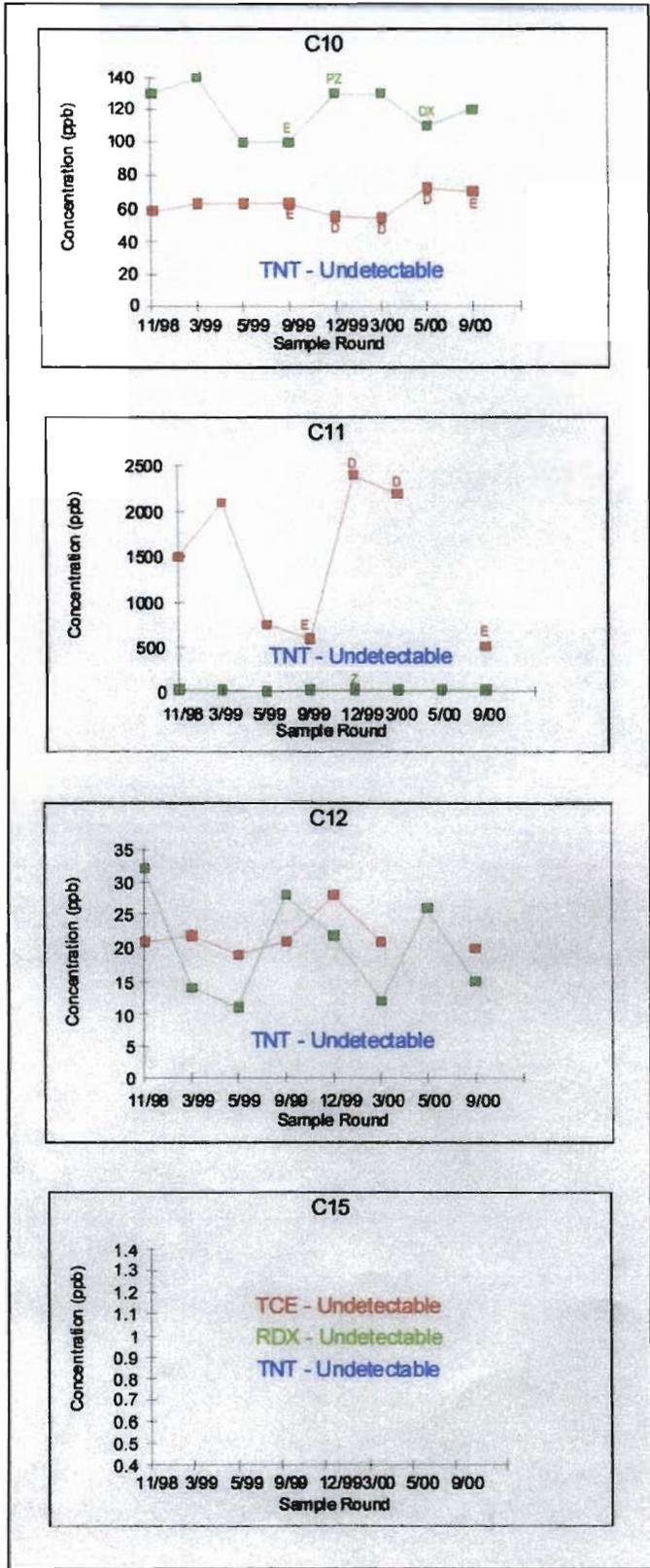


Figure 20. Concentration versus time plots for Wells C10, C11, C12, and C15

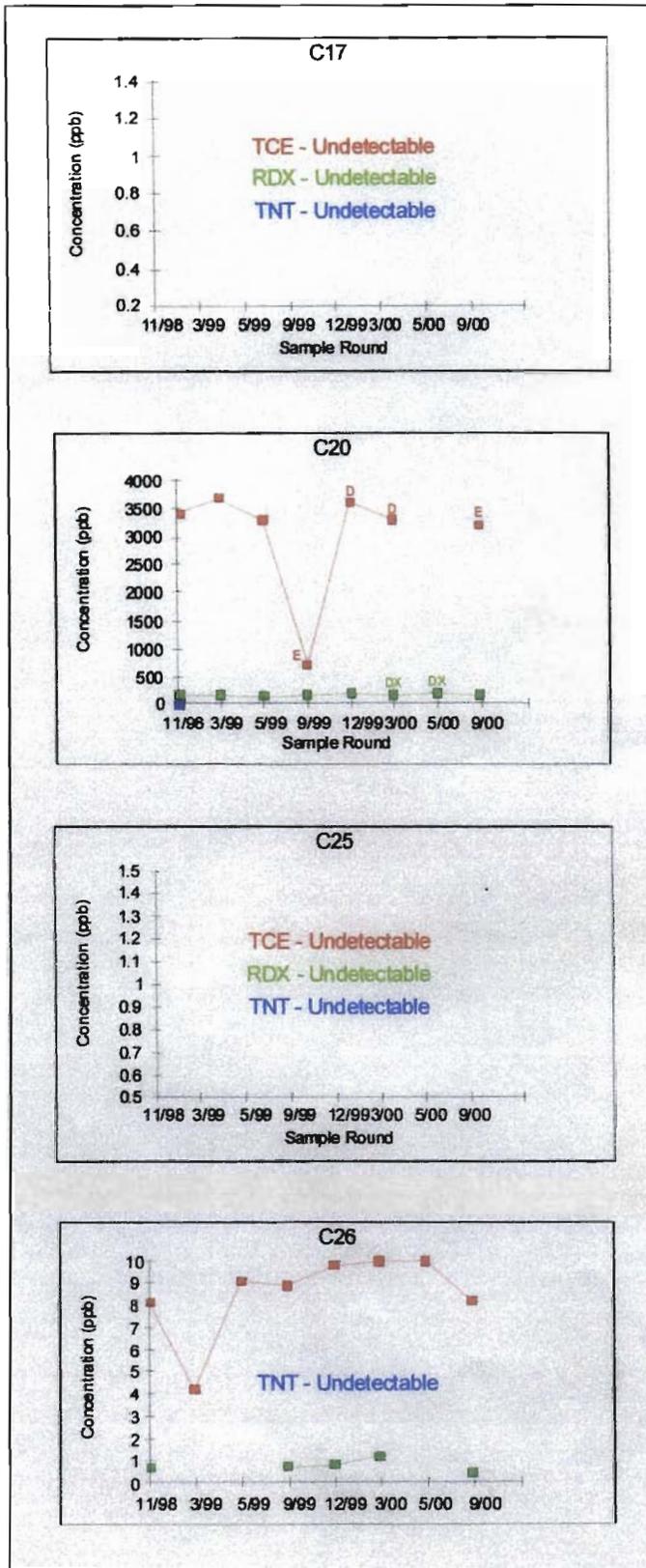


Figure 21. Concentration versus time plots for Wells C17, C20, C25, and C26

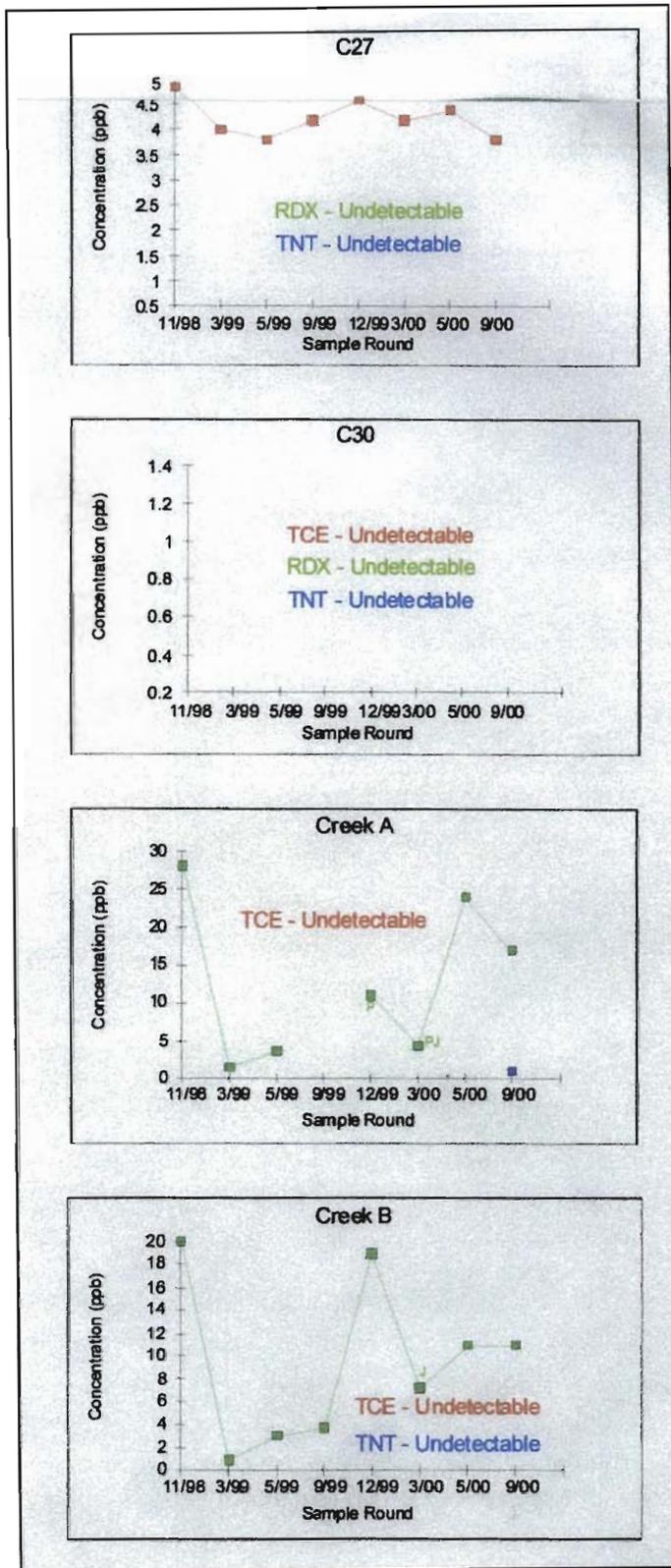


Figure 22. Concentration versus time plots for Wells C27 and C30, Creek A, and Creek B

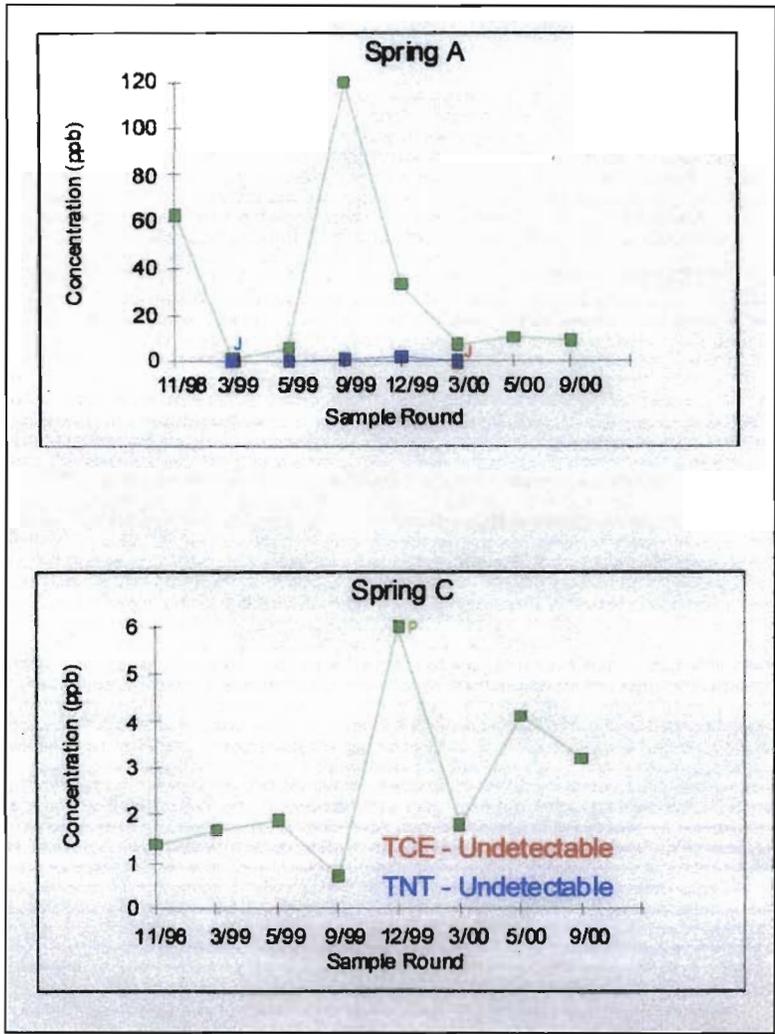


Figure 23. Concentration versus time plots for Spring A and Spring C

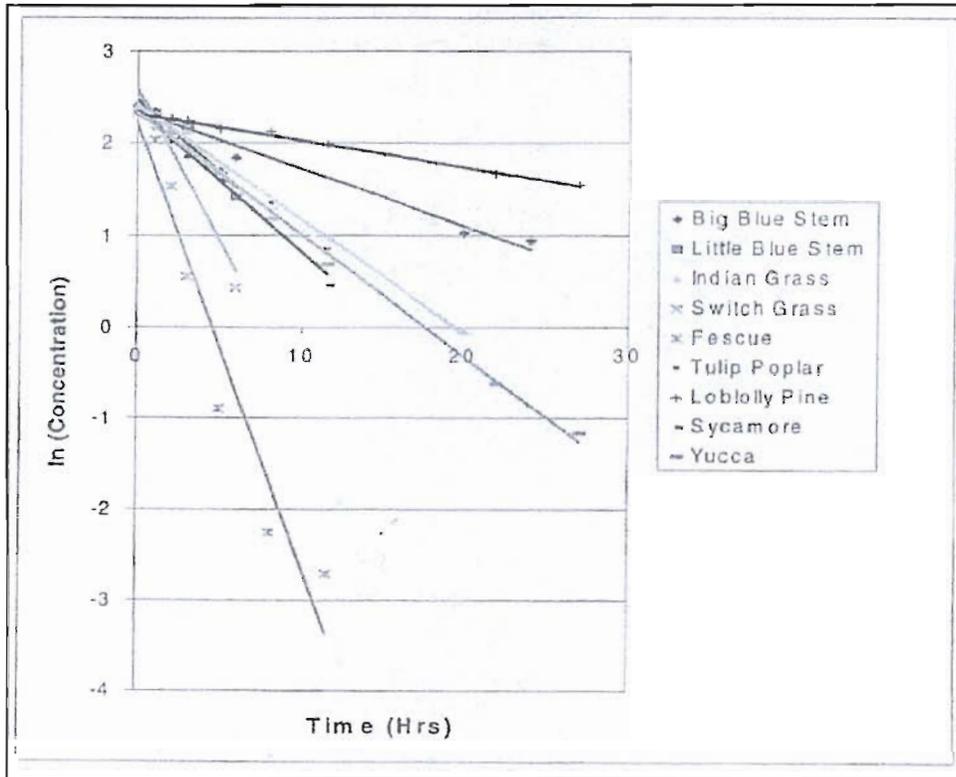


Figure 24. First-order degradation of TNT by selected plant species

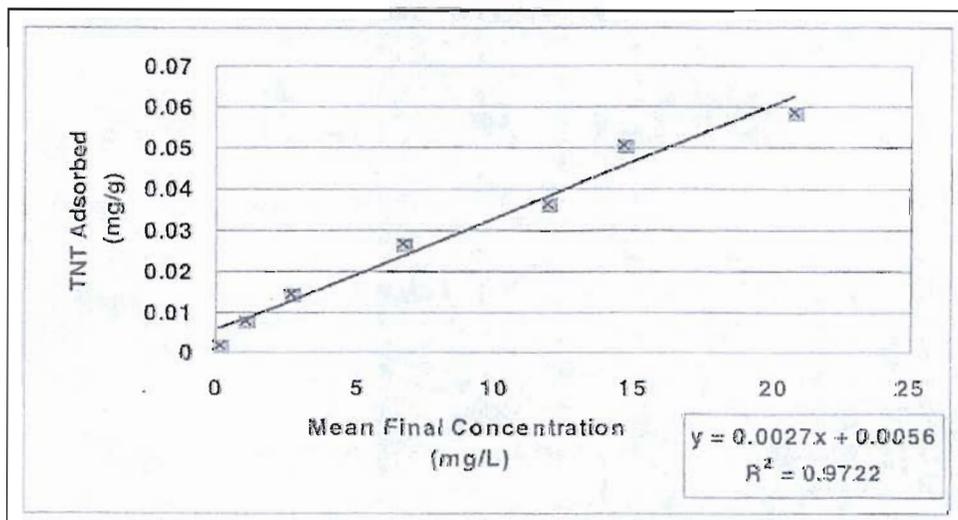


Figure 25. TNT adsorption isotherm for linear reactions with soil obtained at NSWCC

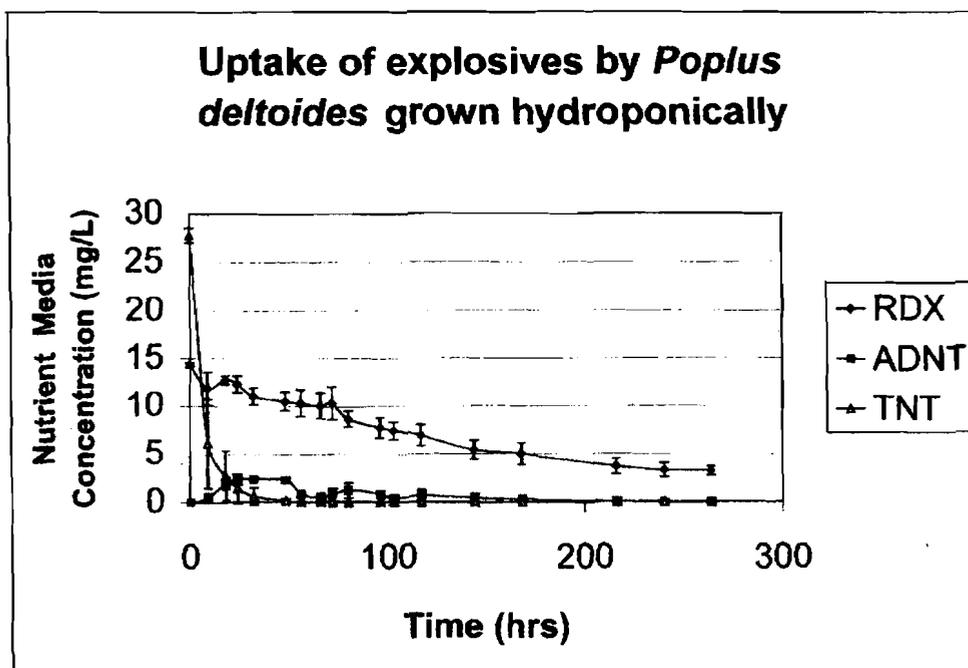


Figure 26. Uptake of explosives by *Populus deltoides* grown hydroponically

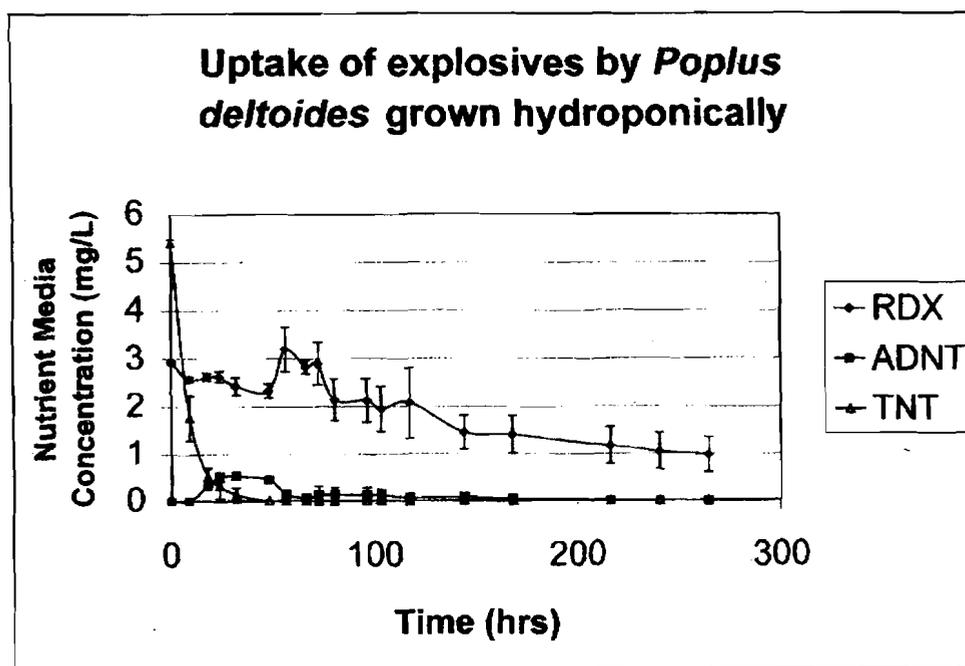


Figure 27. Uptake of explosives by *Populus deltoides* grown hydroponically

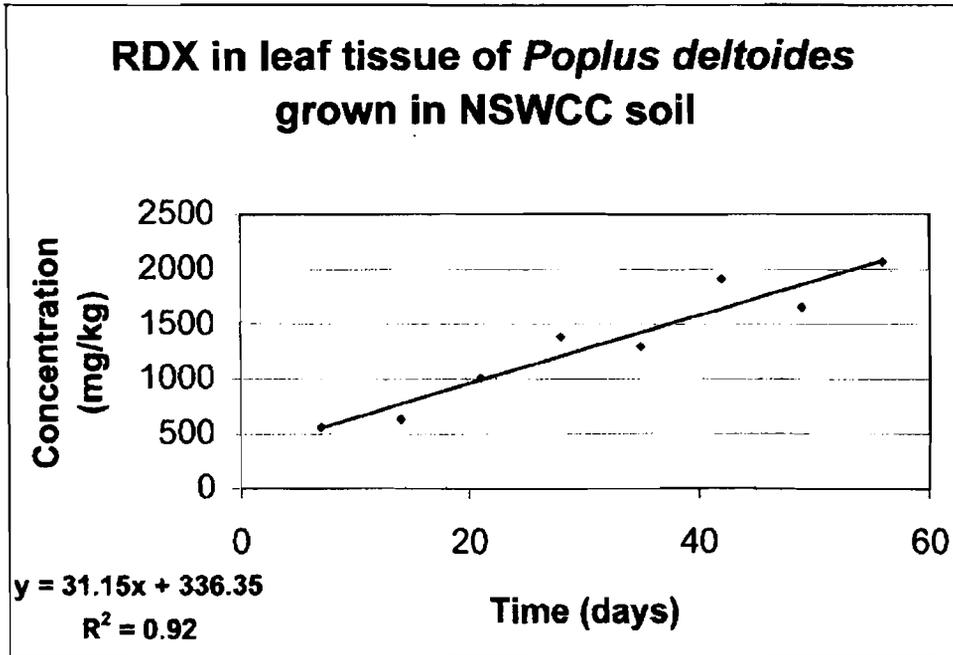


Figure 28. RDX in leaf tissue of *Populus deltoides* grown in NSWCC soil

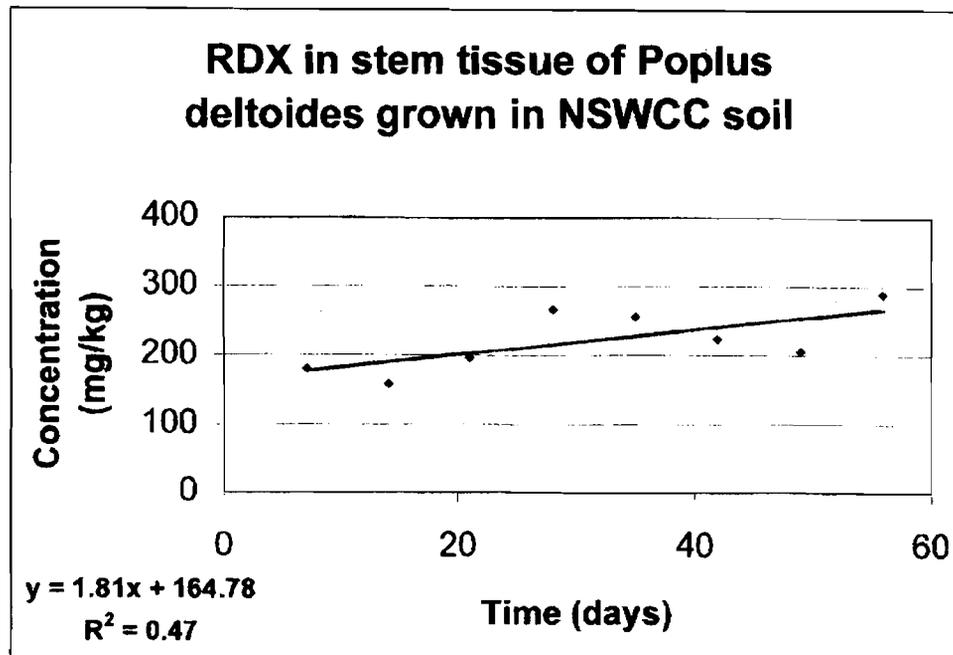


Figure 29. RDX in stem tissue of *Populus deltoides* grown in NSWCC soil

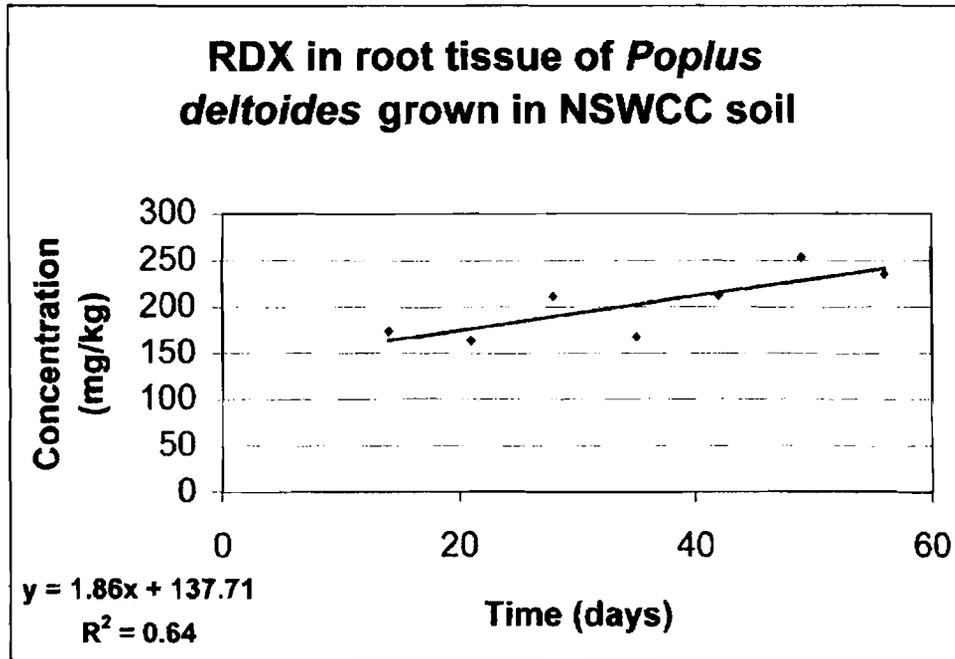


Figure 30. RDX in root tissue of *Populus deltoides* grown in NSWCC soil

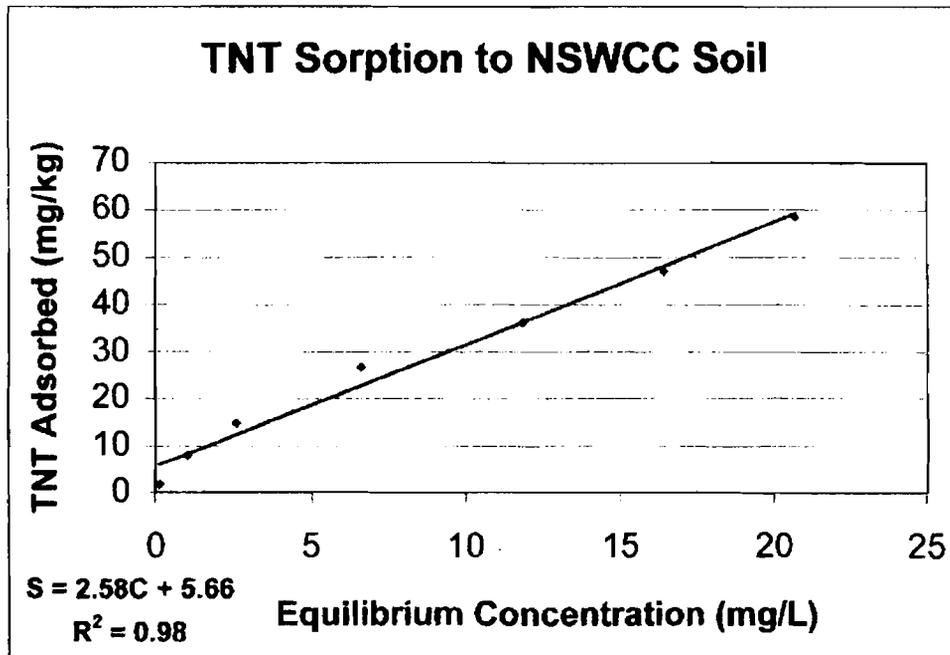


Figure 31. TNT sorption to NSWCC soil

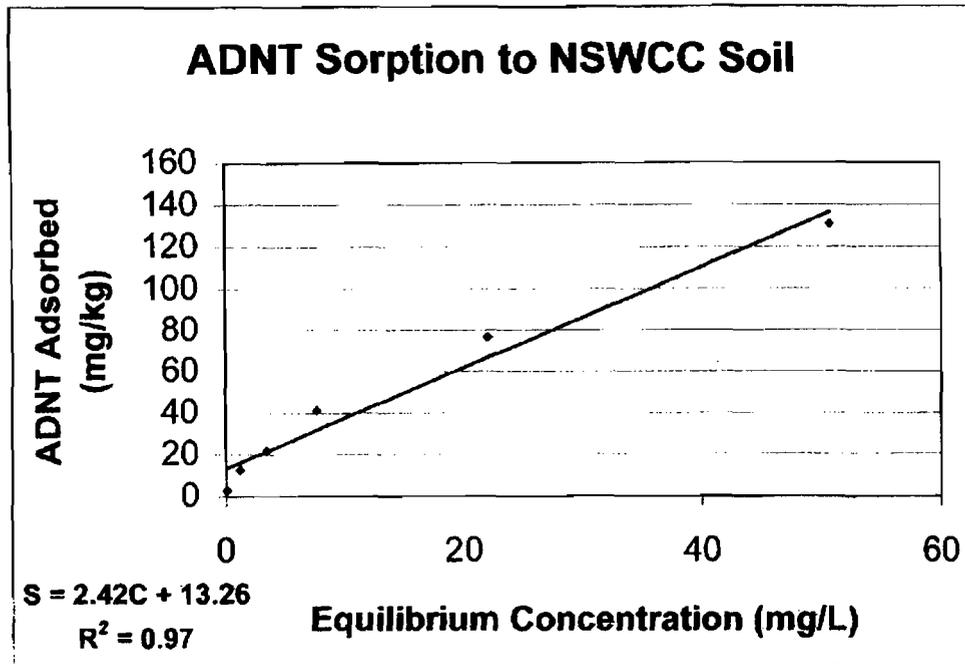


Figure 32. ADNT sorption to NSWCC soil

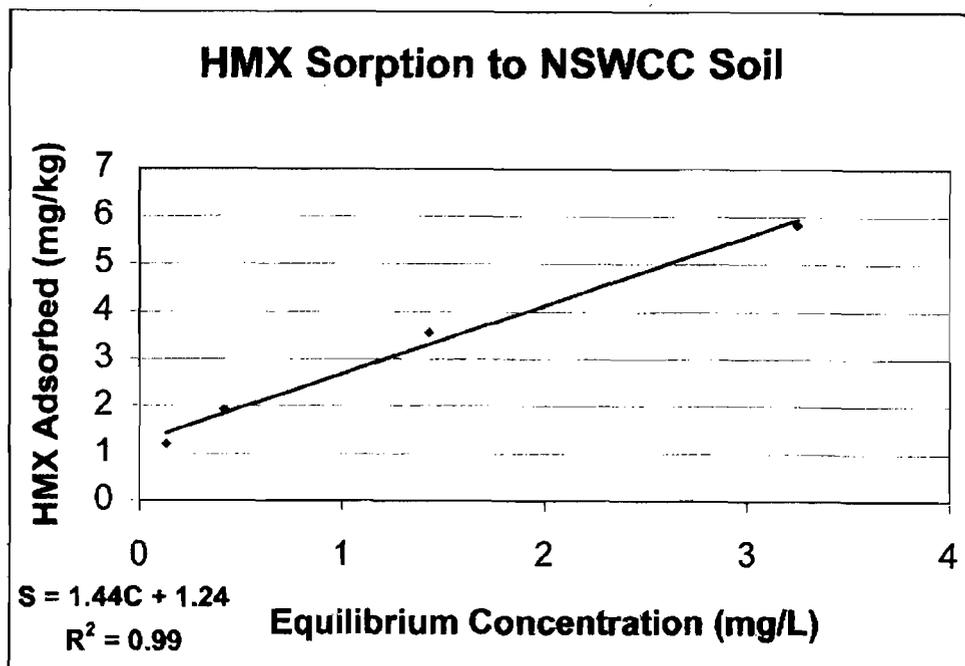


Figure 33. HMX sorption to NSWCC soil

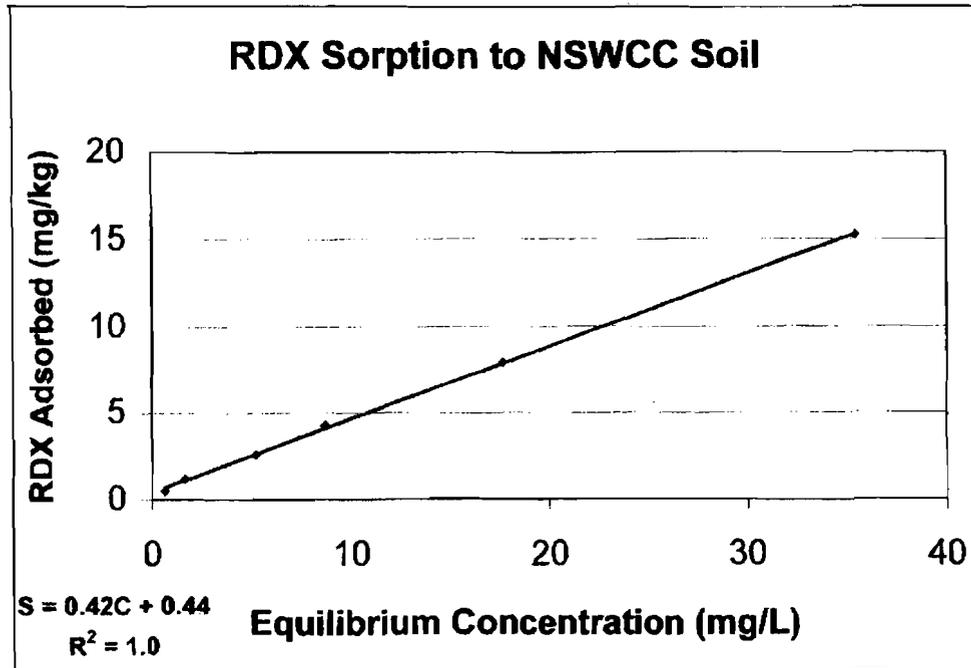
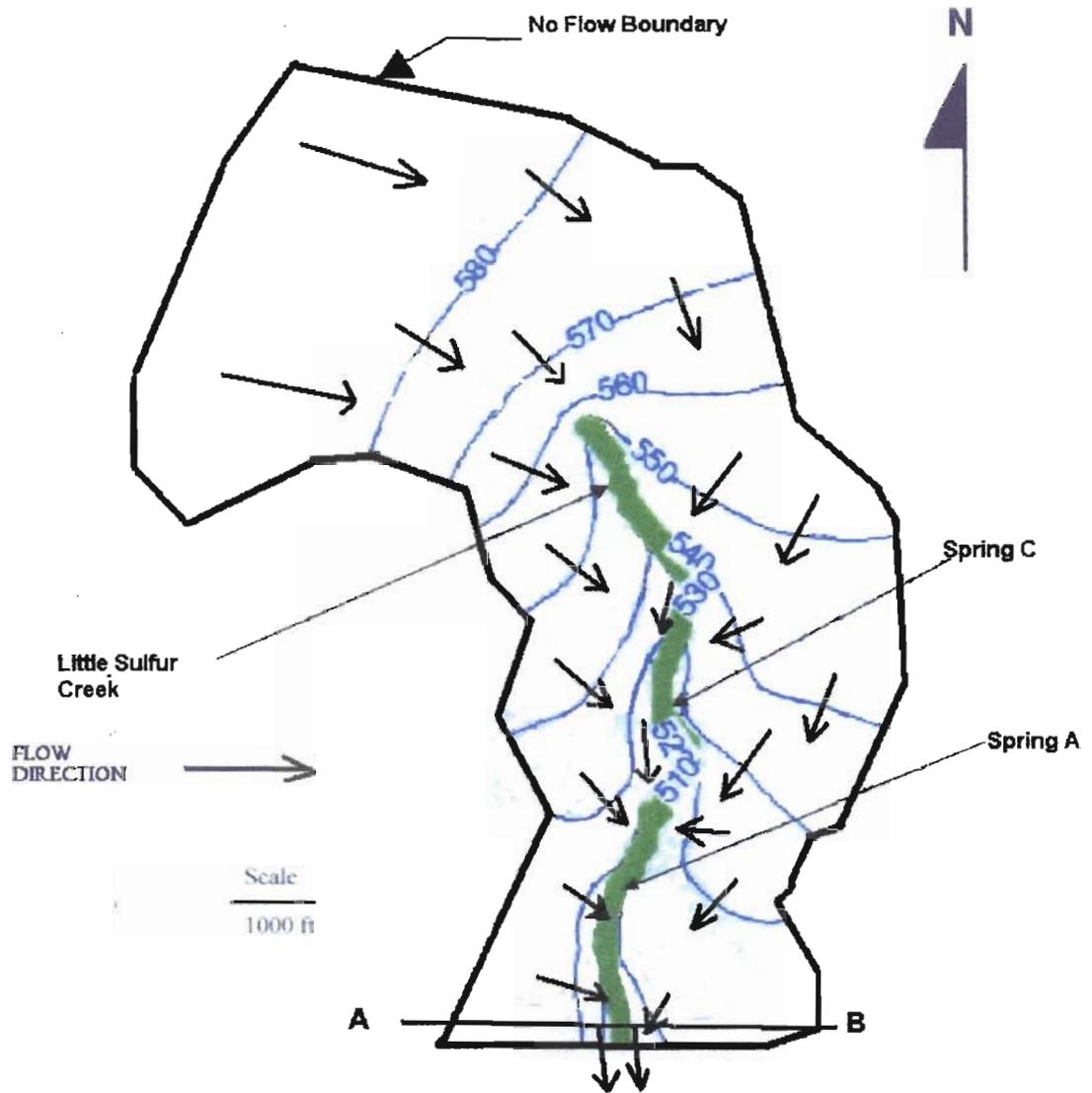
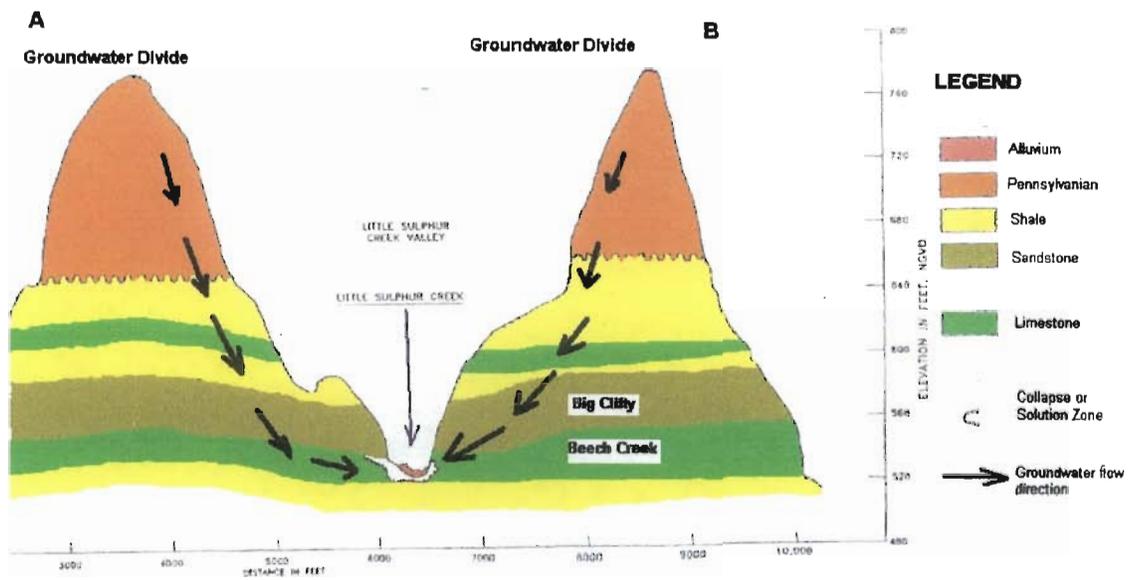


Figure 34. RDX sorption to NSWCC soil



Conceptual Model For Little Sulfur Creek Valley—Plan View

Figure 36. Conceptual model of Little Sulfur Creek Valley, plan view



Conceptual Model For Little Sulfur Creek Valley—Cross Section A-B

Figure 37. Conceptual model of Little Sulfur Creek Valley (Cross section A-B on Figure 36)

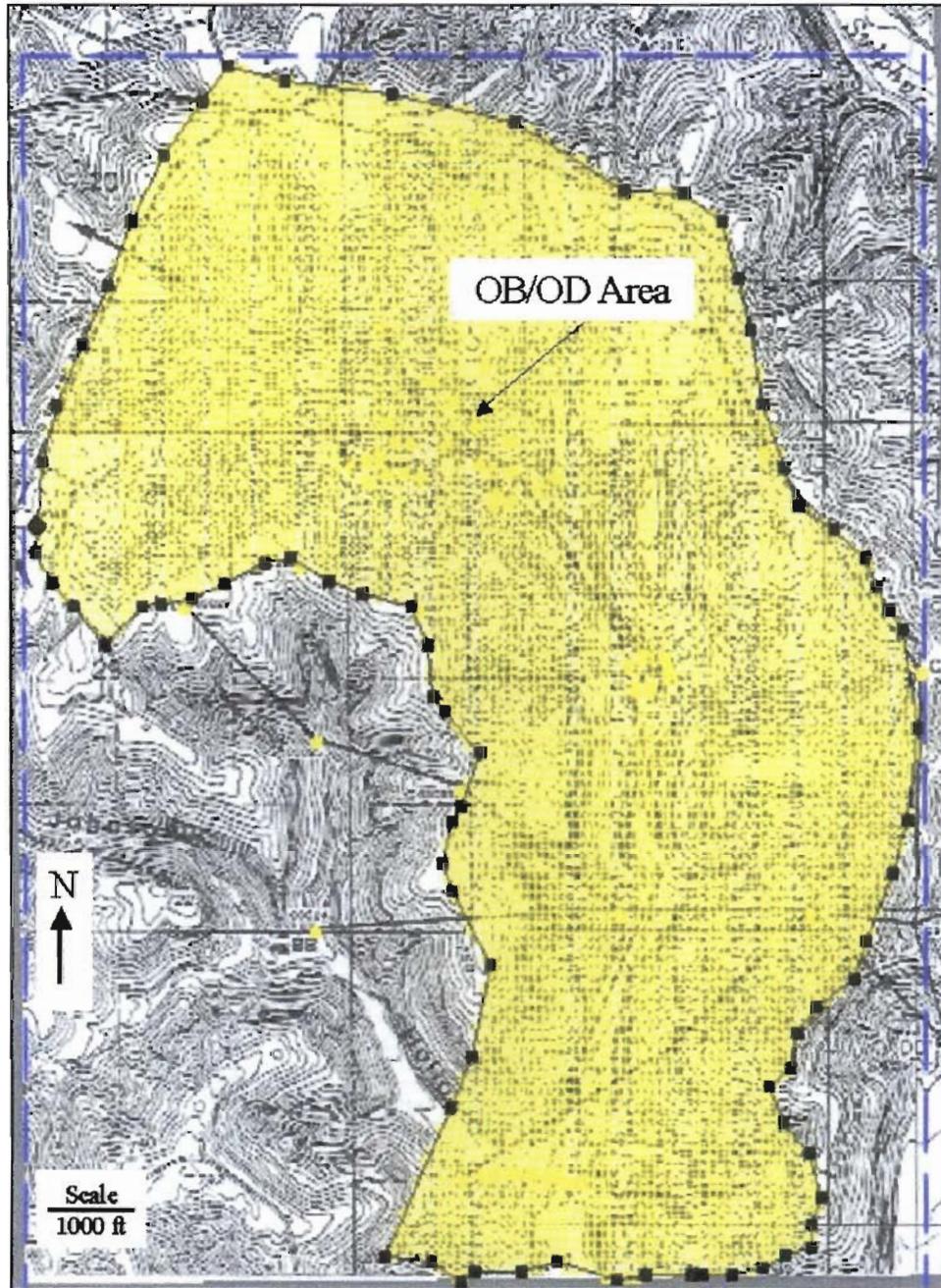


Figure 38. Extent of model for Crane OB/OD area

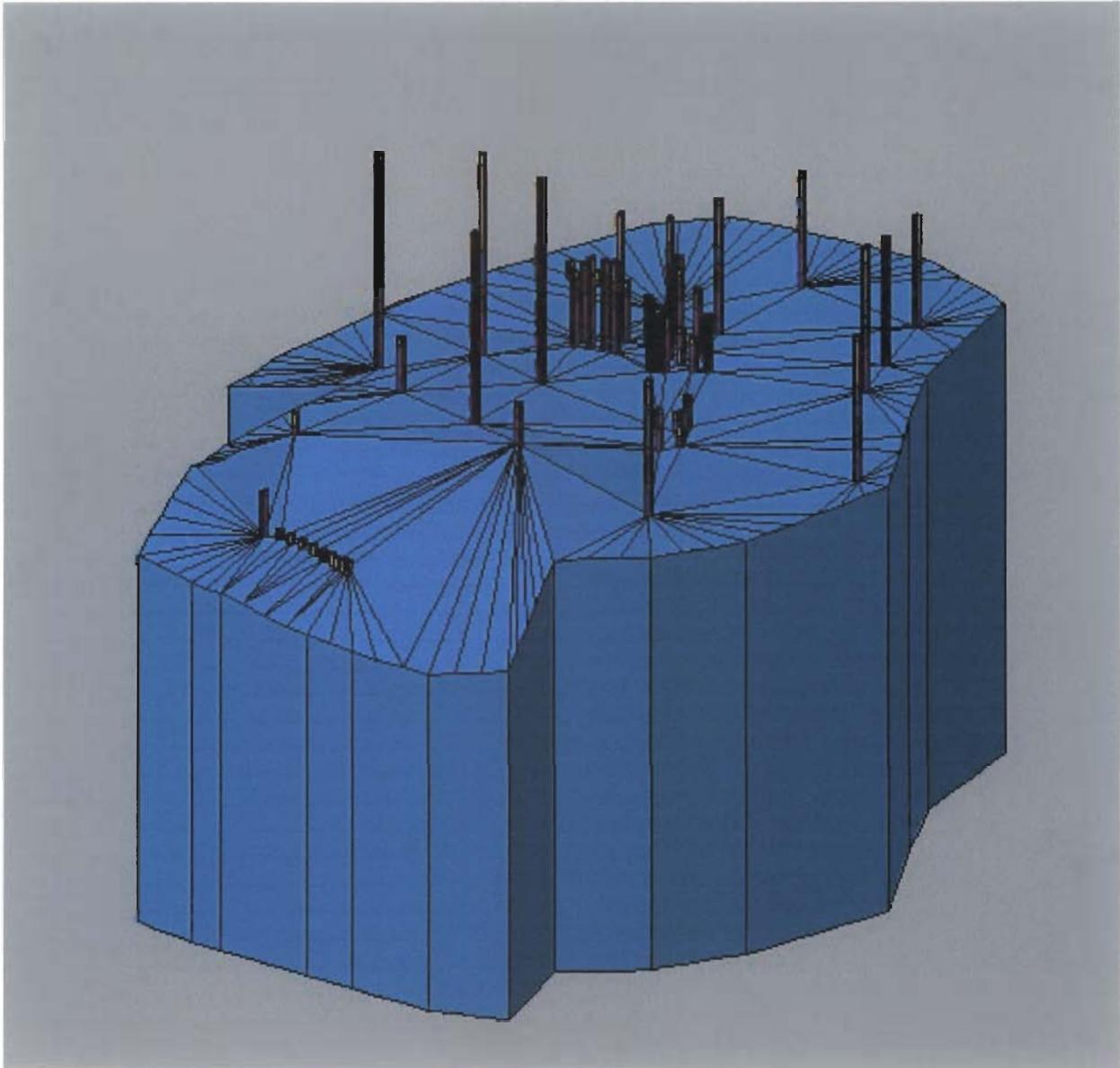


Figure 39. Top of Elwren Formation with boreholes shown

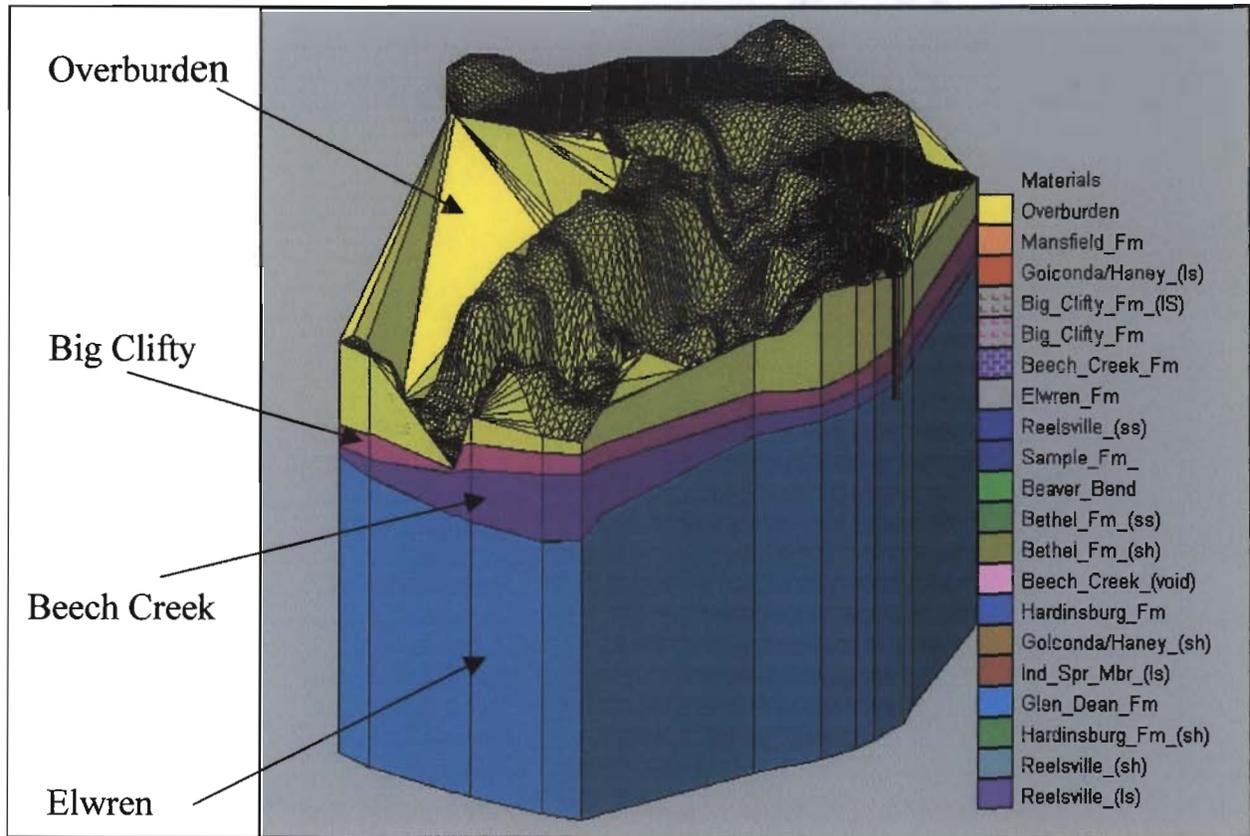


Figure 40. Solid model showing model formations

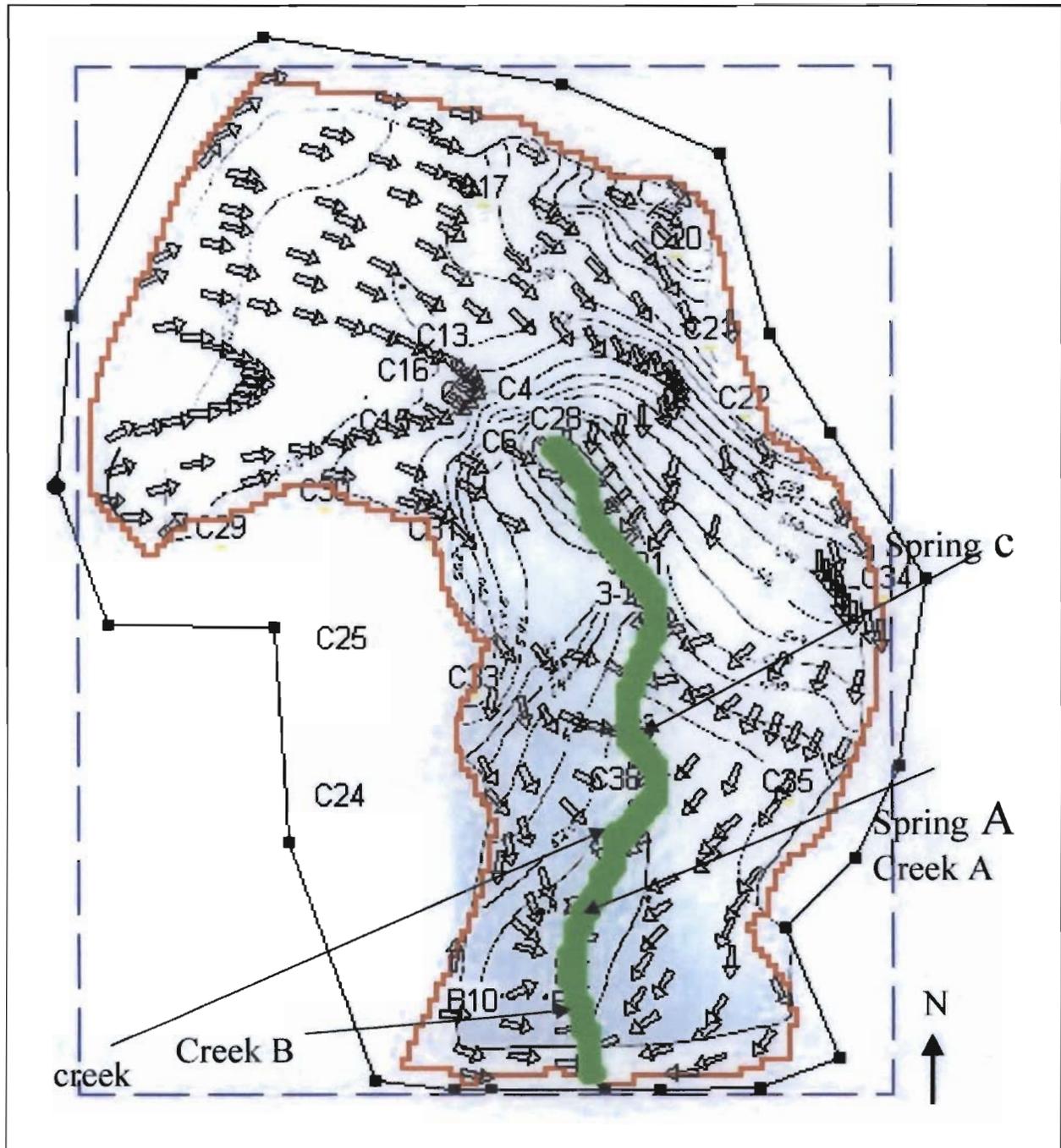


Figure 41. Groundwater directions with stream/wells displayed

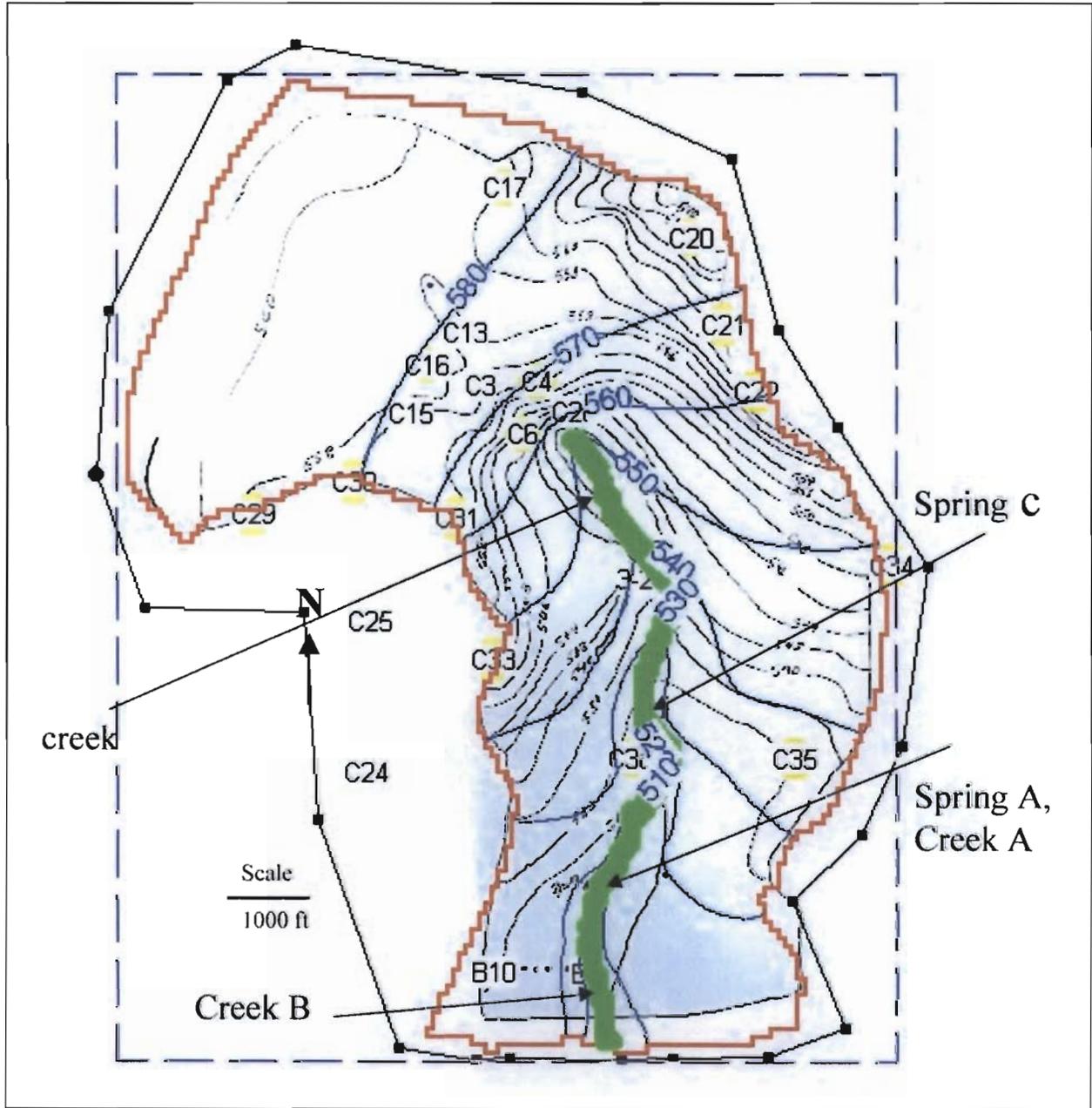


Figure 42. Comparison of simulated hydraulic heads (blue contour lines) and actual contours of hydraulic heads

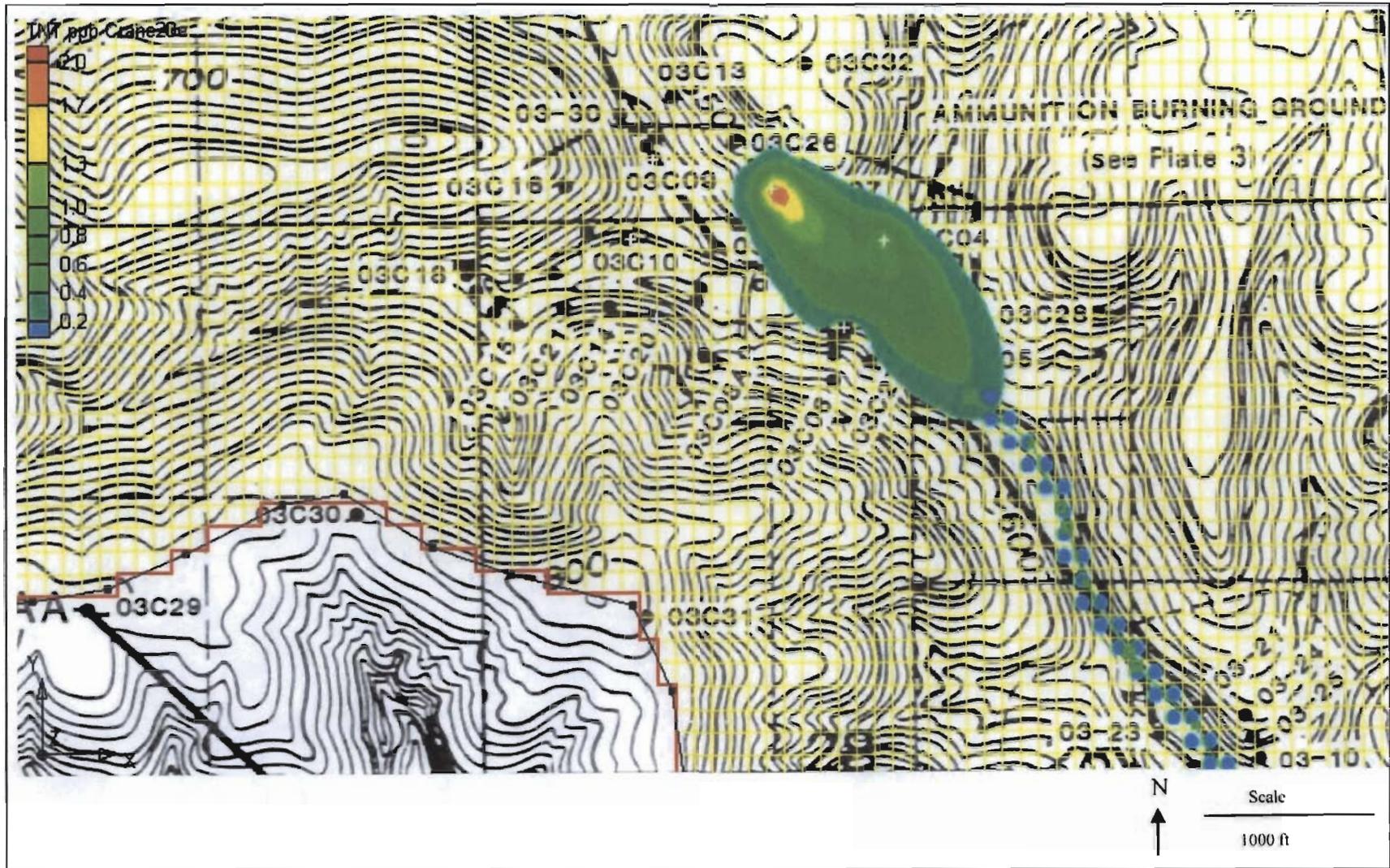


Figure 43. Distribution of TNT plume (simulated) after 57 years

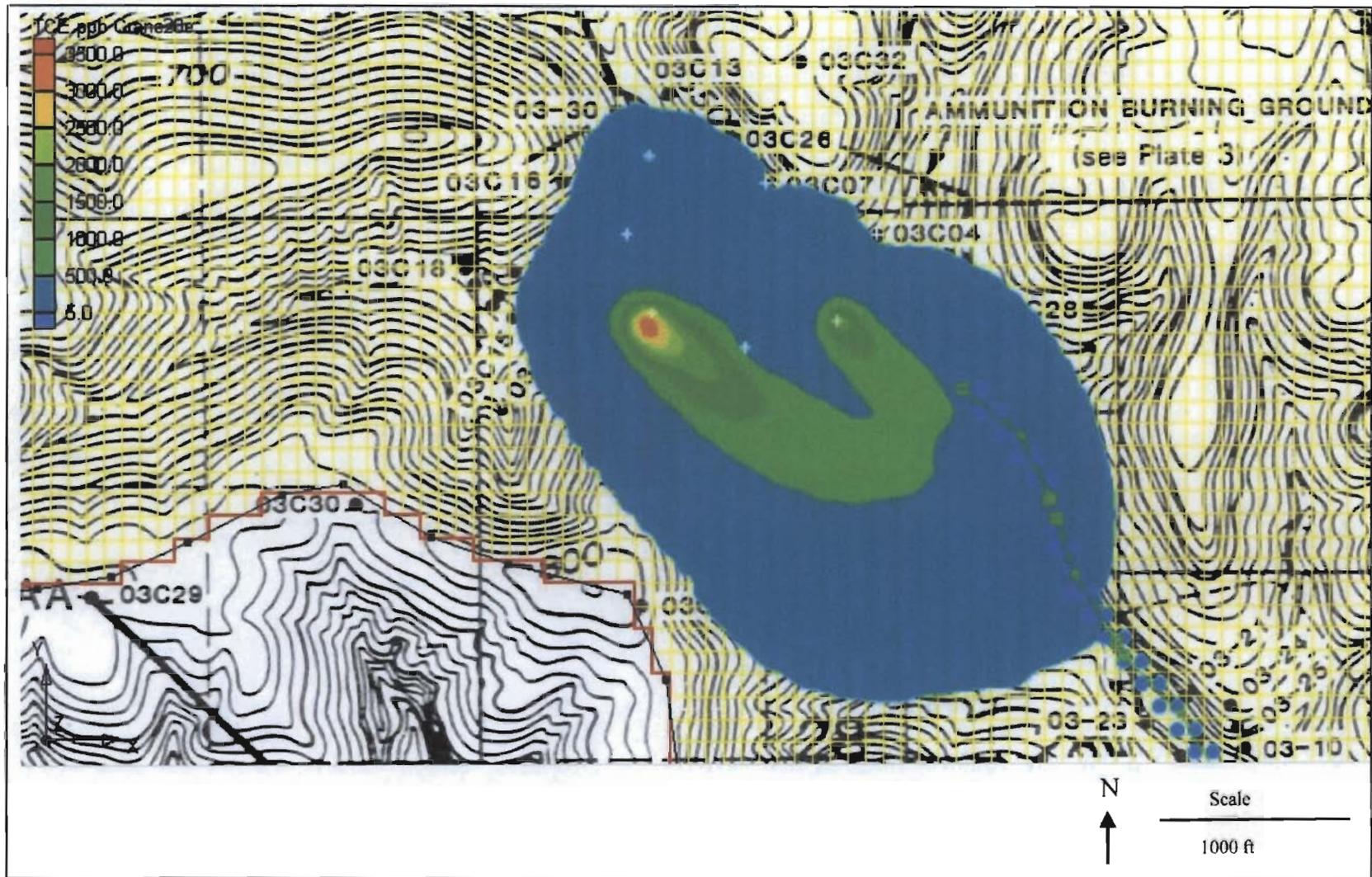


Figure 44. Distribution of TCE plume (simulated) after 57 years

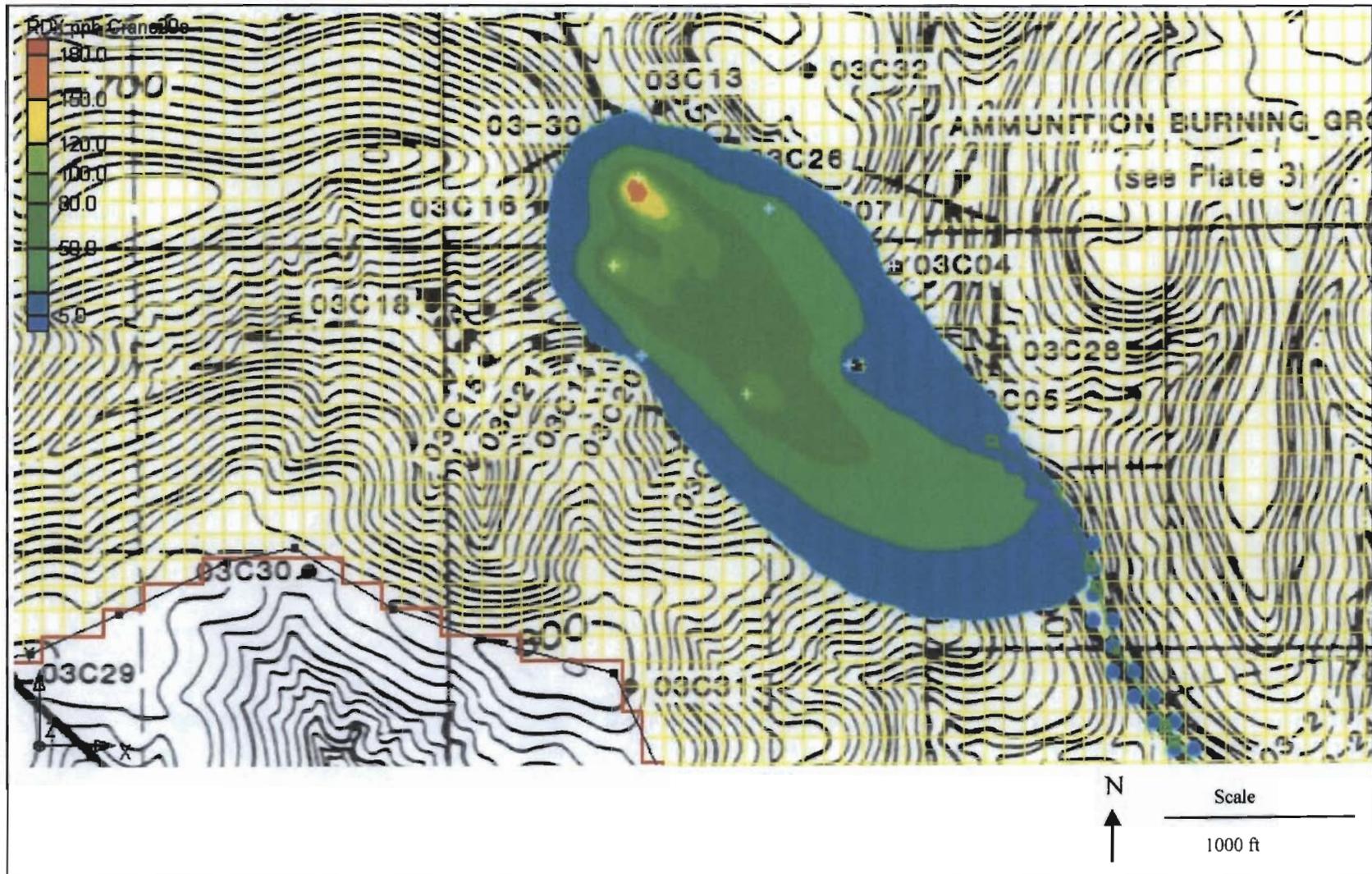


Figure 45. Distribution of RDX plume (simulated) after 57 years

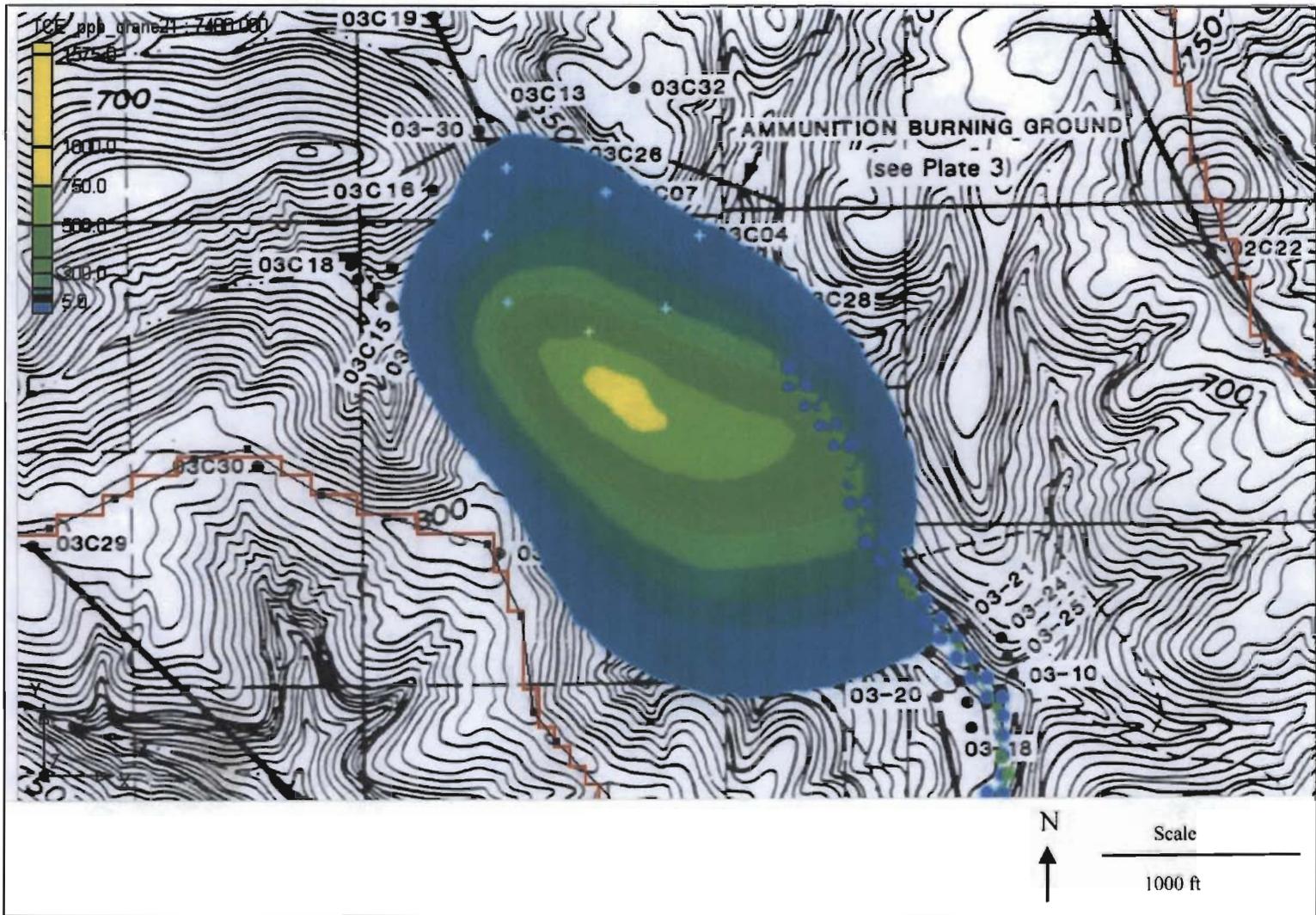


Figure 46. Distribution of TCE plume (simulated) 20 years into the future

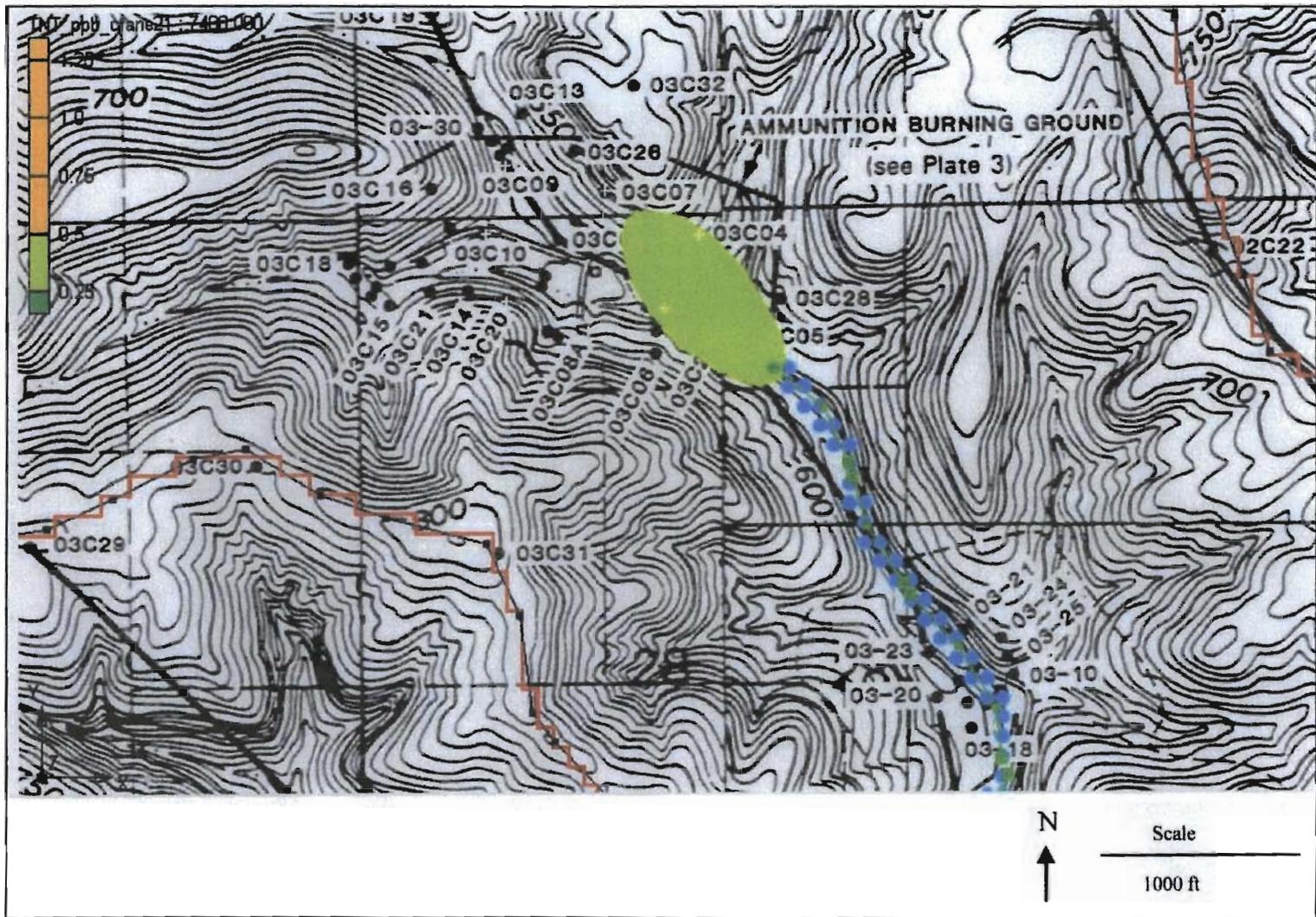


Figure 47. Distribution of TNT plume (simulated) 20 years into the future

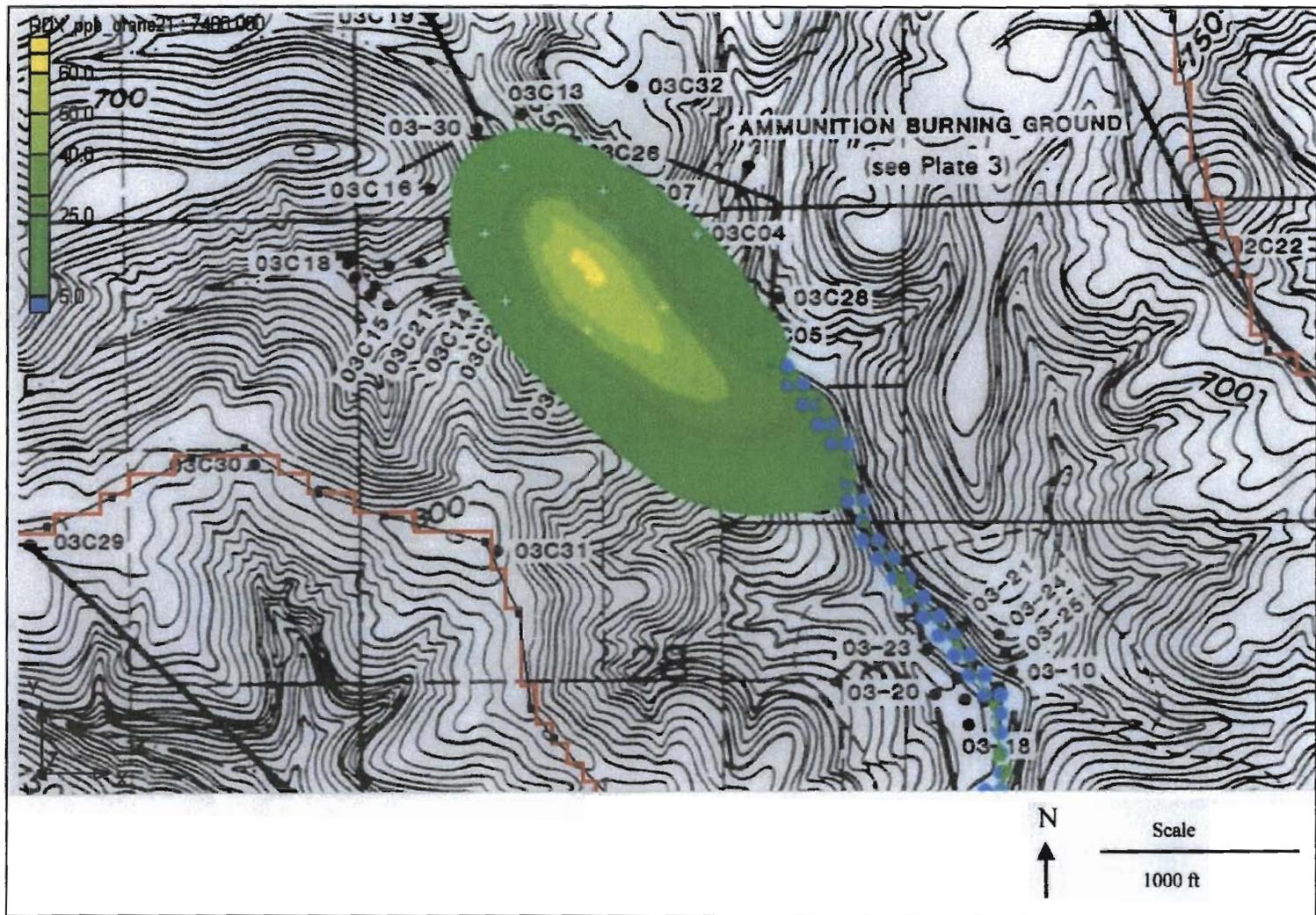


Figure 48. Distribution of RDX plume (simulated) 20 years into the future

Table 1
Monitoring Well Construction Details, Naval Surface Warfare Center, Crane, Indiana

Well I.D.	North Coordinate	East Coordinate	Ground Elevation ^(b) (ft)	Top of Casing Elevation ^(b,c) (ft)	Top/Bottom of Screen (ft BGS)	Screened Formation ^(a)	Total Depth (ft BGS)	Depth to Bedrock (ft BGS)
Ammunition Burning Grounds								
03B02	1302809.5	3048253.0	502.08	503.79	9.6-14.6	Alluvium	15.8	NA
03B04	1302867.5	3048040.1	504.54	506.37	9.5-14.5	Alluvium	16.5	NA
03C02P2	1310168.4	3047545.5	580.79	582.90	38.0-48.0	Beech Creek	49.0	NA
03C03	1310439.5	3046802.9	597.63	599.70	139.0-149.0	Beaver Bend	150.7	NA
03C04	1310497.1	3047530.7	622.34	624.26	73.5-83.5	Beech Creek	85.3	NA
03C07	1310659.1	3047118.4	634.48	636.32	88.7-98.7	Beech Creek	101.6	NA
03C08P2	1309937.9	3046761.2	624.19	629.15	90.0-100.0	Beech Creek	101.6	NA
03C09P2	1310856.1	3046523.3	601.12	603.38	62.0-72.0	Beech Creek	73.0	NA
03C10	1310479.3	3046404.4	605.95	607.92	66.0-76.0	Beech Creek	78.8	NA
03C11	1310261.2	3047188.0	589.94	592.26	47.5-57.5	Beech Creek	59.5	NA
03C12	1310193.9	3047321.7	586.37	587.13	39.0-49.0	Beech Creek	51.2	NA
03C15	1310086.1	3045893.7	618.87	621.10	88.5-98.5	Beech Creek	101.1	NA
03C17	1313000.2	3047118.5	693.92	696.01	138.5-148.5	Beech Creek	149.5	NA
03C20	1310116.8	3046520.8	644.82	646.55	108.0-118.0	Beech Creek	120.0	NA
03C25	1307385.0	3045357.6	594.94	596.68	59.7-69.7	Beech Creek	70.7	NA
03C26	1310931.7	3046881.6	638.78	640.62	94.0-104.0	Beech Creek	105.7	NA
03C27	1309894.9	3047514.8	601.70	603.75	60.5-70.5	Beech Creek	73.3	NA
03C30	1309204.0	3045150.2	776.90	778.72	250.5-260.5	Beech Creek	263.6	NA
Little Sulphur Creek at Boundary	1302793.2	3048273.3	497.20	NA	NA	NA	NA	NA
Little Sulphur Creek below Spring A	1303954.8	3048269.2	506.73	NA	NA	NA	NA	NA
Spring A	1304029.7	3048278.4	507.18	NA	NA	NA	NA	NA
Spring C	1306151.7	3049225.1	528.98	NA	NA	NA	NA	NA

Table 2
Ammunition Burning Grounds, Quarterly Monitoring – Quarters 1 through 8, Naval Surface Warfare Center, Crane, Indiana

Monitoring Point	Field ⁽¹⁾	Volatiles ⁽¹⁾	Dissolved Gases ⁽¹⁾	Explosives ⁽¹⁾	Metals ⁽¹⁾ (Total)	Metals ⁽¹⁾ (Dissolved)	Cyanide	TOX	TOC	Sulfide	Sulfate	Phosphorus (Total and Dissolved)	Chloride
03B02	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03B04	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C02P2	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C03	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C04	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C07	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C08P2	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C09P2	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C10	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C11	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C12	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C15	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C17	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C20	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C25	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
03C26	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C27	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
03C30	A, B	B		A	A, D	A, C, D	*	*	*	*	*	*	*
Little Sulphur Creek Below Spring A	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
Little Sulphur Creek at Boundary	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
Spring A	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*
Spring C	A, B, C	B, C	A	A, B	A, B, D	A, C, D	*	*	*	*	*	*	*

¹ The letters A, B, C, etc., indicate subsets of the parameter group shown in the column headings. Specific parameters included in each subset are listed in Appendix D of this approved FSP.

Table 3
Summary of Sample Analysis and Quality Control Samples,
Quarterly Monitoring-Quarters 1 through 8, Ammunition Burning
Grounds, Naval Surface Warfare Center, Crane, Indiana

Parameter ⁽¹⁾	Samples	Field Duplicates ⁽²⁾	Trip Blanks ⁽³⁾	Ambient Blanks ⁽⁴⁾	Matrix Spike/ Duplicates ⁽⁵⁾	Total ⁽⁶⁾
Laboratory						
TCE & degradation products/volatiles	22	3	TBD	TBD	2/2	29+
Dissolved methane/ ethane/ethene	12	2	NA	TBD	NA	14+
Explosives – subset A	22	3	NA	TBD	2/2	29+
Explosives – subset B	12	2	NA	TBD	1/1	16+
Metals (total)	22	3	NA	TBD	2/2	29+
Metals (dissolved)	22	3	NA	TBD	2/2	29+
Cyanide	22	3	NA	TBD	2/2	29+
Sulfate	22	3	NA	TBD	2/2	29+
Phosphorus (total)	22	3	NA	TBD	2/2	29+
Phosphorus (dissolved)	22	3	NA	TBD	2/2	29+
TOC	22	3	NA	TBD	2/2	29+
TOX	22	3	NA	TBD	2/2	29+
Sulfide	12	2 *	NA	TBD	1/1	16+
Chloride	22	3	NA	TBD	2/2	29+
Field						
Dissolved oxygen ⁽⁷⁾	22	NA	NA	NA	NA	22
PH	22	NA	NA	NA	NA	22
Specific conductance	22	NA	NA	NA	NA	22
Temperature	22	NA	NA	NA	NA	22
Turbidity	22	NA	NA	NA	NA	22
ORP	22	NA	NA	NA	NA	22
Alkalinity	22	3	NA	NA	NA	25
Carbon Dioxide	12	2	NA	NA	NA	14
Dissolved oxygen ⁽⁸⁾	12	2	NA	NA	NA	14
Ferrous Iron	12	2	NA	NA	NA	14
Hydrogen sulfide	12	2	NA	NA	NA	14
Nitrate	12	2	NA	NA	NA	14
Nitrite	12	2	NA	NA	NA	14
Water level	18	NA	NA	NA	NA	18

¹ See Table 2 of this approved FSP in conjunction with Table 1-3 of the approved QAPP for ABG-specific analysis requirements.

² Field duplicates will be collected at a minimum frequency of 1 per 10 samples. Field duplicates are not applicable (NA) for field measurements obtained by using a flow-through meter or a water-level meter.

³ Trip blanks will be submitted for analysis at a frequency of one per cooler containing samples for volatile organics analysis. Because the number of sample coolers shipped varies, totals are to be determined (TBD).

⁴ Ambient blanks will be collected at the discretion of the FOL, to delineate site conditions. Because site conditions vary, totals are to be determined (TBD). Ambient blanks are not applicable for field analyses (NA).

⁵ Matrix spike (MS) and duplicate samples will be collected at a frequency of 1 per 20 samples. For inorganics, an MS and a sample duplicate will be collected and, for organics, an MS and a matrix spike duplicate (MSD) will be collected. MS/MSDs and sample duplicates are not applicable for field analyses (NA).

⁶ Plus sign (+) indicates potential for the total number of samples to increase, due to TBD variables.

⁷ Dissolved oxygen is measured by a flow-through meter for determination of stabilization conditions.

⁸ Dissolved oxygen is analyzed by field kit for monitoring of natural attenuation.

NA Not Applicable
TBD To be Determined
TCE Trichloroethene
TOC Total organic carbon
TOX Total organic halogens
ORP Oxidation-reduction potential

**Table 4
Summary of Sample Analysis and Quality Control Samples, Quarterly
Monitoring-Quarters 1 through 8, Ammunition Burning Grounds,
Naval Surface Warfare Center, Crane, Indiana**

Parameter ⁽¹⁾	Samples	Field Duplicates ⁽²⁾	Trip Blanks ⁽³⁾	Ambient Blanks ⁽⁴⁾	Matrix Spike/ Duplicates ⁽⁵⁾	Total ⁽⁶⁾
Laboratory						
TCE & degradation products/volatiles	22	3	TBD	TBD	2/2	29+
Dissolved methane/ethane/ethene	12	2	NA	TBD	NA	14+
Explosives – subset A	22	3	NA	TBD	2/2	29+
Explosives – subset B	12	2	NA	TBD	1/1	16+
Metals (total)	22	3	NA	TBD	2/2	29+
Metals (dissolved)	22	3	NA	TBD	2/2	29+
Cyanide	22	3	NA	TBD	2/2	29+
Sulfate	22	3	NA	TBD	2/2	29+
Phosphorus (total)	22	3	NA	TBD	2/2	29+
Phosphorus (dissolved)	22	3	NA	TBD	2/2	29+
TOC	22	3	NA	TBD	2/2	29+
TOX	22	3	NA	TBD	2/2	29+
Sulfide	12	2	NA	TBD	1/1	16+
Chloride	22	3	NA	TBD	2/2	29+
Field						
Dissolved oxygen ⁽⁷⁾	22	NA	NA	NA	NA	22
PH	22	NA	NA	NA	NA	22
Specific conductance	22	NA	NA	NA	NA	22
Temperature	22	NA	NA	NA	NA	22
Turbidity	22	NA	NA	NA	NA	22
ORP	22	NA	NA	NA	NA	22
Alkalinity	22	3	NA	NA	NA	25
Carbon Dioxide	12	2	NA	NA	NA	14
Dissolved oxygen ⁽⁸⁾	12	2	NA	NA	NA	14
Ferrous Iron	12	2	NA	NA	NA	14
Hydrogen sulfide	12	2	NA	NA	NA	14
Nitrate	12	2	NA	NA	NA	14
Nitrite	12	2	NA	NA	NA	14
Water level	18	NA	NA	NA	NA	18

¹ See Table 2 of this approved FSP in conjunction with Table 1-3 of the approved QAPP for ABG-specific analysis requirements.

² Field duplicates will be collected at a minimum frequency of 1 per 10 samples. Field duplicates are not applicable (NA) for field measurements obtained by using a flow-through meter or a water-level meter.

³ Trip blanks will be submitted for analysis at a frequency of one per cooler containing samples for volatile organics analysis. Because the number of sample coolers shipped varies, totals are to be determined (TBD).

⁴ Ambient blanks will be collected at the discretion of the FOL, to delineate site conditions. Because site conditions vary, totals are to be determined (TBD). Ambient blanks are not applicable for field analyses (NA).

⁵ Matrix spike (MS) and duplicate samples will be collected at a frequency of 1 per 20 samples. For inorganics, an MS and a sample duplicate will be collected and, for organics, an MS and a matrix spike duplicate (MSD) will be collected. MS/MSDs and sample duplicates are not applicable for field analyses (NA).

⁶ Plus sign (+) indicates potential for the total number of samples to increase, due to TBD variables.

⁷ Dissolved oxygen is measured by a flow-through meter for determination of stabilization conditions.

⁸ Dissolved oxygen is analyzed by field kit for monitoring of natural attenuation.

NA Not Applicable
TBD To be Determined
TCE Trichloroethene
TOC Total organic carbon
TOX Total organic halogens
ORP Oxidation-reduction potential

Table 5
Quarterly Results for FY1999 and FY2000 for TCE, RDX, and TNT

Location	Sample Date	TCE	RDX	TNT
B02	11/05/1998	0.5 U	0.53 U	0.53 U
B02	03/10/1999	0.5 U	0.58 U	0.58 U
B02	05/18/1999	0.5 U	0.95 UJ	0.95 UJ
B02	09/14/1999	0.5 U	0.3 U	0.3 U
B02	12/29/1999	0.5 U	1.2 U	1.2 U
B02	03/28/2000	0.5 U	0.56 U	0.6 U
B02	06/23/2000	0.5 U	0.74 U	0.79 U
B02	09/07/2000	0.5 U	0.22 U	0.22 U
B04	11/09/1998	0.5 U	0.42 U	0.42 U
B04	02/23/1999	0.5 U	0.94 U	0.94 U
B04	05/17/1999	0.5 U	0.52 U	0.52 U
B04	09/14/1999	0.5 U	0.64 U	0.64 U
B04	01/11/2000	0.5 U	0.70 U	0.74 U
B04	03/27/2000	0.5 U	0.63 U	0.68 U
B04	06/26/2000	0.5 U	1.1 U	1.1 U
B04	09/08/2000	0.5 U	0.88 U	0.88 U
C02P2	11/09/1998	28	21	0.48 U
C02P2	02/26/1999	7.7	2.9	0.49 U
C02P2	05/19/1999	3.2	1.9	0.71 U
C02P2	09/14/1999	10	17	0.95 U
C02P2	12/15/1999	12	3.8 PZ	1.2 U
C02P2	03/06/2000	12	12 J	0.42 U
C02P2	06/08/2000	9.2 U	17	1.1 U
C02P2	09/18/2000	11	12	0.52 U
C03	11/06/1998	0.5 U	0.78 U	0.78 U
C03	02/27/1999	0.5 U	1.0 U	1.0 U
C03	05/18/1999	0.5 U	0.20 U	0.20 U
C03	09/20/1999	0.5 U	0.7 U	0.7 U
C03	12/20/1999	0.5 U	0.87 U	0.92 U
C03	04/01/2000	0.5 U	1.1 U	1.2 U
C03	06/19/2000	0.5 U	1 U	1.1 U
C03	09/12/2000	0.5 U	0.68 U	0.68 U
C04	11/11/1998	0.5 U	0.71 U	0.71 U
C04	02/27/1999	0.5 U	0.46 U	0.46 U
C04	05/21/1999	0.6	1 U	1 U
C04	09/20/1999	0.5 U	1.5 U	1.5 U
C04	01/05/2000	0.5 U	0.88 U	0.94 U
C04	06/19/2000	0.5 U	0.57 U	0.61 U
C04	09/13/2000	0.5 U	1.1 U	1.1 U
C04	3/14/00 - 3/18/00	0.5 U	0.5 U	0.53 U

(Sheet 1 of 4)

Notes:

U – The analyte of interest was not detected, to the limit of detection indicated.

J – The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

P – When a dual column technique is employed, this flag indicates that calculated results from the two columns differ by more than 25 percent.

Z – The value reported is from the C18 column and there is coelution with another target analyte or the CN/C8 columns in series.

Table 5 (Continued)

Location	Sample Date	TCE	RDX	TNT
C07	11/11/1998	4.1	36	0.65 U
C07	02/26/1999	4.1	28	0.42 U
C07	02/26/1999	4.7	23	1.2 U
C07	05/19/1999	3	19	0.64 U
C07	09/20/1999	4.3	21	0.23 U
C07	03/14/2000	4.5	34	1.3 U
C07	06/15/2000	2.9	27	1.3 U
C07	09/08/2000	4.6	30	0.64 U
C08P2	11/10/1998	59	100	1.2 U
C08P2	03/12/1999	71	110	1.2 U
C08P2	05/24/1999	61	81	0.44 U
C08P2	09/20/1999	62 E	86	0.79 U
C08P2	03/30/2000	63 D	90	0.44 U
C08P2	06/20/2000	77 D	95 DX	0.46 U
C08P2	09/13/2000	69 E	87	0.94 U
C09P2	11/08/1998	160 J	170	1.2 U
C09P2	03/01/1999	160	130	0.44 U
C09P2	05/19/1999	150	150	0.75 U
C09P2	09/20/1999	160 E	120 E	0.31 U
C09P2	12/17/1999	170 D	190 PZ	1.8 U
C09P2	03/25/2000	120 D	160 DX	0.75 U
C09P2	06/06/2000	110 U	180	1 U
C09P2	09/15/2000	140 E	160 E	0.46 U
C10	11/08/1998	59	130	1.4 U
C10	02/25/1999	63	140	1.5 U
C10	05/22/1999	63	100	0.65 U
C10	09/14/1999	63 E	100 E	0.49 U
C10	12/20/1999	55 D	130 PZ	1.4 U
C10	04/01/2000	54 D	130	0.95 U
C10	06/23/2000	72 D	110 DX	0.55 U
C10	09/08/2000	70 E	120	0.87 U
C11	11/06/1998	1500	27	1.2 U
C11	02/25/1999	2100	34	1.0 U
C11	05/21/1999	760	12	0.71 U
C11	09/20/1999	590 E	25	0.51 U
C11	12/21/1999	2400 D	32 Z	0.90 U
C11	03/22/2000	2200 D	31	1.2 U
C11	06/06/2000	2500 U	29	0.58 U
C11	09/15/2000	510 E	35	1.6 U

*(Sheet 2 of 4)***Notes:**

U – The analyte of interest was not detected, to the limit of detection indicated.

J – The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

D – The value reported is derived from the analysis of a diluted sample or sample extract.

P – When a dual column technique is employed, this flag indicates that calculated results from the two columns differ by more than 25 percent.

E – The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

X – The sample has been analyzed at several dilutions. The value reported has been determined to be the most appropriate quantitative value.

Z – The value reported is from the C18 column and there is coelution with another target analyte or the CN/C8 columns in series.

Table 5 (Continued)

Location	Sample Date	TCE	RDX	TNT
C12	11/08/1998	21	32	0.68 U
C12	02/25/1999	22	14	0.74 U
C12	05/22/1999	19	11	0.30 U
C12	09/14/1999	21	28	0.75 U
C12	12/27/1999	28	22	1.2 U
C12	03/15/2000	21	12	0.46 U
C12	06/05/2000	20 U	26	0.81 U
C12	9/13-9/14 2000	20	15	0.53 U
C15	11/10/1998	0.5 U	0.75 U	0.75 U
C15	03/01/1999	0.5 U	0.49 U	0.49 U
C15	03/08/1999	0.5 U	1.3 U	1.4 U
C15	05/23/1999	0.5 U	1.1 U	1.1 U
C15	09/14/1999	0.5 U	1.4 U	1.4 U
C15	03/23/2000	0.5 U	0.99 U	1.1 U
C15	06/07/2000	0.5 U	0.55 U	0.58 U
C15	09/18/2000	0.5 U	0.77 U	0.77 U
C17	11/09/1998	0.5 U	0.95 U	0.95 U
C17	03/08/1999	0.5 U	1.2 U	1.2 U
C17	03/11/1999	0.5 U	1.0 U	1.1 U
C17	05/18/1999	0.5 U	0.36 U	0.36 U
C17	09/14/1999	0.5 U	1.4 U	1.4 U
C17	04/01/2000	0.5 U	0.5 U	0.53 U
C17	05/25/2000	0.5 U	0.68 U	0.73 U
C17	09/12/2000	0.5 U	1.4 U	1.4 U
C20	11/10/1998	3400	190	0.54
C20	02/24/1999	3600 D	200	1.7 U
C20	03/11/1999	3700	180	0.56 U
C20	05/22/1999	3300	150	0.68 U
C20	09/20/1999	730 E	170	1.1 U
C20	03/23/2000	3300 D	190 DX	0.68 U
C20	06/01/2000	3300 U	210 DX	0.73 U
C20	09/18/2000	3200 E	190	1.2 U
C25	11/07/1998	0.5 U	1.4 U	1.4 U
C25	02/24/1999	0.5 U	1.2 U	1.2 U
C25	05/25/1999	0.5 U	1 U	1 U
C25	09/14/1999	0.5 U	0.79 U	0.79 U
C25	12/14/1999	0.5 U	1.4 U	1.5 U
C25	03/24/2000	0.5 U	0.68 U	0.73 U
C25	05/25/2000	0.5 U	0.84 U	0.9 U
C25	09/07/2000	0.5 U	0.88 U	0.88 U
C26	11/10/1998	8.1	0.7	0.65 U
C26	03/02/1999	9.8	0.87	0.60 U
C26	03/02/1999	4.2	1.4 U	1.4 U
C26	05/23/1999	9.1	0.81 U	0.81 U
C26	09/20/1999	8.9	0.8	0.61 U
C26	03/29/2000	10	1.2	1 U
C26	06/21/2000	10	1.1 U	1.2 U
C26	09/14/2000	8.2	0.52	0.42 U

*(Sheet 3 of 4)***Notes:**

U – The analyte of interest was not detected, to the limit of detection indicated.

D – The value reported is derived from the analysis of a diluted sample or sample extract.

E – The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

X – The sample has been analyzed at several dilutions. The value reported has been determined to be the most appropriate quantitative value.

Table 5 (Continued)

Location	Sample Date	TCE	RDX	TNT
C27	11/09/1998	4.9	0.92 U	0.92 U
C27	03/02/1999	4	1.3 U	1.3 U
C27	05/24/1999	3.8	0.55 U	0.55 U
C27	09/14/1999	4.2	0.86 U	0.86 U
C27	12/16/1999	4.6	1.2 U	1.2 U
C27	03/28/2000	4.2	0.82 U	0.87 U
C27	06/21/2000	4.4	1.2 U	1.3 U
C27	09/12/2000	3.8	1.1 U	1.1 U
C30	11/11/1998	0.5 U	1.4 U	1.4 U
C30	03/08/1999	0.5 U	0.87 U	0.92 U
C30	03/08/1999	0.5 U	0.56 U	0.56 U
C30	05/24/1999	0.5 U	0.79 U	0.79 U
C30	09/14/1999	0.5 U	0.25 U	0.25 U
C30	03/21/2000	0.5 U	1.2 U	1.3 U
C30	06/28/2000	0.5 U	1.1 U	1.1 U
C30	09/19/2000	0.5 U	0.61 U	0.65 U
CREEK A	11/05/1998	0.5 U	28	0.71 U
CREEK A	02/28/1999	0.5 U	1.6	0.70 U
CREEK A	05/20/1999	0.5 U	3.6	0.55 U
CREEK A	01/10/2000	0.5 U	11 P	1.1 U
CREEK A	03/08/2000	0.5 U	4.5 PJ	1.3 U
CREEK A	06/09/2000	0.5 U	24	0.44 U
CREEK A	09/20/2000	0.5 U	17	0.91
CREEK B	11/05/1998	0.5 U	20	0.90 U
CREEK B	02/28/1999	0.5 U	1.0	0.65 U
CREEK B	05/20/1999	0.5 U	3.1	0.60 U
CREEK B	09/20/1999	0.5 U	3.8	0.52 U
CREEK B	12/28/1999	0.5 U	19	1.2 U
CREEK B	03/08/2000	0.5 U	7.2 J	0.53 U
CREEK B	06/09/2000	0.5 U	11	0.49 U
CREEK B	09/20/2000	0.5 U	11	0.94 U
SPRING A	11/05/1998	0.5 U	63	0.86U
SPRING A	02/28/1999	0.6	1.5	0.49 J
SPRING A	05/20/1999	0.5 U	6	0.84
SPRING A	09/20/1999	0.5 U	120	1.8
SPRING A	01/11/2000	0.5 U	33	2.1
SPRING A	03/29/2000	0.3 J	7.4	0.7
SPRING A	06/26/2000	0.5 U	11	0.96 U
SPRING A	09/29/2000	0.5 U	9.2	0.92 U
SPRING C	11/05/1998	0.5 U	1.4	0.79 U
SPRING C	02/28/1999	0.5 U	1.7	1.6 U
SPRING C	05/20/1999	0.5 U	1.9	0.66 U
SPRING C	09/20/1999	0.5 U	0.77	0.4 U
SPRING C	01/11/2000	0.5 U	6.0 P	0.66 U
SPRING C	03/14/2000	0.5 U	1.8	0.96 U
SPRING C	06/28/2000	0.5 U	4.1	0.79 U
SPRING C	09/29/2000	0.5 U	3.2	0.35 U

*(Sheet 4 of 4)***Notes:**

U – The analyte of interest was not detected, to the limit of detection indicated.

J – The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

P – When a dual column technique is employed, this flag indicates that calculated results from the two columns differ by more than 25 percent.

Table 6
Soil Analysis of Samples Obtained at NSWCC

% Sand	42.0
% Silt	44.0
% Clay	14.0
Soil Type	Loam
Bulk Density (g/cm ³)	1.50
CEC	13.42
pHb	7.75
pHw	7.4
OM (%)	3.280
Ca (kg/ha)	418.88
K (kg/ha)	96.98
Mg (kg/ha)	474.02
Mn (kg/ha)	101.60
Na (kg/ha)	104.90
Zn (kg/ha)	30.56
P (kg/ha)	12.03
TNT (kg/ha)	0.00

Table 7
Summary of Rate Equations for First-Order TNT Reactions (Chang 1981)

Order	Differential Form	Integrated Form	Half-Life	Units of the Rate Constant
1	$-d[A]/dt = k[A]$	$[A] = [A]_0 e^{-kt}$	$(\ln 2)/k$	s ⁻¹

Table 8
Freundlich Equation for Linear Soil Adsorption (Hasset and Banwart 1989)

$$C_s = K_f C_w^{1/n}$$

C_s = Amount adsorbed

C_w = Equilibrium concentration of sorbate

K_f = Partition constant

$1/n$ = Empirical constant

Table 9
Species Specific Degradation Constants and Half-Lives for First-Order Reactions with TNT

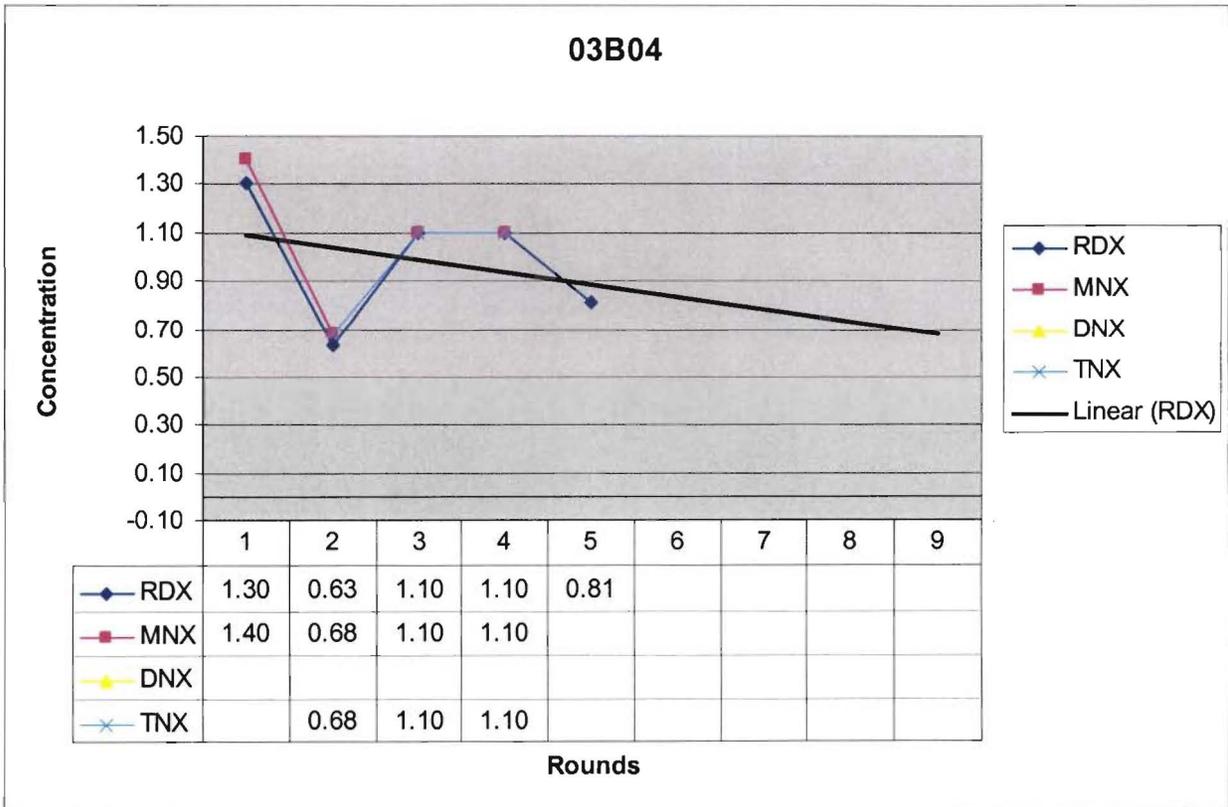
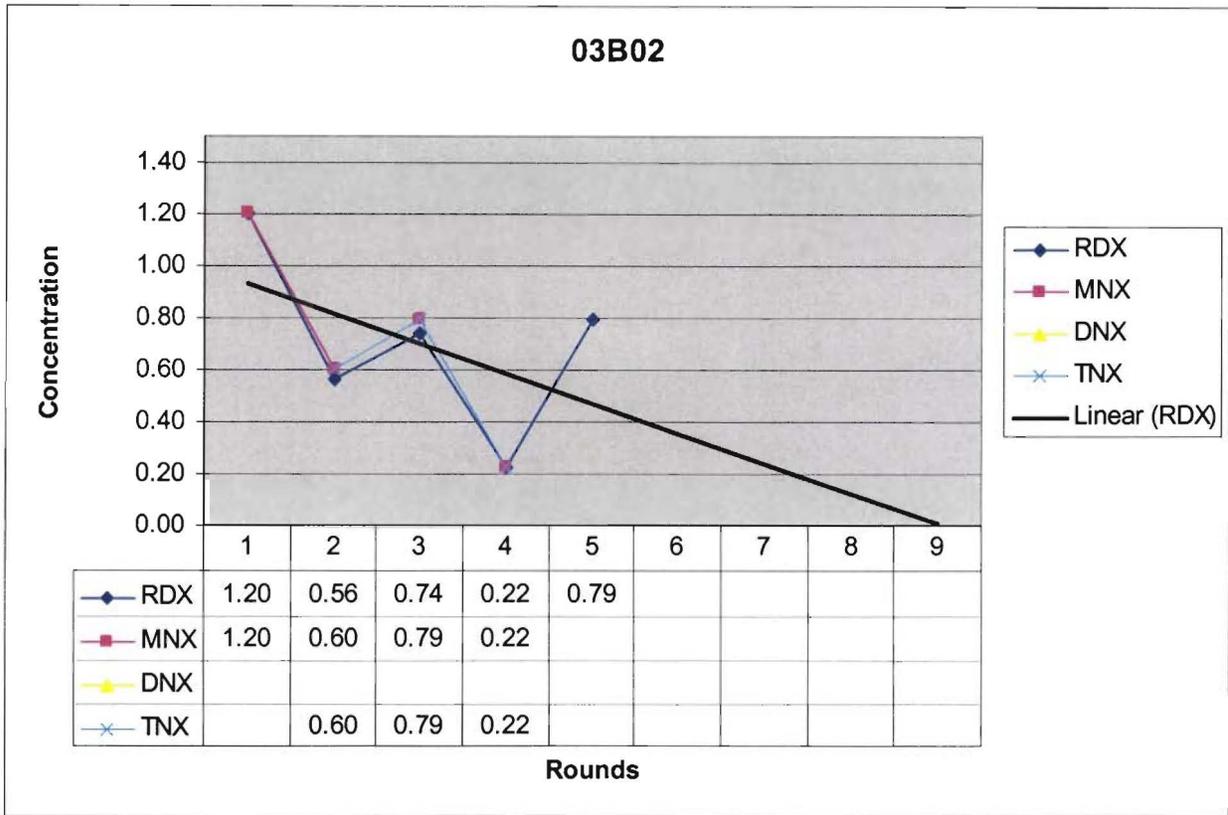
Plant	Degradation Constant (hr ⁻¹)	Half-Life (hr)
Fescue	0.4830	1.44
Switch Grass	0.3287	2.11
Little Blue Stem	0.1608	4.31
Sycamore	0.1550	4.47
Yucca	0.1326	5.22
Indian Grass	0.1237	5.60
Tulip Poplar	0.1226	5.65
Big Blue Stem	0.0625	11.09
Loblolly Pine	0.0288	24.07

Table 10						
Concentrations of Explosives and Their Degradation Products in the Crane Soil Sample, ppm						
RDX	TNX	TNT	TNB	4A-DNT	2A-DNT	HMX
1490	0.195	24.1	0.573	9.31	7.42	179
Analytes assayed but not detected include DNB, 2,6-DNT, 2,4-DNT, NB, 2-NT, 3-NT, 4-NT.						

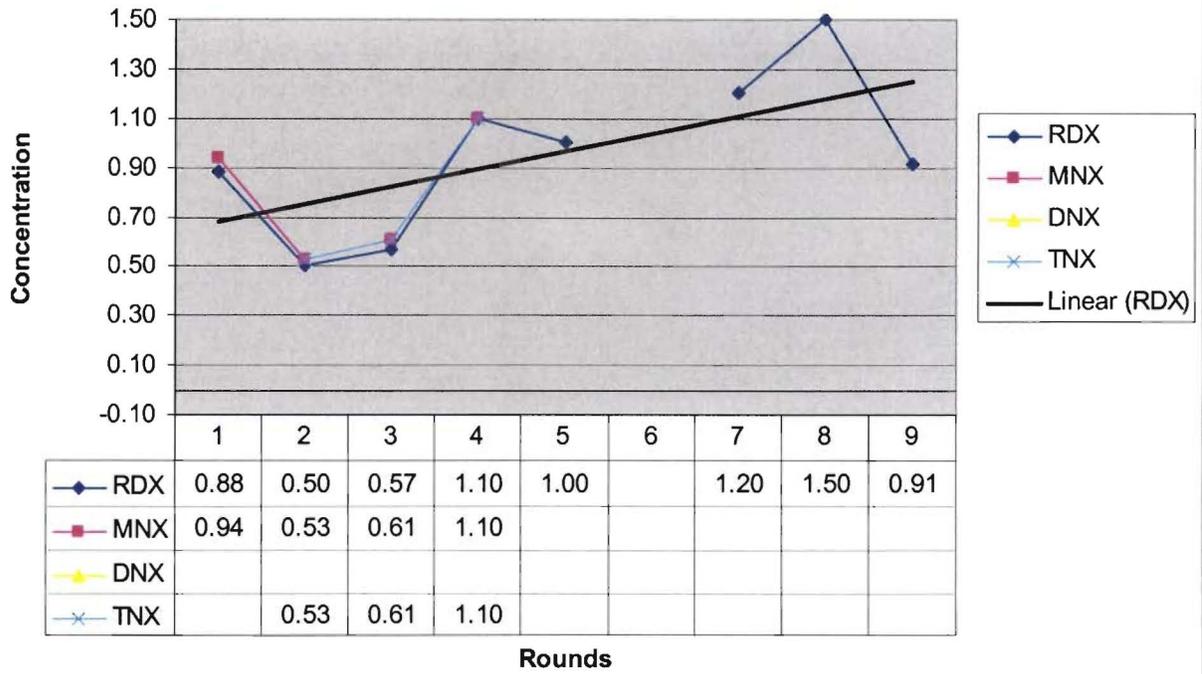
Table 11			
Parameters Used in the Crane MODFLOW and MT3D Model			
MODFLOW PARAMETERS			
	Formation		
	Alluvium	Big Clifty	Beech Creek
Horizontal Hydraulic Conductivity	0.3	2.0	2.0
Vertical Hydraulic Conductivity	0.3	0.2	0.2
Drain Conductance = 100 ft ² /day/ft			
MT3D PARAMETERS			
	Compound		
	TCE	TNT	RDX
Distribution Coefficient (Kd) (L/mg)	0.003	0.15	0.21
Rate Constant (1/day)	0.003	1.0 x 10 ⁻⁵	8.13 x 10 ⁻⁵
Longitudinal Dispersivity = 100 ft			
Transverse Dispersivity = 33 ft			
Vertical Dispersivity = 3.3 ft			
Bulk Density = 68 lb/ft ³			
Porosity = 0.30			

Appendix A

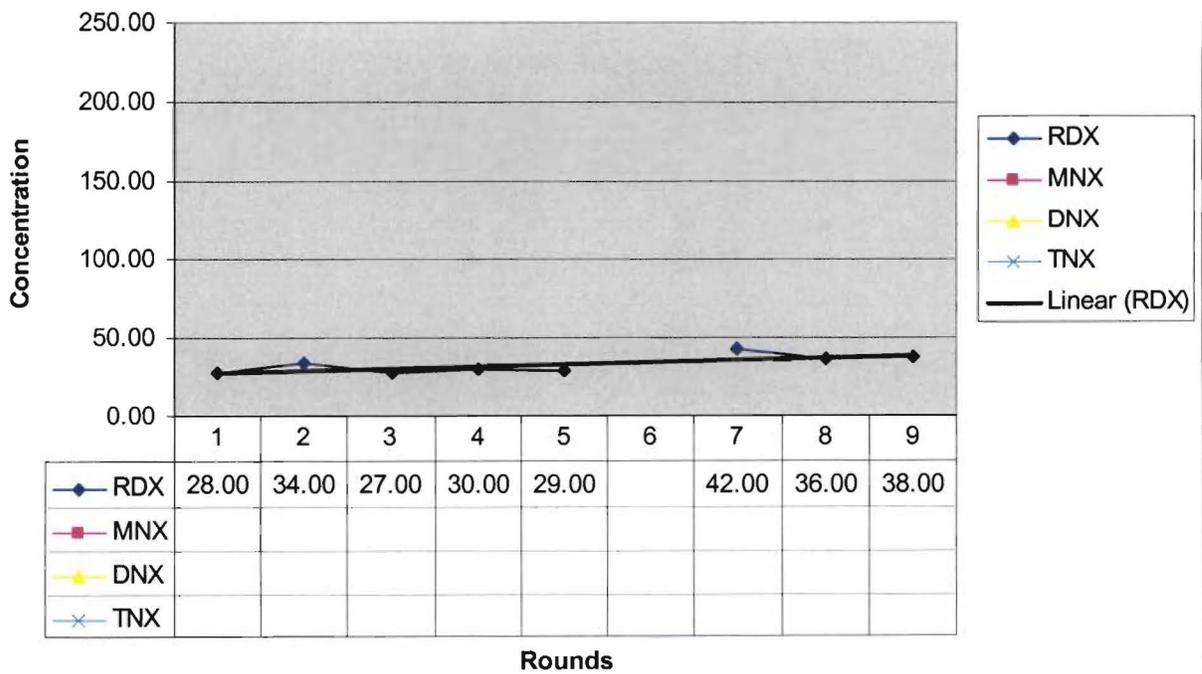
Trend Analysis for RDX and Breakdown Products

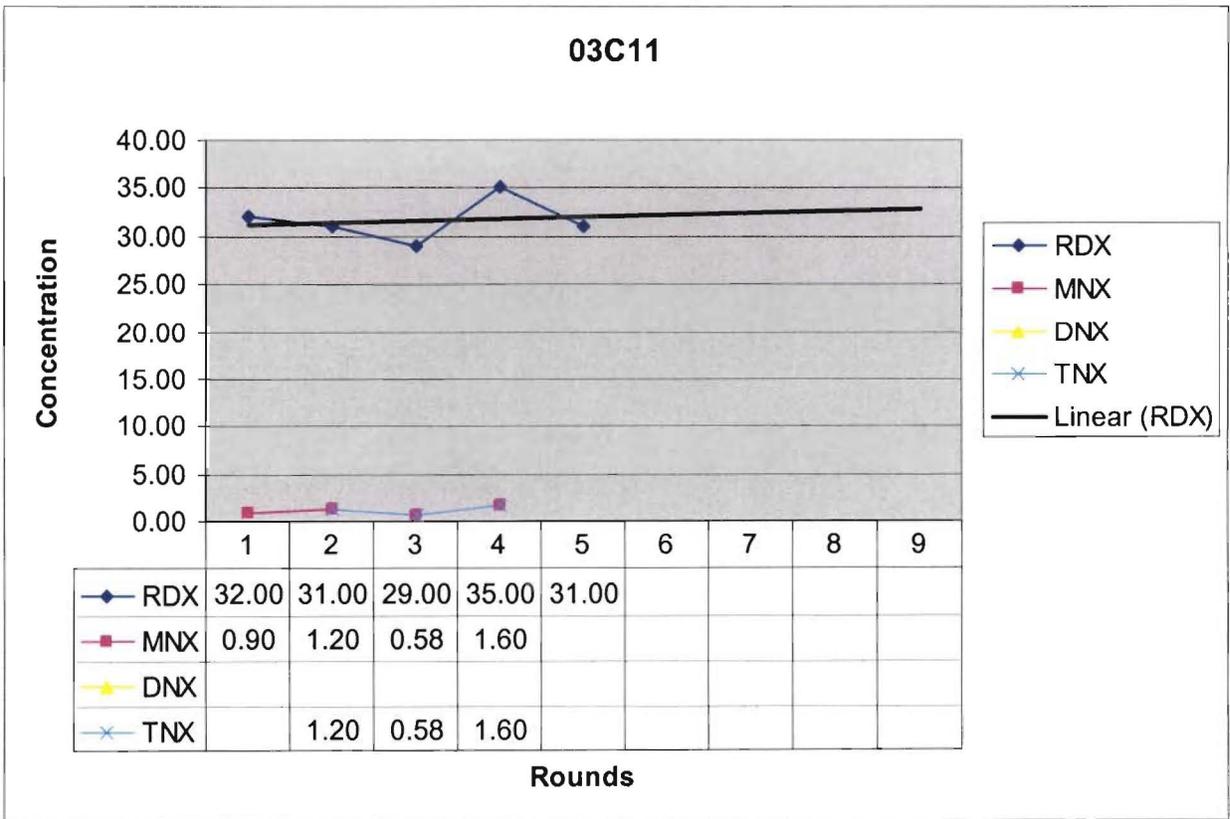
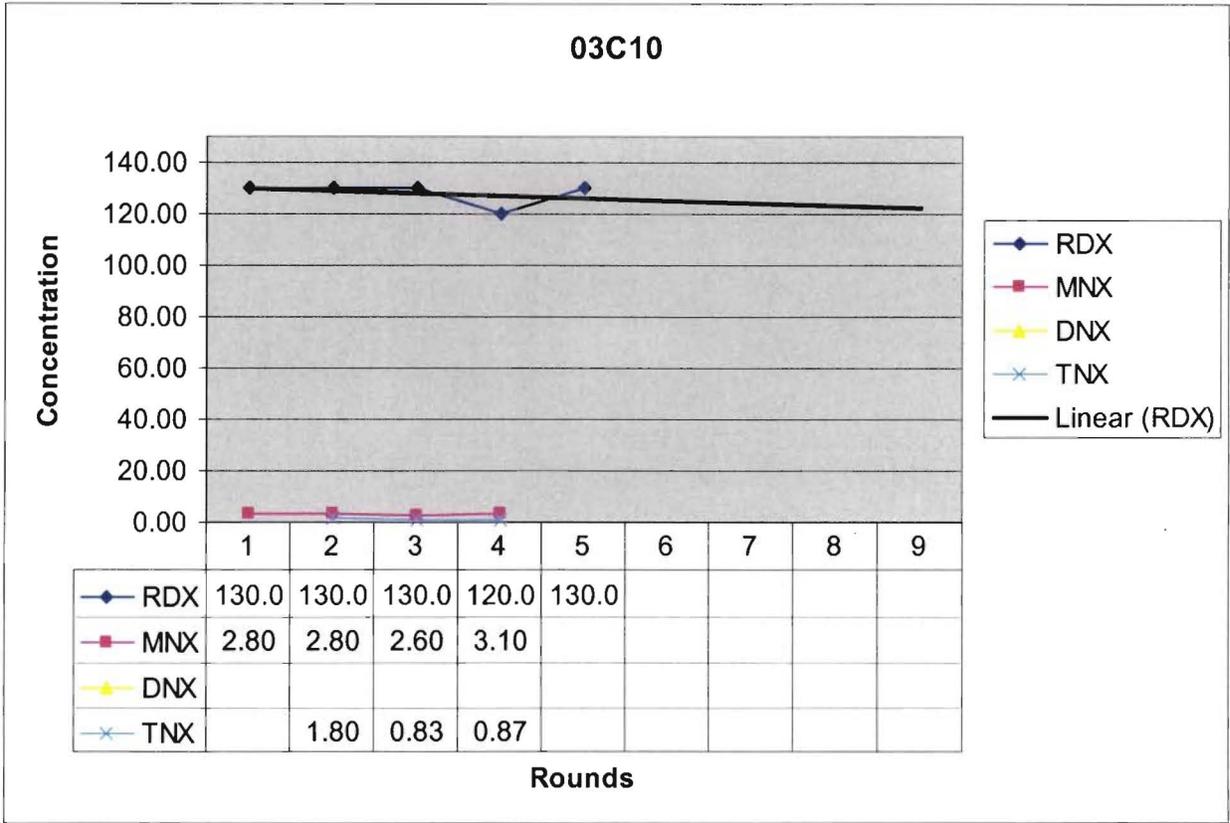


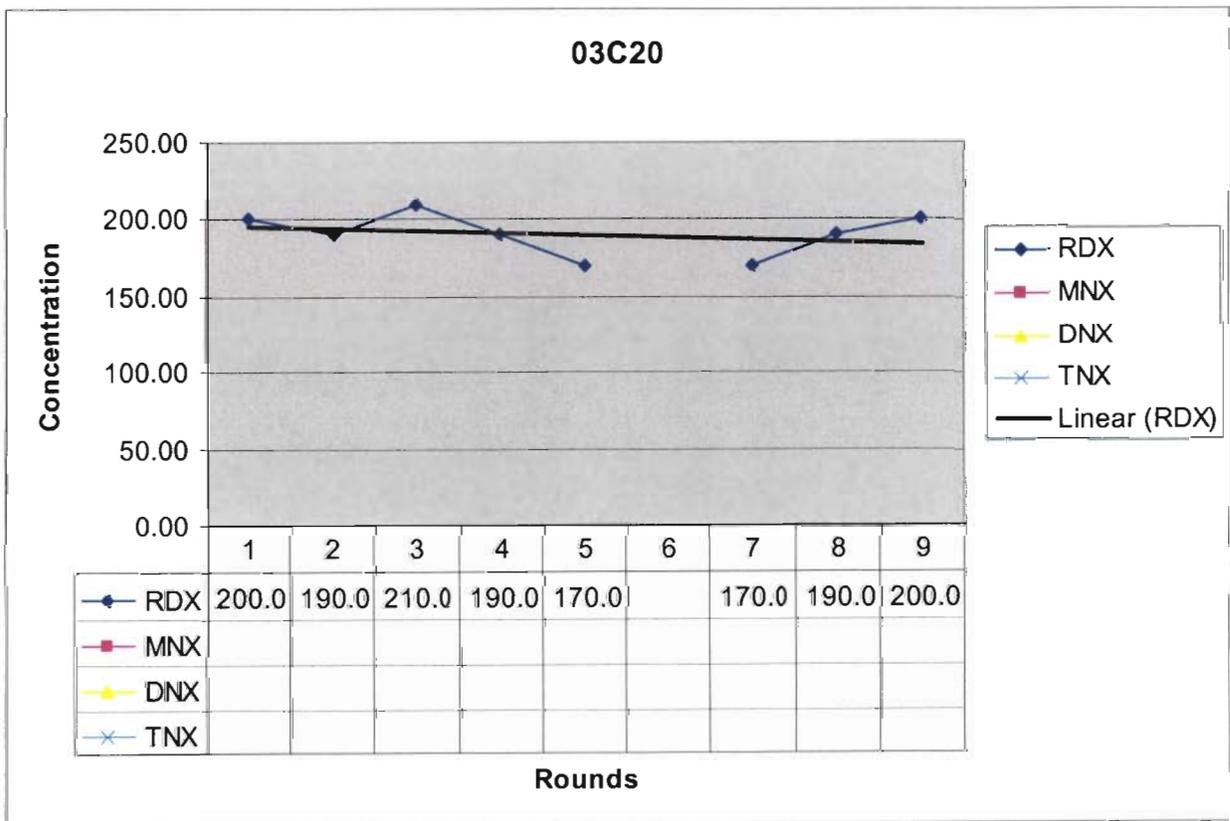
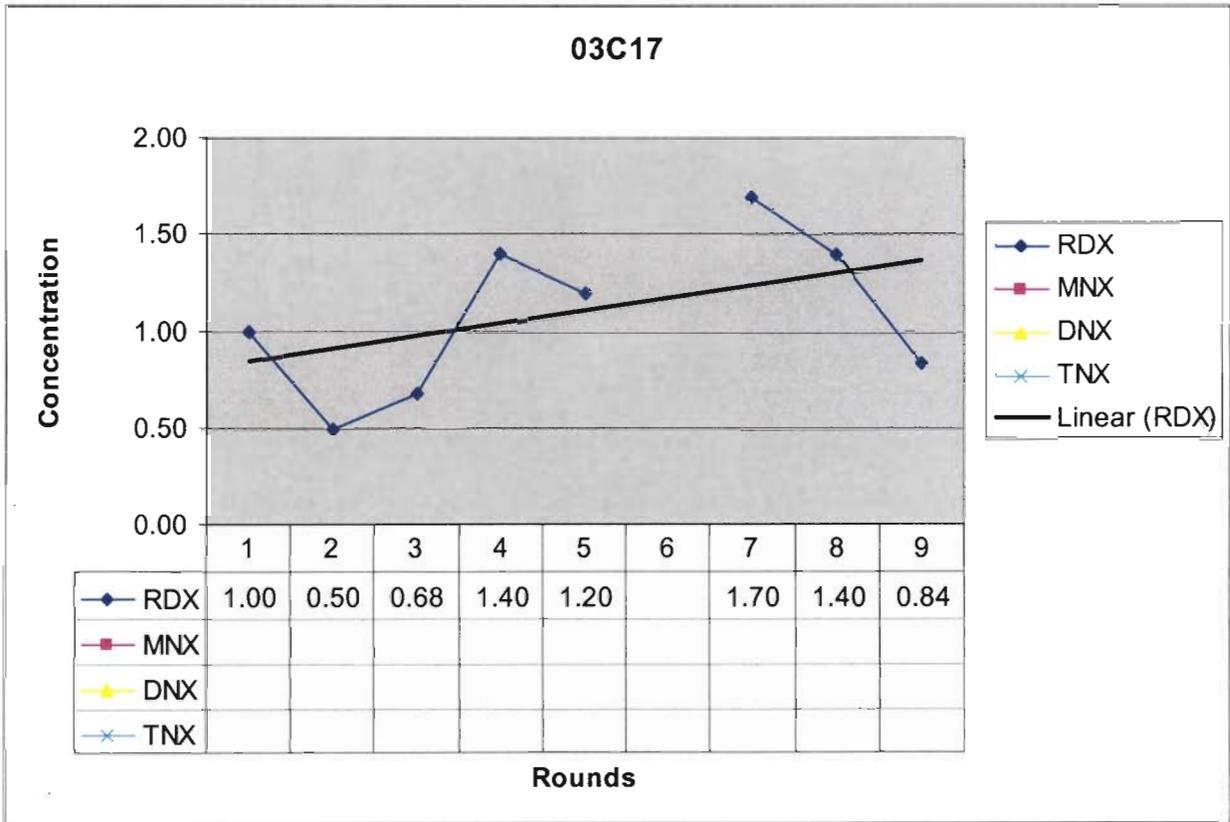
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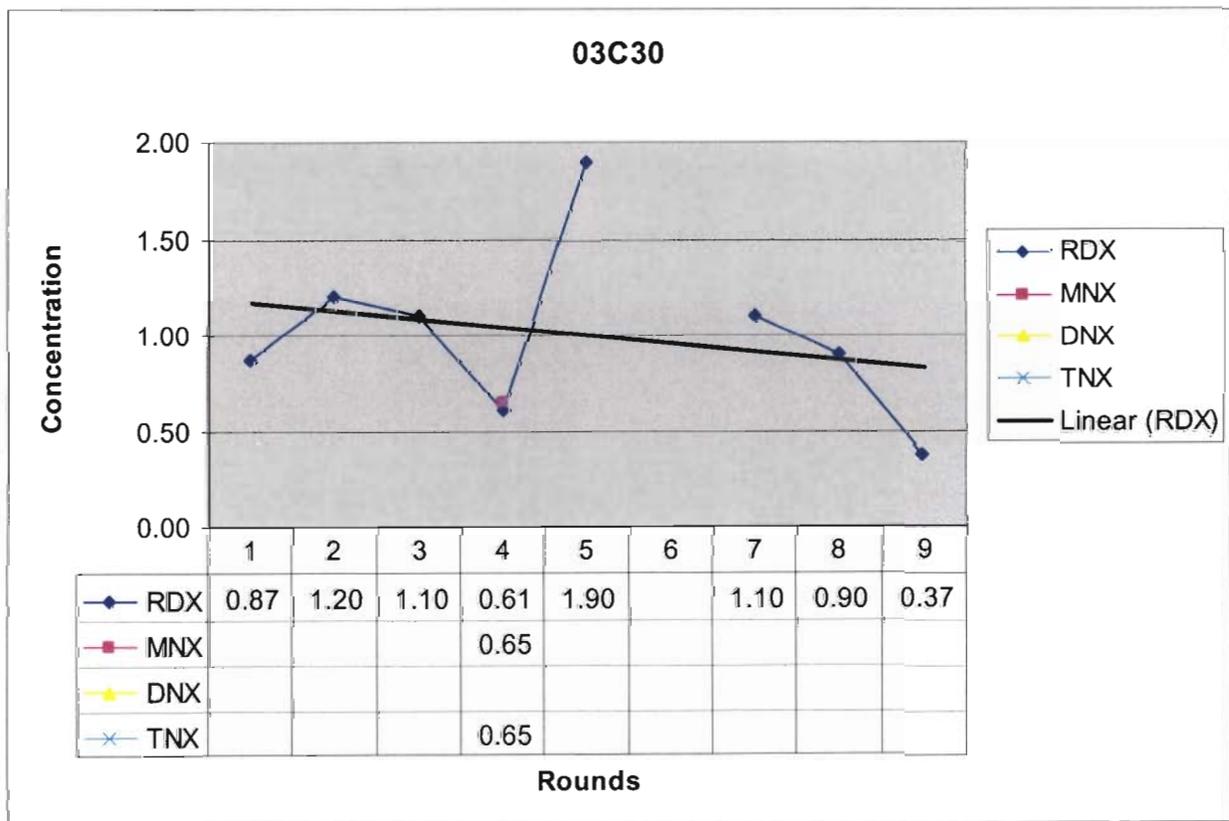
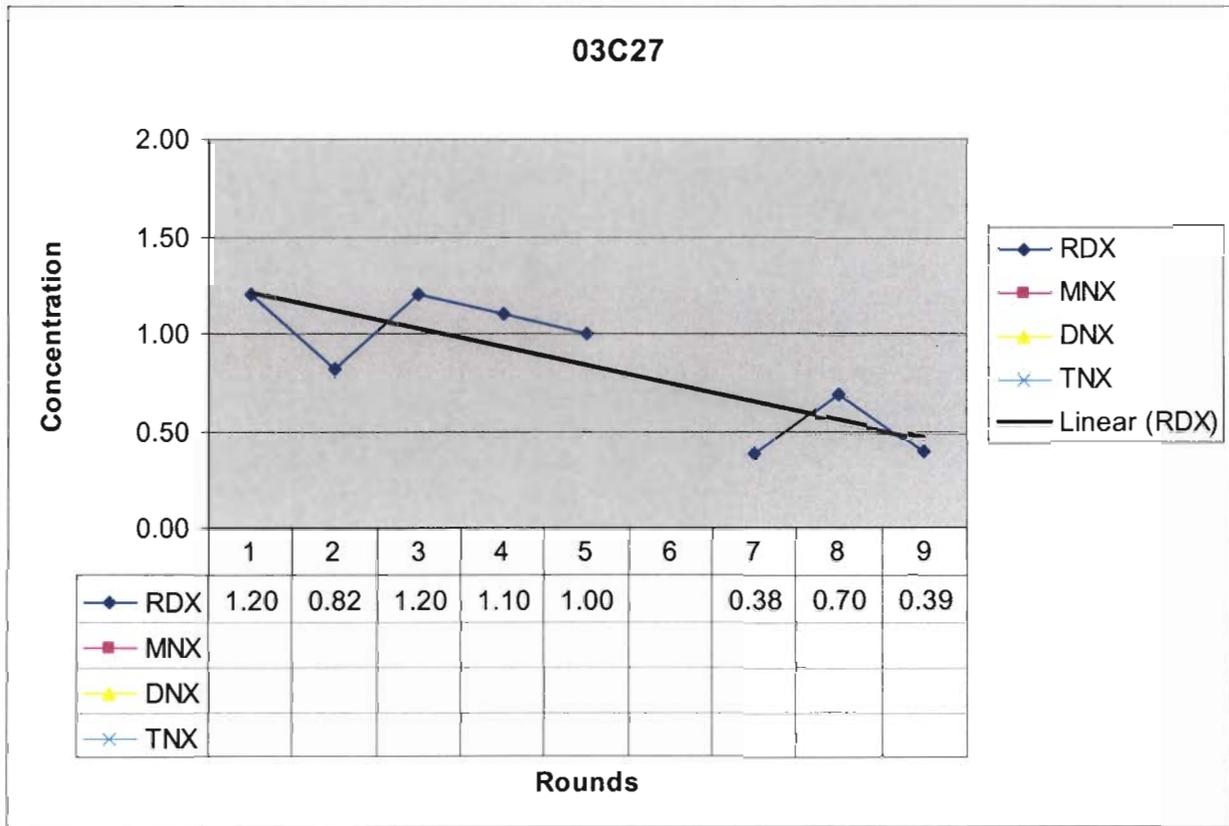


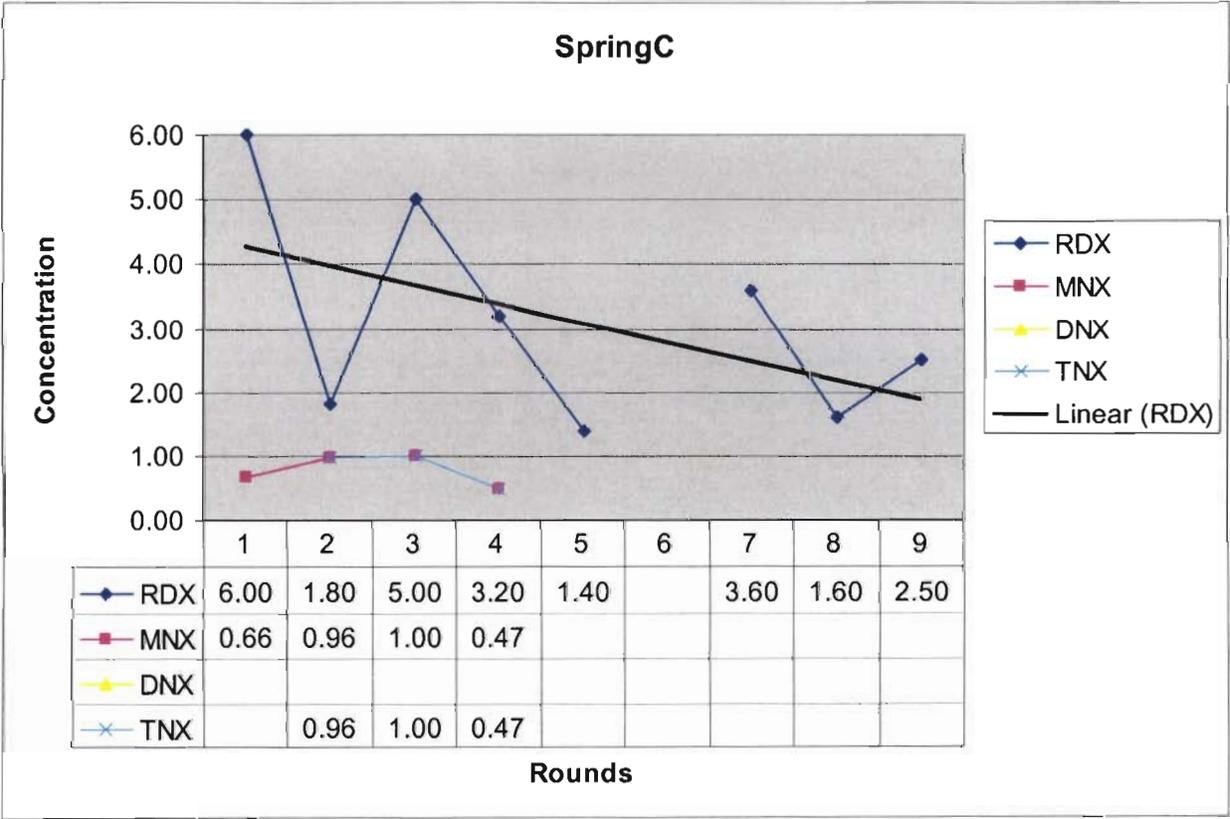
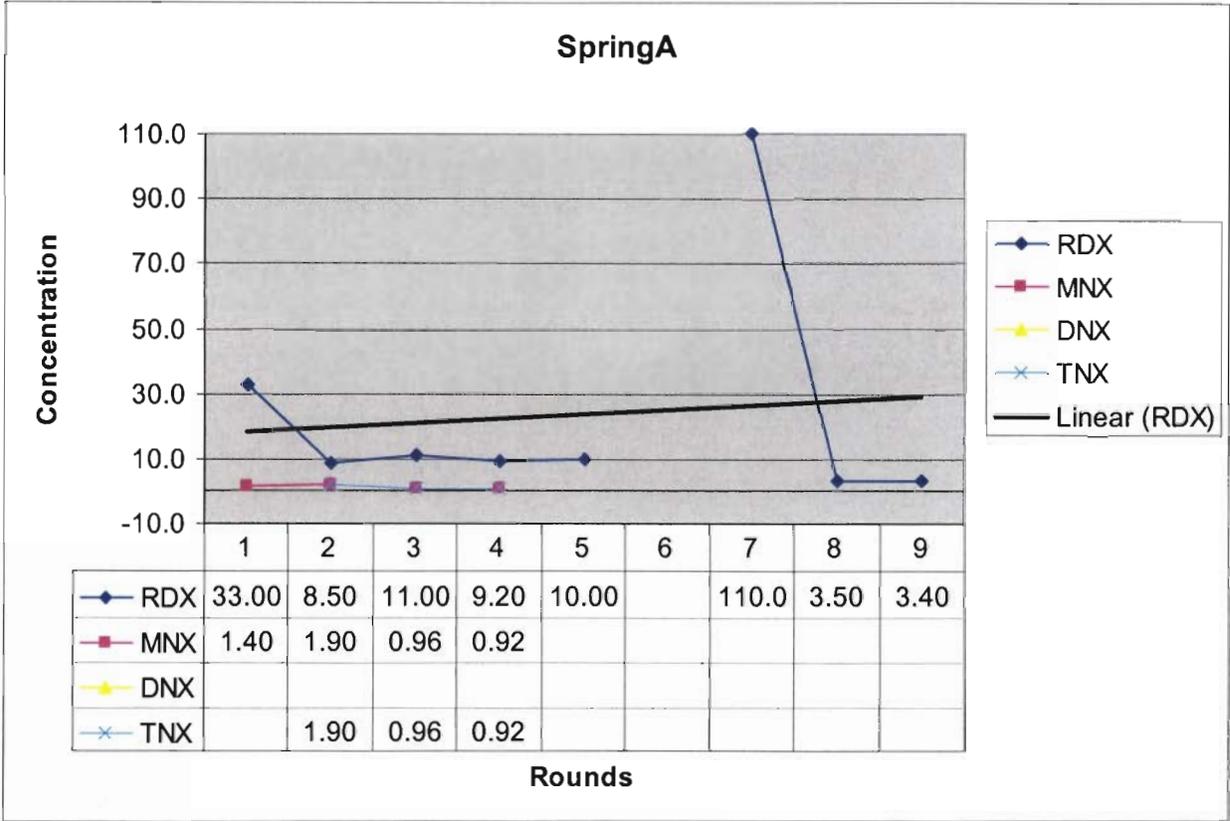
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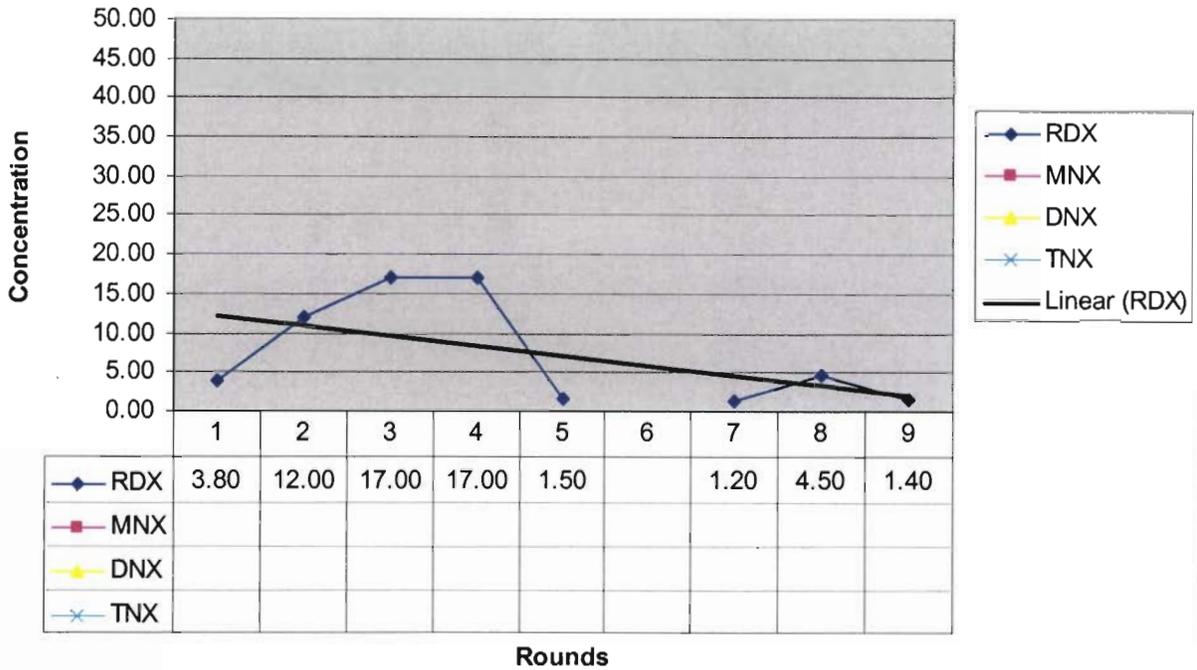




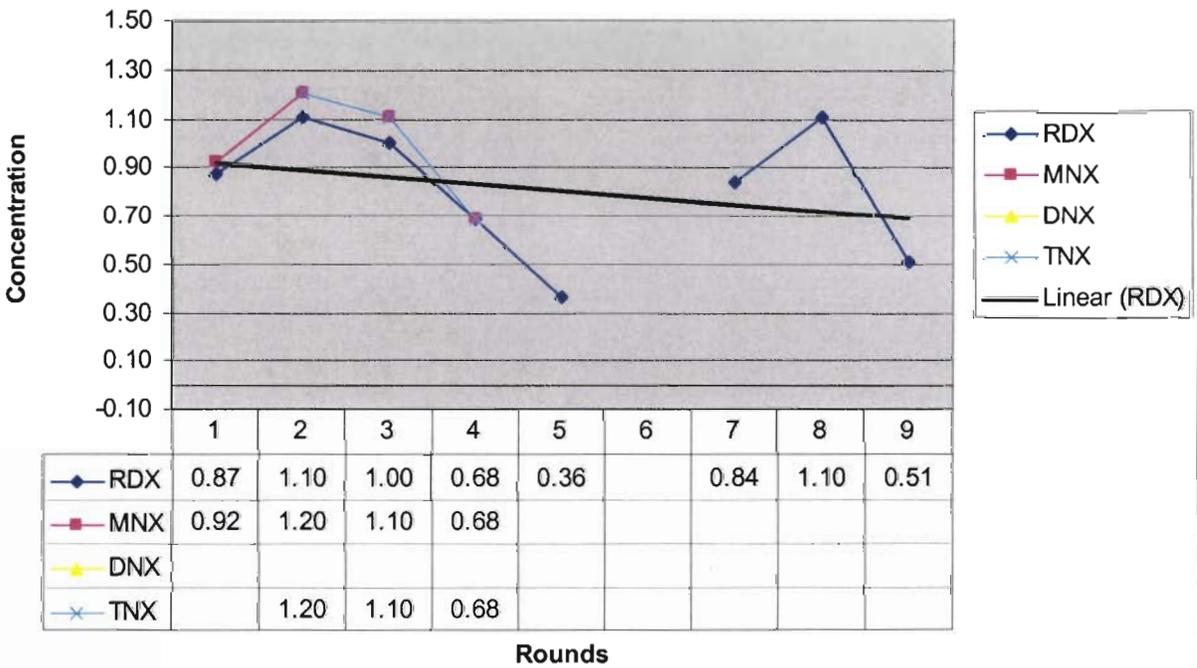




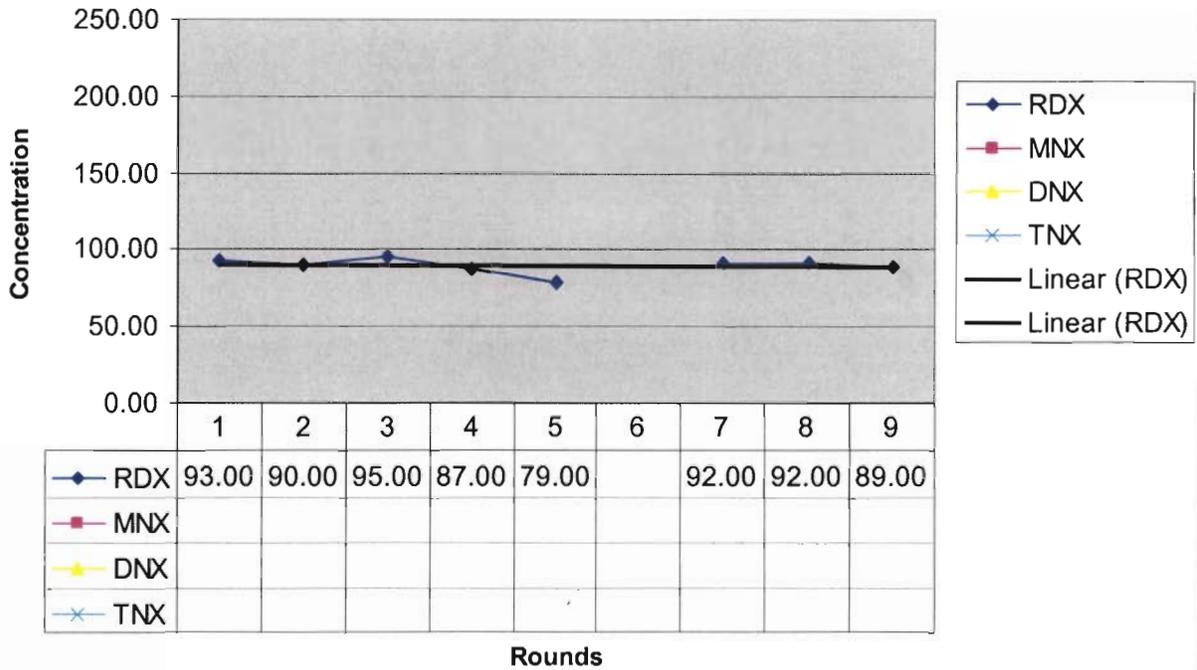
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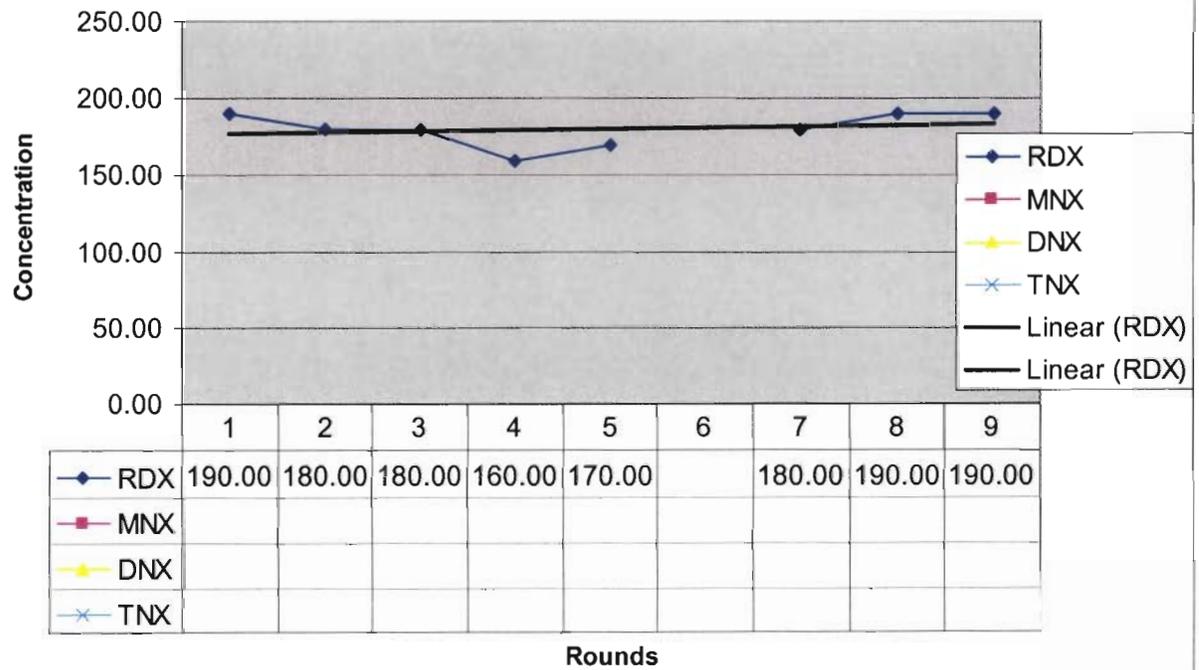
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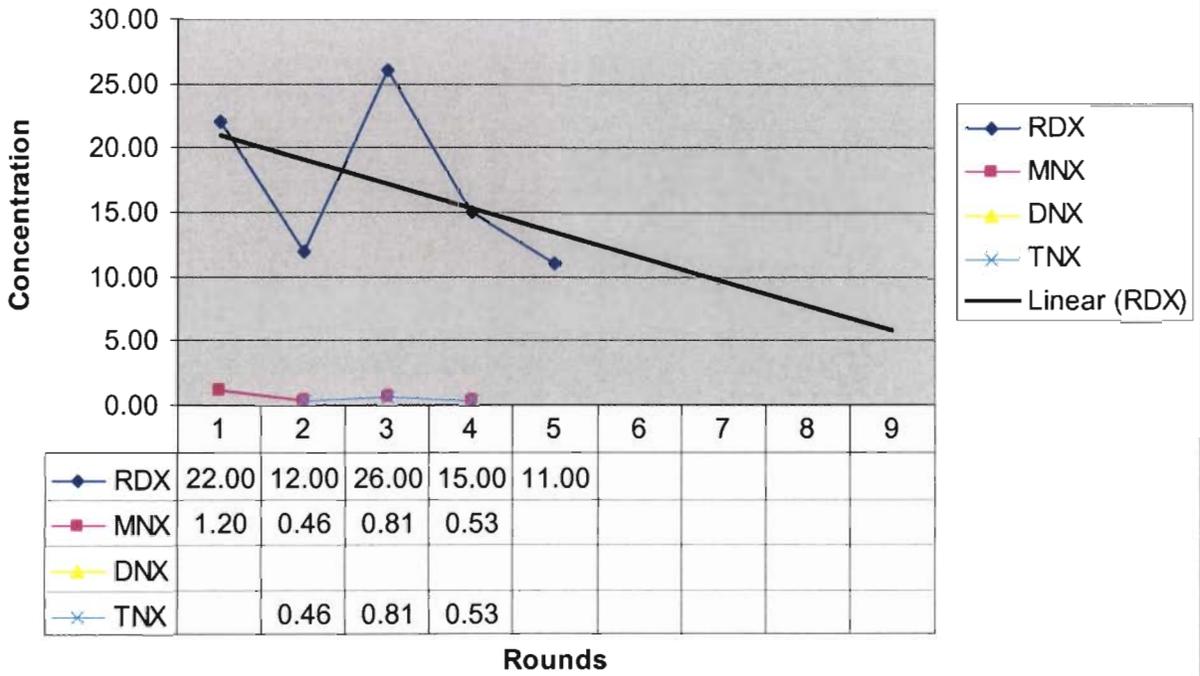
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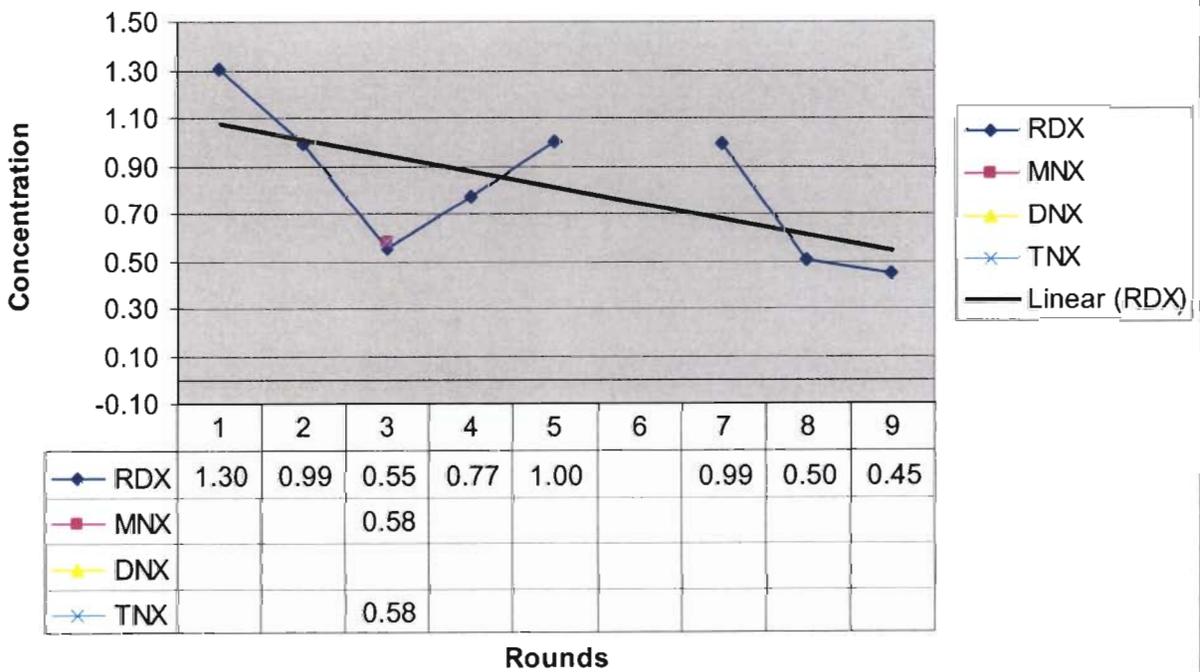
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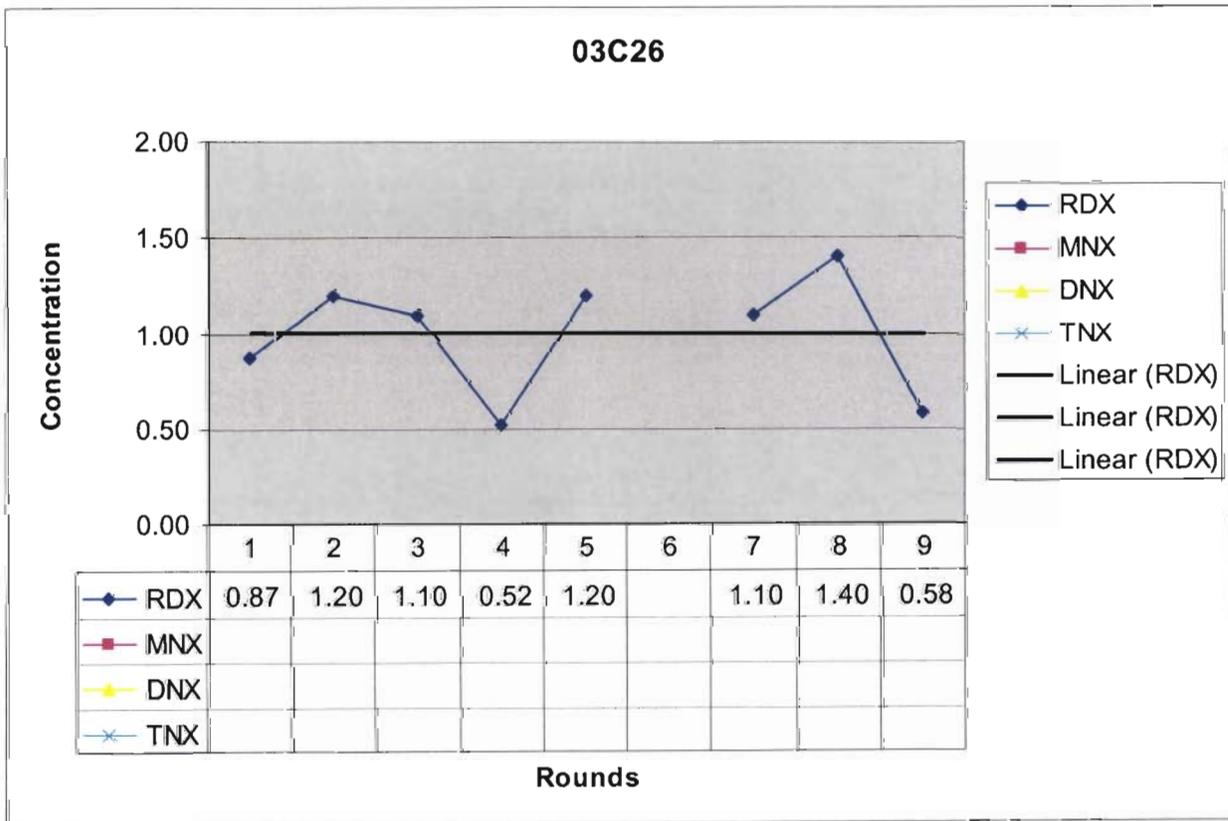
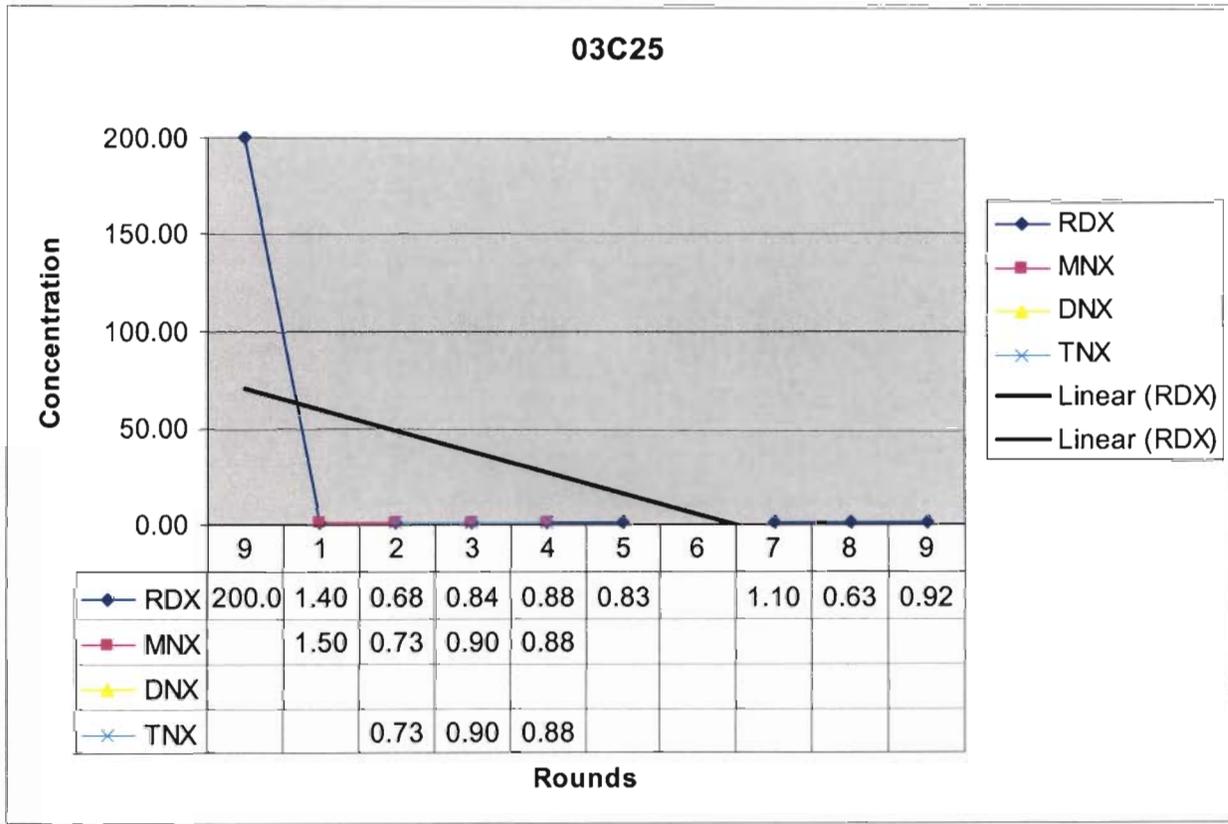


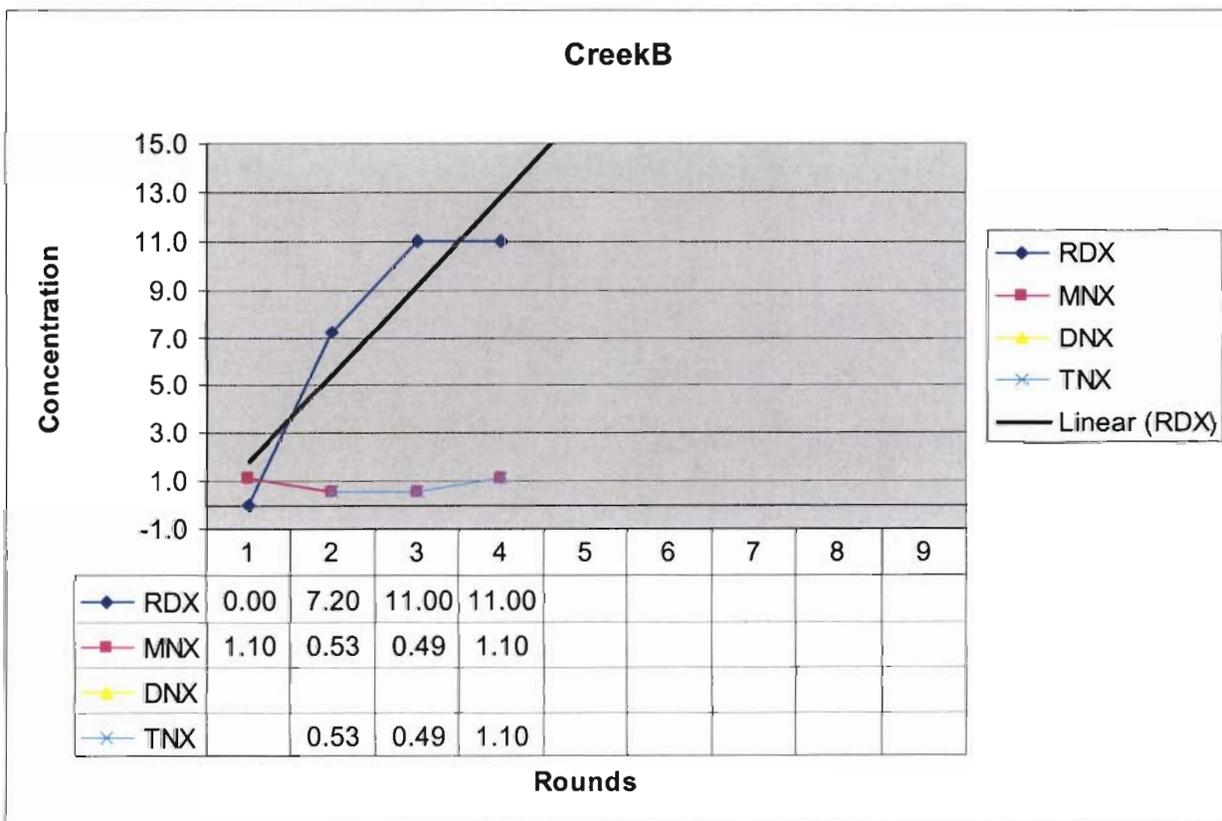
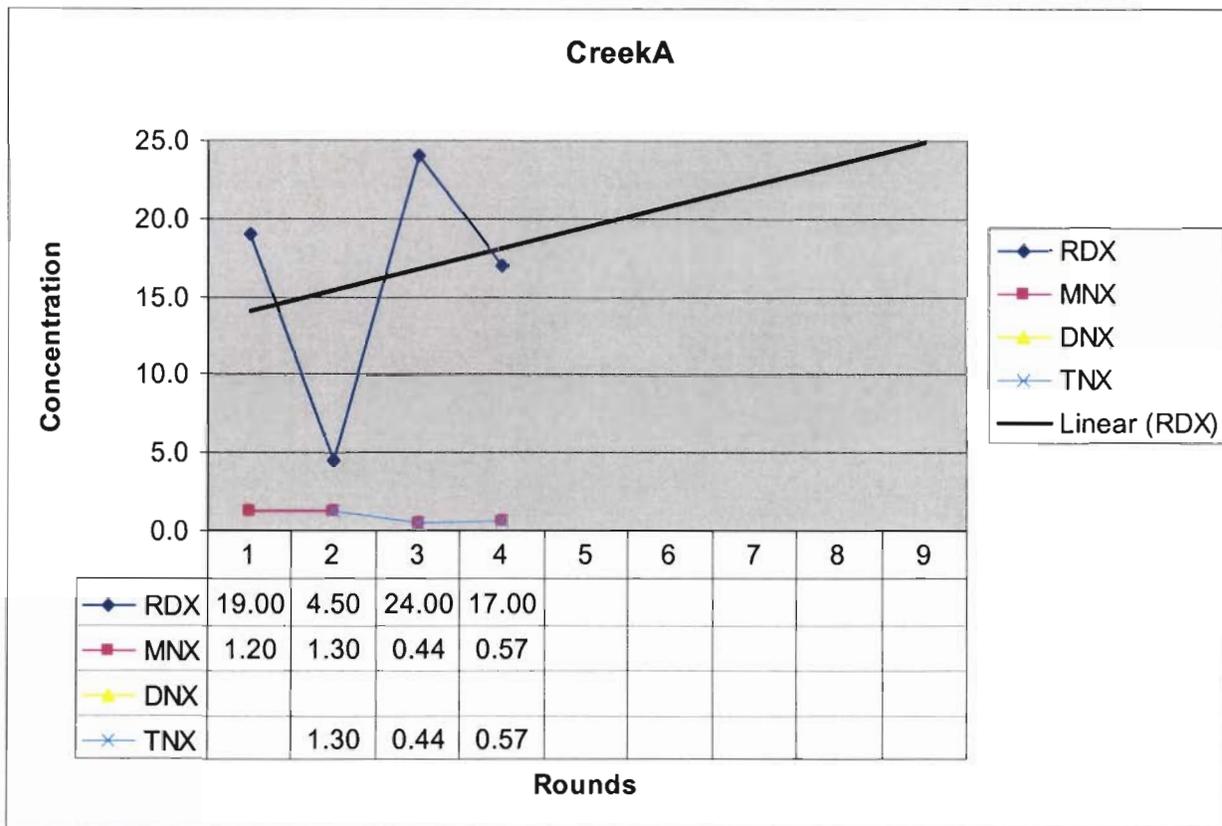
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03C15

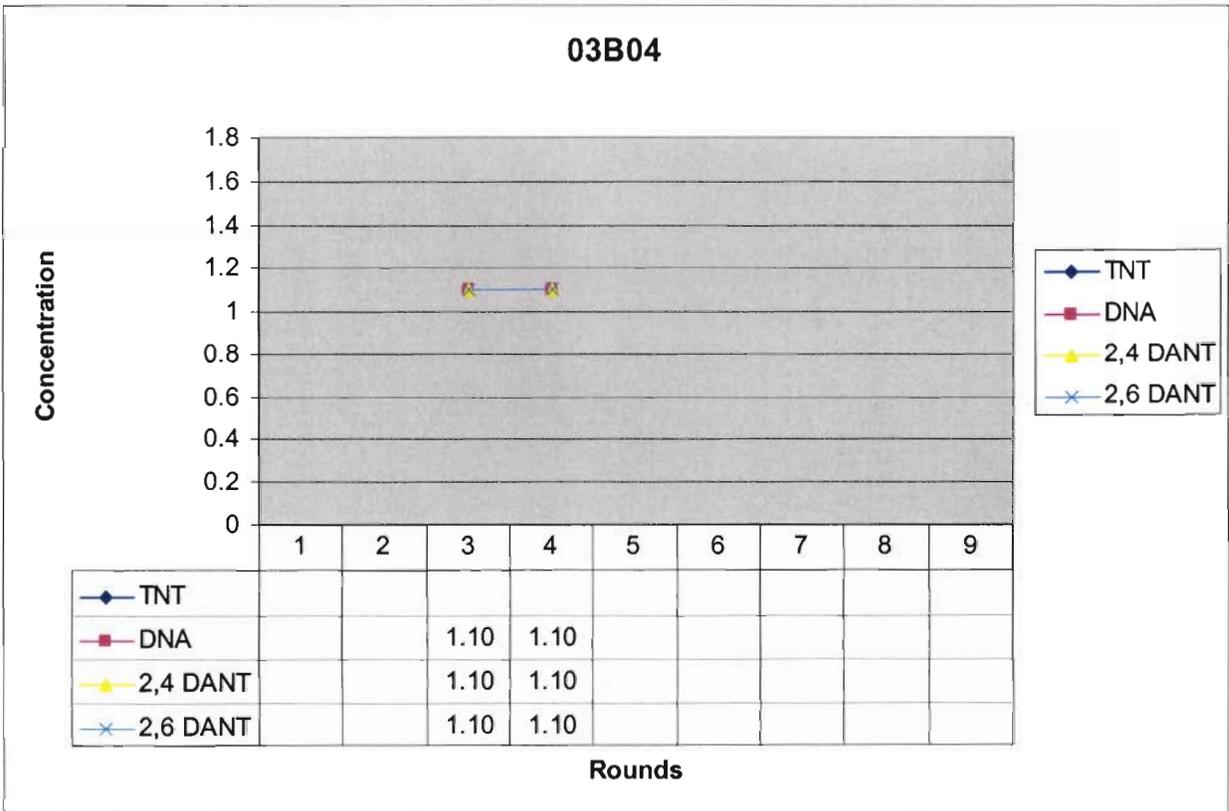
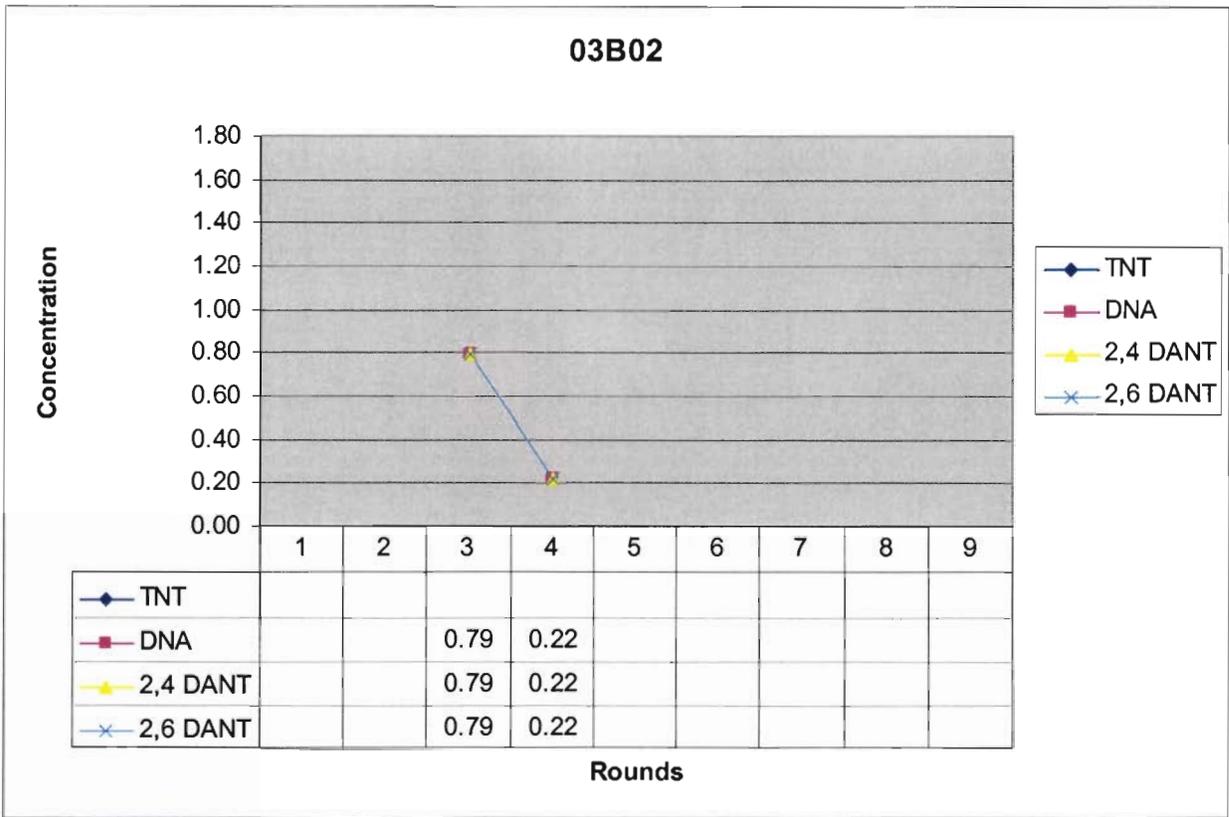




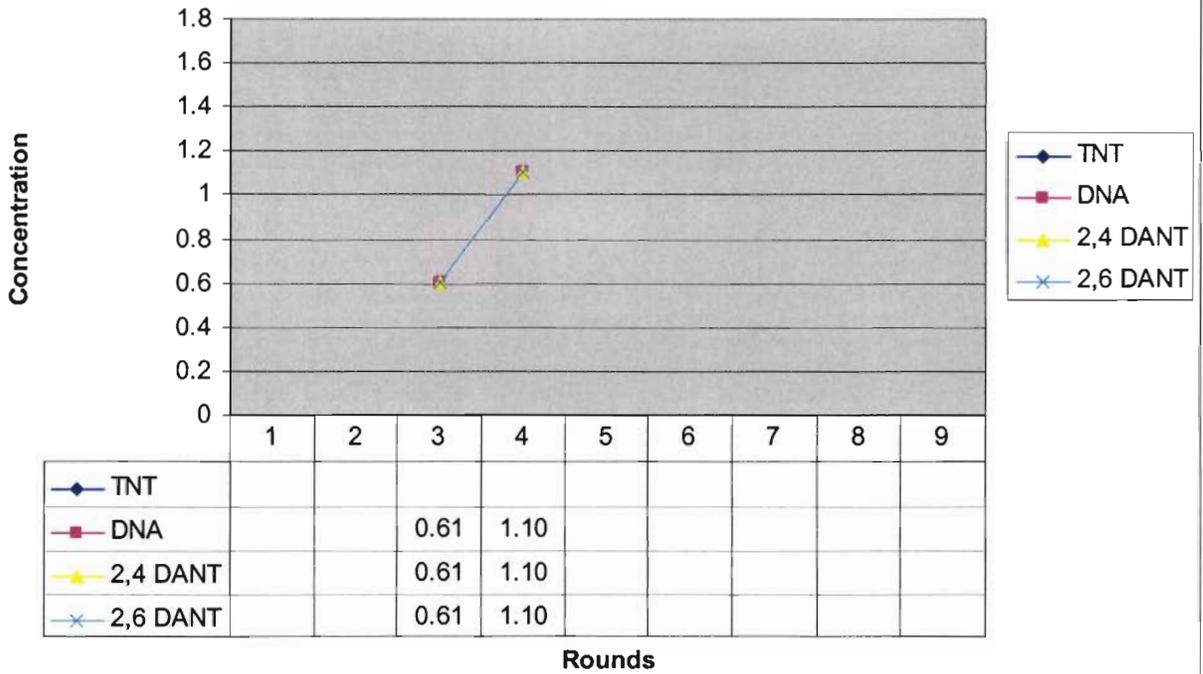


Appendix B

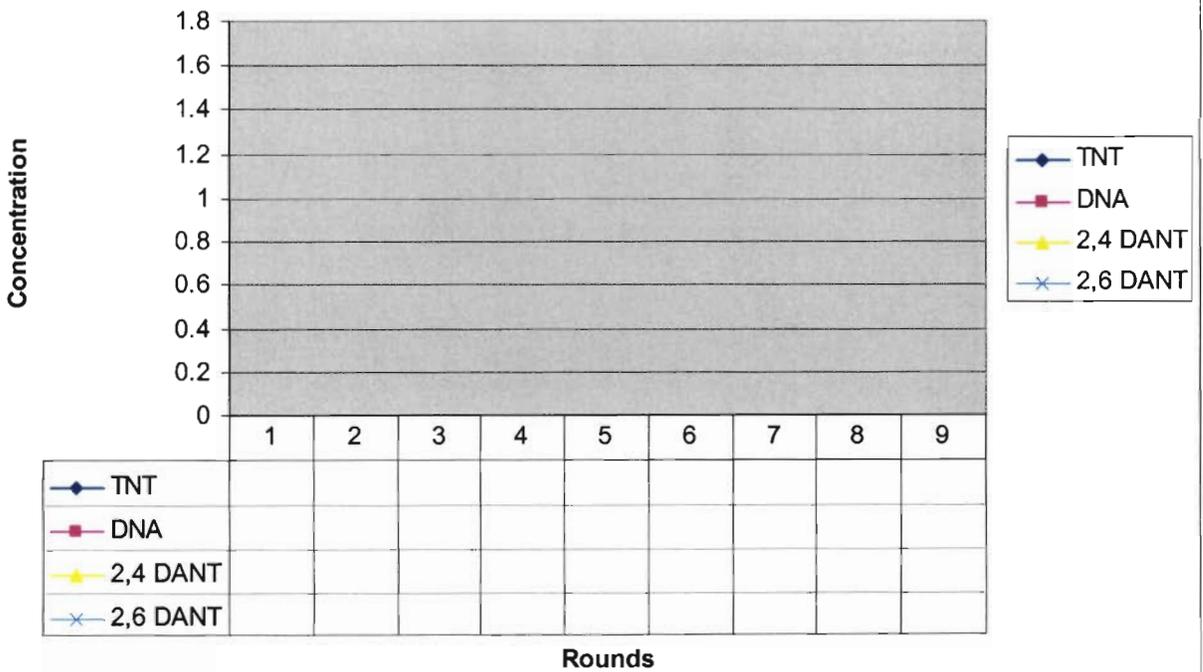
Trend Analysis for TNT and Breakdown Products

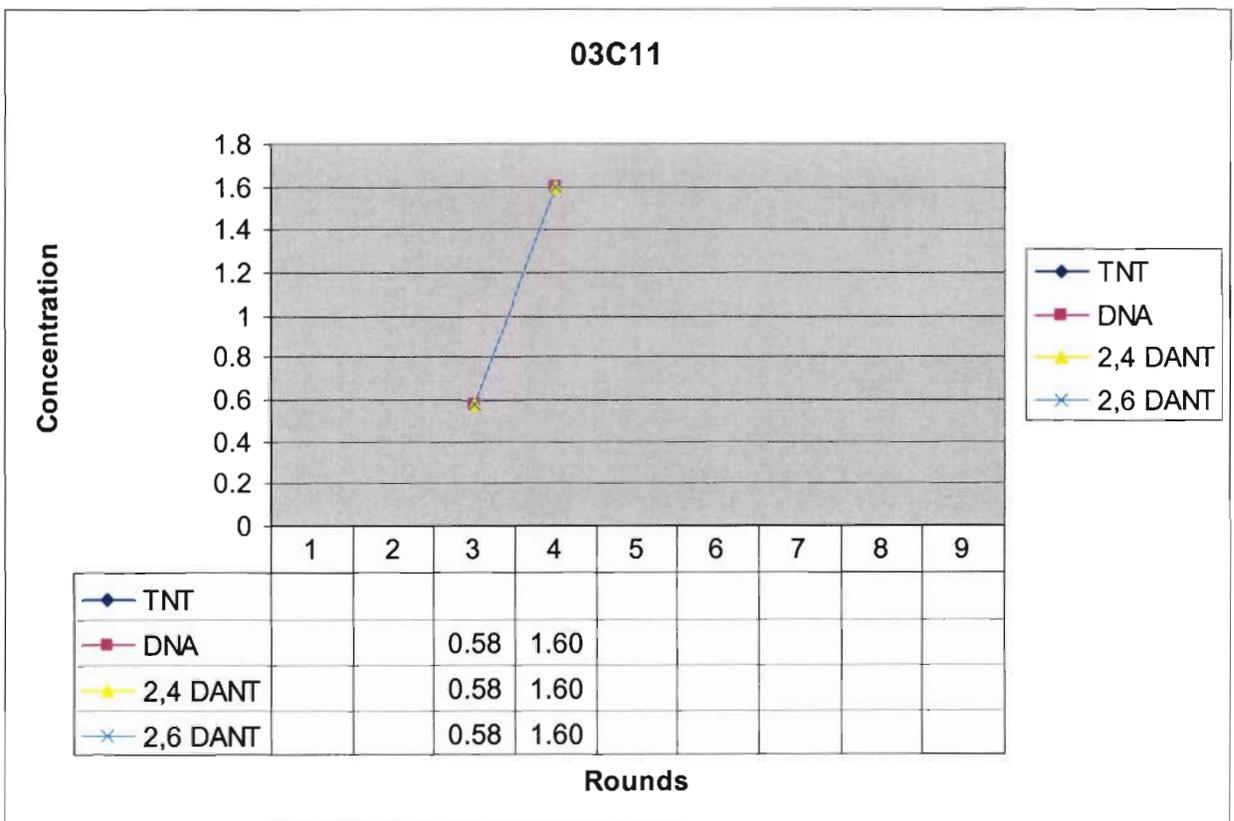
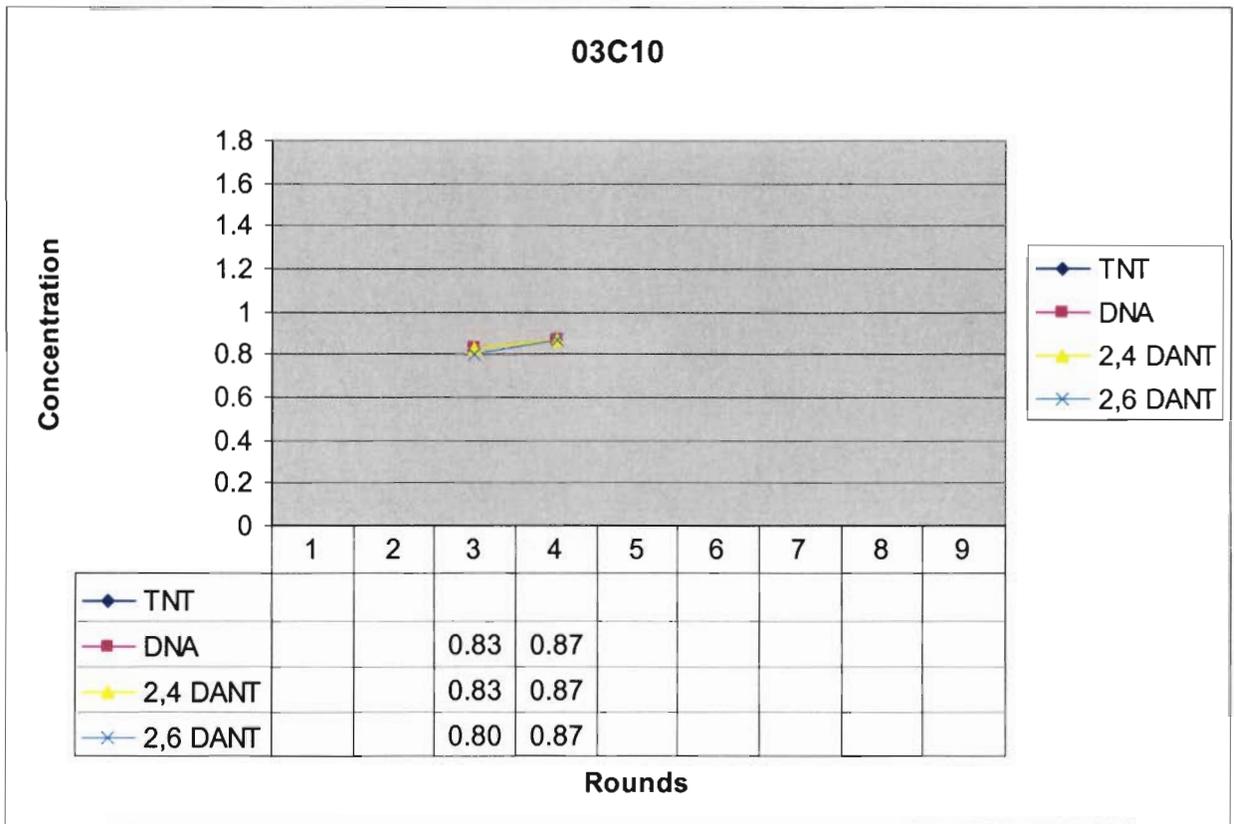


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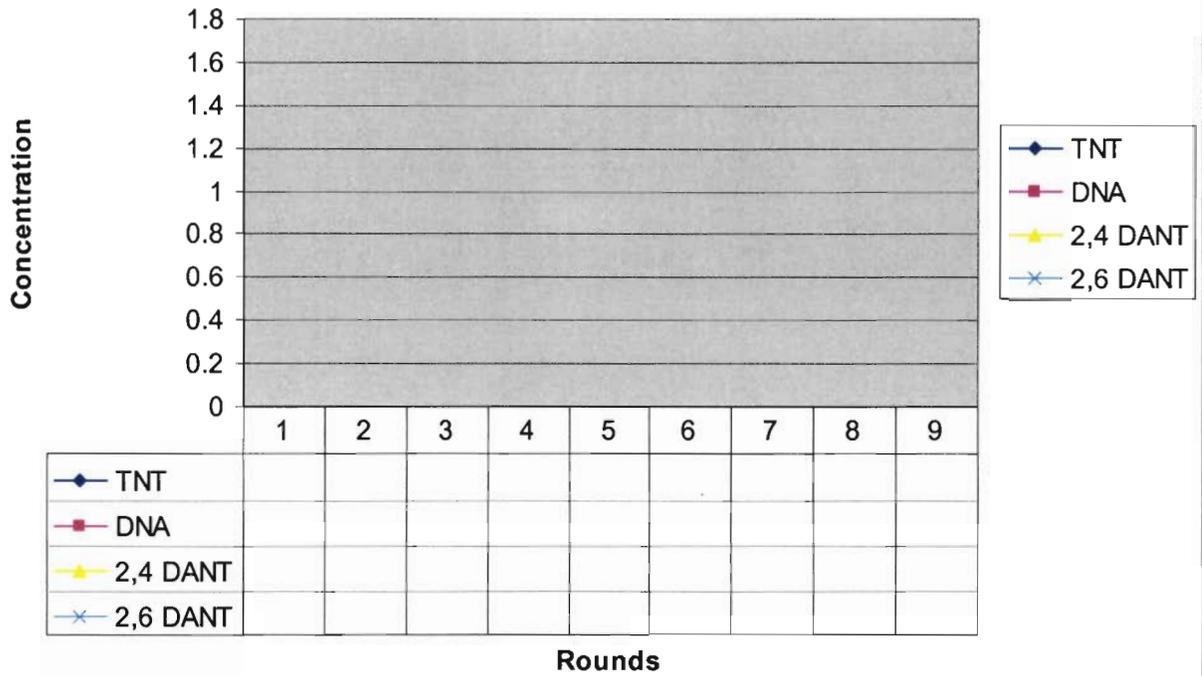


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03C17



03C20

