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Evaluation of Peroxone Oxidation Techniques for Removal of Explosives From Cornhusker Army Ammunition Plant Waters

by *Elizabeth C. Fleming, Mark E. Zappi, Jerry Miller,
Rafael Hernandez, Evelyn Toro*

WES

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Prepared for Headquarters, U.S. Army Corps of Engineers
and U.S. Army Environmental Center



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Final report

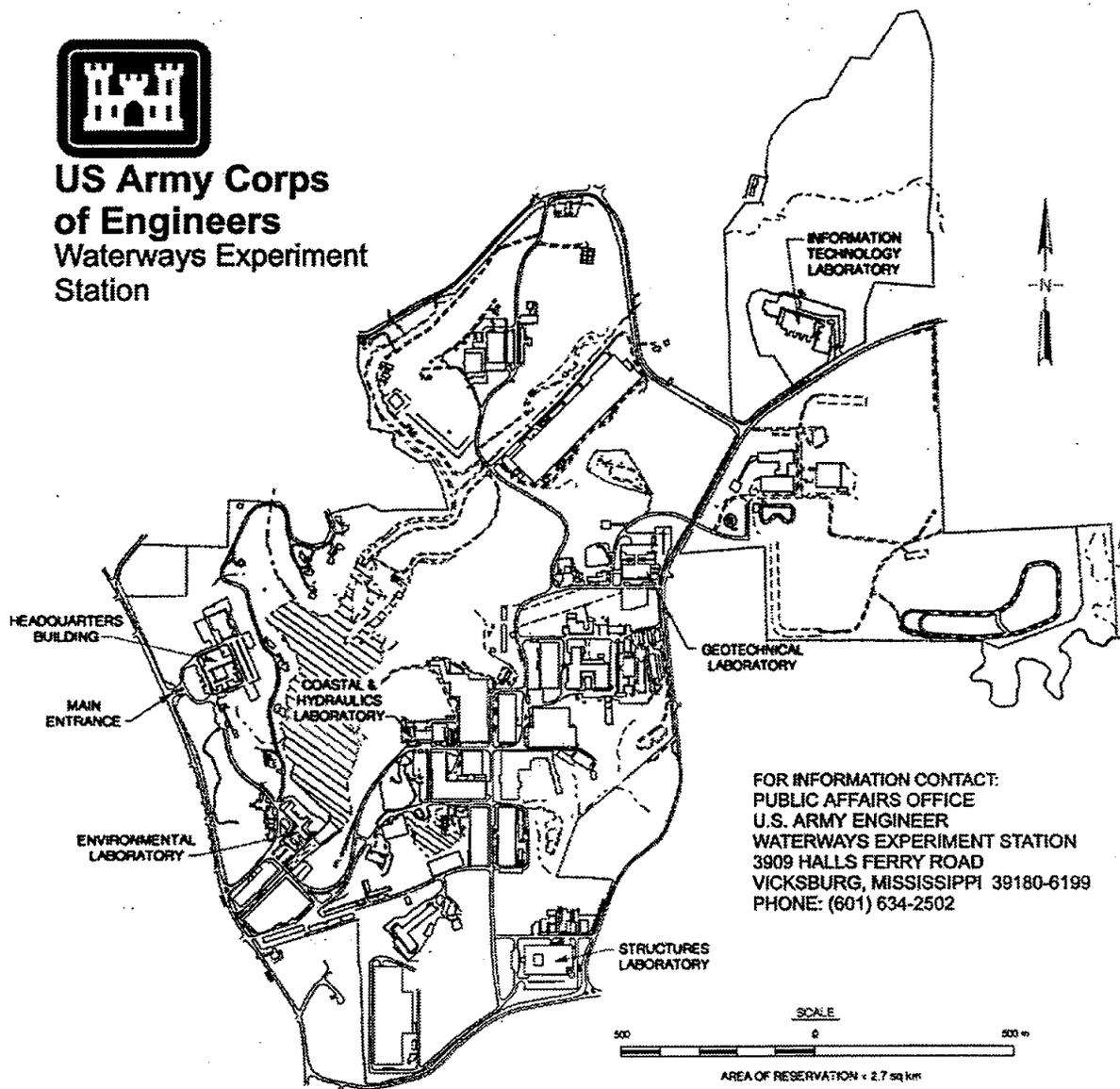
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Preface

The work reported herein was performed for the Strategic Environmental Research and Development Program (SERDP), Washington, DC, and the U.S. Army Environmental Center during fiscal year 1995 by the U.S. Army Engineer Waterways Experiment Station (WES). WES acknowledges the support given by SERDP and appreciates the opportunity to participate in the SERDP projects. Dr. John Harrison was acting Executive Director, SERDP. Dr. M. John Cullinane, WES, was the Program Manager.

This report was prepared by Ms. Elizabeth C. Fleming, Dr. Mark E. Zappi, Mr. Jerry Miller, Mr. Rafael Hernandez, and Ms. Evelyn Toro, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES. This work was performed under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander of WES.

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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 (metric) units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
feet	0.3048	meters
gallons (U.S. liquid)	3.785412	liters
inches	2.54	centimeters
miles (U.S. statute)	1.609347	kilometers
pounds (mass)	0.4535924	kilograms

1 Introduction

The Cornhusker Army Ammunition Plant (CAAP) is located in Grand Island, NE, and occupies approximately 11,936 acres.¹ Figure 1 illustrates the general location of the CAAP, approximately 147 miles east of Omaha, NE. The installation was constructed in 1942 to support World War II efforts for the primary purpose of manufacturing bombs. After intermittent periods of standby and operational status, the facility is currently on standby status and has been since 1 July 1974. In 1981 and 1982, the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, Maryland, identified cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), and 2,4-dinitrotoluene (2,4-DNT) contamination on-post.

Groundwater is the primary source of drinking water in the Grand Island area. Initial reports concluded that explosives contamination had migrated into the groundwater and contaminated approximately 246 residential drinking water sources (Fleming, Cerar, and Christenson 1996). Bottled water was supplied to the residents until a permanent alternative water-supply system could be constructed. The USAEC led an effort to treat the explosives-contaminated soils using incineration. Approximately 40,000 tons of contaminated soils were incinerated and the project was completed in August 1988. Concurrently, the U.S. Army constructed alternative water-supply facilities for those residents whose drinking water had been contaminated to an extent exceeding the TNT drinking water standard of 35 parts per billion (ppb). The alternative drinking water-supply system, namely the Northwest Grand Island Water Supply Extension, was completed in December 1986.

The U.S. Environmental Protection Agency (USEPA) and the U.S. Army published a health advisory that lowered the drinking water criteria from 35 ppb to 2 ppb and the criteria for ingestion was 10 ppb (Fleming, Cerar, and Christenson 1996). Based upon the lower limits, groundwater samples were recollected, and the number of residents requiring supplied water increased from 246 to 314. The U.S. Army extended the water-supply system to include the additional 68 residents. On 22 July 1987, the CAAP was included on the National Priorities List (NPL).

¹A table of factors for converting non-SI units of measurement to SI units is presented on page viii.

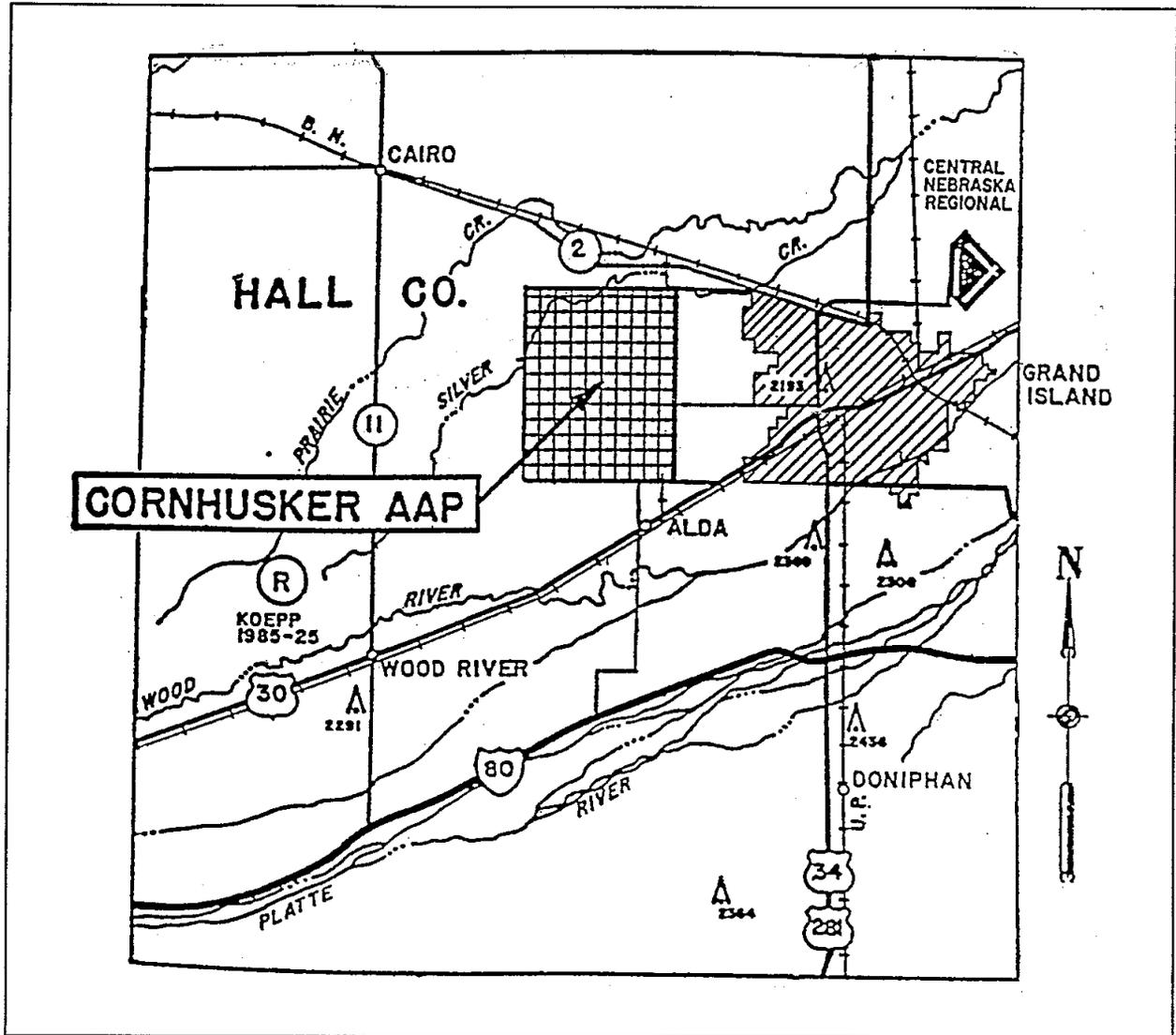


Figure 1. General location of CAAP

The U.S. Army Engineer Waterways Experiment Station (WES) selected the CAAP for evaluations of peroxone oxidation technologies since it is an NPL site and because of the extent and concentrations of explosives, namely HMX, RDX, trinitrobenzene (TNB), TNT, 4-amino-dinitrotoluene (4A-DNT), 2-amino-dinitrotoluene (2A-DNT), and 2,4-DNT present. WES performed bench- and pilot-scale evaluations of three waters from the CAAP site, from Wells 22 and 66, and a "New Well," which was constructed during the peroxone evaluations. The general location of the New Well is illustrated in Figure 2. The newly constructed well will be referred to as the New Well throughout this report. This report addresses the results obtained during the pilot-scale evaluations. The average influent concentrations collected during treatment evaluations of HMX, RDX, TNB, TNT, 4A-DNT,

2A-DNT, and 2,4-DNT in Wells 22, 66, and New Well waters during the pilot-scale evaluations are presented in Table 1 below:

Table 1 Average Concentrations of Explosives in Wells 66, 22, and the New Well								
Well No.¹	HMX µg/l	RDX µg/l	TNB µg/l	DNB µg/l	TNT µg/l	4A-DNT µg/l	2A-DNT µg/l	2,4-DNT µg/l
22	2.79	13.6	17.0	<2.0	11.5	17.0	13.9	3.6 ²
66	5.3	16.3	92.1	0.7	373.7	45.8	57.6	5.2
New Well	16.5	97.6	515.7	1.7	1,378.3	285.4	319.8	3.5

¹ Concentrations of Tetryl and 2,6-dinitrotoluene (2,6-DNT) were below the analytical detection limit of 0.2 ppb. DNB and HMX concentrations were less than 2.0 µg/l and 400 µg/l criteria, respectively.
² Indicates only one replicate. Remaining concentrations were less than the analytical detection limit of 2.0 µg/l.

Study Objectives

The main objective of this study was to determine the technical feasibility of using peroxone systems for treatment of contaminated groundwaters at the CAAP using a pilot-scale peroxone system. Site-specific objectives of this study were to determine whether concentrations of the eight aforementioned explosives contained in the CAAP waters could be treated to below the health advisory levels in the treatment times evaluated. The health advisory level for HMX is 400 ppb, and the health advisory levels for the remaining explosives were 2 ppb.

Another objective of this study was to determine whether peroxone oxidation techniques, considered a dark advanced oxidation process (AOP), may be an alternative to ultraviolet (UV) light-illuminated oxidation methods of remediation of explosives-contaminated waters. If effective, peroxone may eliminate the costs associated with operation of UV technologies, which sometimes limit their application economically. Also, UV-based technologies are adversely affected by the presence of turbidity, while dark AOPs such as peroxone are not.

A third objective of this study was to evaluate the pilot-scale system design and develop operating procedures/protocols for peroxone for further testing at Department of Defense (DoD) sites. Based upon the results of the CAAP evaluations, a design package is being developed by the U.S. Army Engineer District, Omaha, Omaha, NE. (The data from this study were also used by USAEC for a field demonstration to be conducted at the CAAP using peroxone techniques under the Environmental Securities Testing and Certification Program).

Other specific objectives of this study were as follows:

- To determine the retention time required for treatment.

- To determine the optimal treatment conditions, i.e., hydrogen peroxide and ozone dosages and continuous versus batch application of hydrogen peroxide (to be discussed in more detail in Chapter 4: Discussion of Results).
- To determine the removal efficiencies of each of the treatment techniques.
- To provide further information to the Omaha District for development of the peroxone design package, which includes economic evaluations of peroxone treatment.

Project Approach

This project was performed in six phases.

- Interpretation of bench-scale data to determine treatment conditions for the peroxone oxidation pilot-scale unit (POPS) study.
- Selection of treatment conditions for the POPS evaluations.
- Mobilization of the POPS unit to CAAP.
- Evaluation of POPS treatment of three CAAP waters.
- Demobilization of the POPS unit.
- Transfer of POPS CAAP data to the Omaha District for development of the peroxone design package and to the USAEC for design of the CAAP demonstration project.

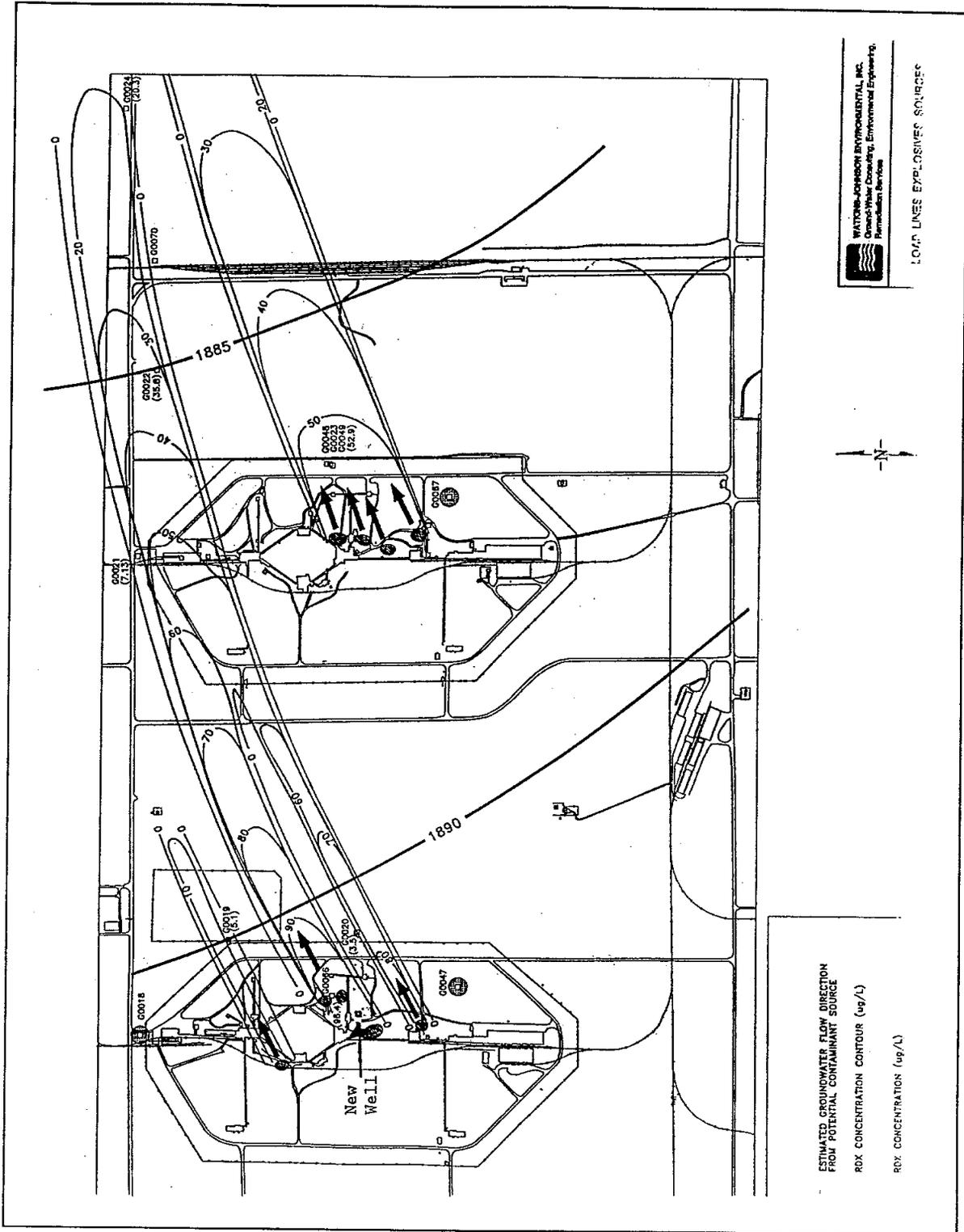


Figure 2. General location of New Well

2 Technology Description

Advanced Oxidation Processes

Peroxone is termed a dark AOP because it does not involve the addition of UV light as opposed to illuminated AOPs. Although the addition of UV light to an AOP system generally results in more rapid reaction kinetics, the capital and operations and maintenance costs associated with UV light add significantly to the costs associated with their use. Typical UV light systems generally cost from \$1.00 to \$5.00 per 1,000 gal of water treated (Zappi et al., in preparation). Estimates of the cost of implementation of peroxone treatment techniques range from \$0.05 to \$1.00 per 1,000 gal. In the past, many explosives treatment systems have involved the use of granular activated carbon (GAC), which also may range in cost from \$1.00 to \$5.00 per 1,000 gal of water treated; this technique also results in phase change of the explosive as opposed to destruction of the explosive using AOPs.

AOPs involve the use of oxidizers such as ozone or hydrogen peroxide to oxidize organics to nontoxic compounds. Oxidizers may be used singly or in combination (as in the case of peroxone). There are two pathways for destruction of organic contaminants by oxidation products: direct attack by electrophilic addition or indirect attack by free radicals produced by reaction with water and water constituents. The reaction of ozone or hydrogen peroxide alone with OH, CH₃, and OCH₃ groups is strong but is considerably weaker with NO₂, CO₂H, and CHO groups (Langlais, Reckhow, and Brink 1991). The studies of CAAP waters presented in this report support the theory that CH₃ group reactions are strong. According to research into TNT degradation, TNB is an intermediate of TNT oxidation, and the CH₃ is probably the first portion of the TNT molecule to be attacked. The structures of the explosives evaluated in this study are illustrated below (Figure 3). Notice the primary difference between TNT and TNB is the CH₃ group. This will be discussed further in Chapter 4 of this report.

The reaction of hydrogen peroxide and ozone results in the production of hydroxyl radicals that are nonselective in their reactions. The hydroxyl

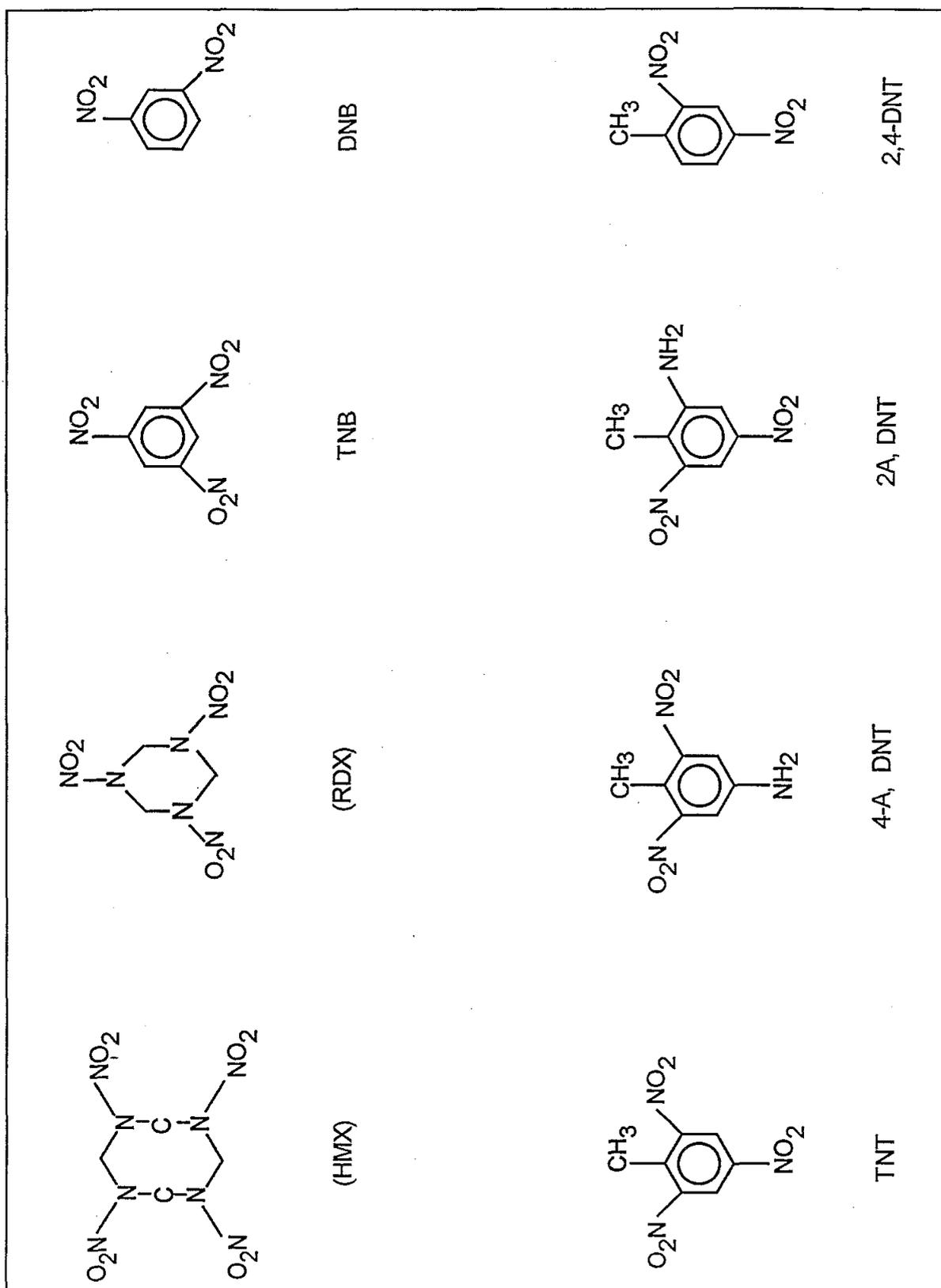


Figure 3. Chemical structures of explosives studied

radical (OH) is a highly reactive oxidizer and is produced during the reaction of hydrogen peroxide and ozone according to the following equations:



In the aforementioned equations, hydrogen peroxide (H_2O_2) disassociates in water to form peroxide (HO_2^-) and a hydrogen ion (H^+). Peroxide reacts with ozone to form an ozonide (O_3^-) and hydroxy peroxide (HO_2). Hydroxyperoxide disassociates into hydrogen ion and superoxide (O_2^-) that reacts with ozone to form ozonide and oxygen. The ozonide reacts with hydrogen ion to form a hydroxyl radical (OH) and oxygen. Because the hydroxyl radical is highly reactive, it is able to react with organic species, and in the case of explosives compounds, resulting in destruction of the explosive to a nontoxic compound (investigations into the products of decomposition of TNT, RDX, and aminodinitrotoluenes will be presented in Chapter 4). However, there are inhibitors or “scavengers” of hydroxyl radicals that tend to consume the hydroxyl radical before the superoxide anion (O_2^-) is regenerated (see Equation 3 above). Typical scavengers include bicarbonate and carbonate ions, alkyl groups, tertiary alcohols, and humic substances (Langlais, Reckhow, and Brink 1991). Typical concentrations of bicarbonate and carbonate ions naturally present in waters range from 50 to 100 mg/l and 0 to 10 mg/l, respectively (Metcalf and Eddy 1991). In addition to the aforementioned scavengers, the oxidizers themselves, i.e., ozone and hydrogen peroxide, may act as scavengers, if added in inappropriate doses, i.e., overdosing the system. Once the hydroxyl radical is scavenged by the inhibitors, it is not available for degradation of the target contaminants.

Previous studies of peroxone oxidation of geosmin and 2-methylisoborneol (2MIB) were presented in a paper by Koch et al. (1992). The results of their studies indicated that 80 to 90 percent of geosmin and 2MIB could be removed using peroxone and that the use of peroxone may result in significant cost savings. The Metropolitan Water District of Southern California (1991) also evaluated peroxone using pilot-scale systems for removal of 2MIB and geosmin and determined a hydrogen peroxide-to-ozone ratio of 0.1 to 0.2 was optimal for their application.

Studies were conducted by Bellamy et al. (1991) to determine whether peroxone was an effective treatment method for volatile organic compound

(VOC)-contaminated groundwater. Their studies indicated that dichloroethene (DCE), trichloroethene (TCE), and perchloroethene (PCE) could be reduced to below the required standard of $5 \mu\text{g}/\ell$. Glaze and Kang (1988) evaluated oxidation of TCE and PCE using ozonation alone and peroxone. They found addition of hydrogen peroxide to the ozone process (peroxone) increased the rate of TCE destruction by a factor of two to three and increased the rate of PCE destruction by a factor of two to six, depending on the ozone dosage.

Zappi (1995) evaluated removal of TNT from $1 \text{ mg}/\ell$ TNT-spiked solutions using peroxone on the bench-scale level. The optimal treatment conditions for removal of TNT were $100 \text{ mg}/\ell$ hydrogen peroxide and sparging 2-percent ozone for those evaluations. The results reported herein are slightly different, stressing the need for treatability studies in order to determine treatment parameters on a case-by-case basis. Further information will be provided in Chapter 4. Studies by Zappi (1995) also revealed that excess oxidizers may result in adverse effects upon the peroxone system by scavenging hydroxyl (OH) species generated for the purpose of explosives degradation.

Radical Formation in Peroxone Systems

The reactions between ozone and hydrogen peroxide that result in the formation of the hydroxyl radical have been under investigation since the early 1950s when Taube et al. (1952) first described potential radical formation reactions. The ozone-hydrogen peroxide reactions were later defined by the engineering community as peroxone. A thorough literature review was undertaken at WES as an attempt to quantify and qualify key mechanistic reactions that result in the formation of hydroxyl radicals during AOP treatment. This effort was used to present the following information detailing hydroxyl radical formation mechanisms and related radical scavenging reactions.

Figure 4 presents a mechanistic diagram that details hydroxyl radical fate during AOP treatments that utilize both ozone and hydrogen peroxide. Radical production mechanisms illustrated in Figure 4 include UV photolysis, peroxone, and hydroxide ion-based ozone decomposition. Hydroxyl radical sinks or scavenging mechanisms (Note: scavengers other than the contaminant are represented as " S_i " in the figure) include reactions with ozone, hydrogen peroxide, contaminants (illustrated as Species A), and/or common water constituents such as carbonate and cationic species. From these series of reactions that obviously include initiation, propagation, and termination reactions, a steady-state hydroxyl radical concentration is developed. Mechanisms can be grouped into two types: dark and illuminated. Since peroxone involves only dark reactions, then only the dark mechanisms are discussed below.

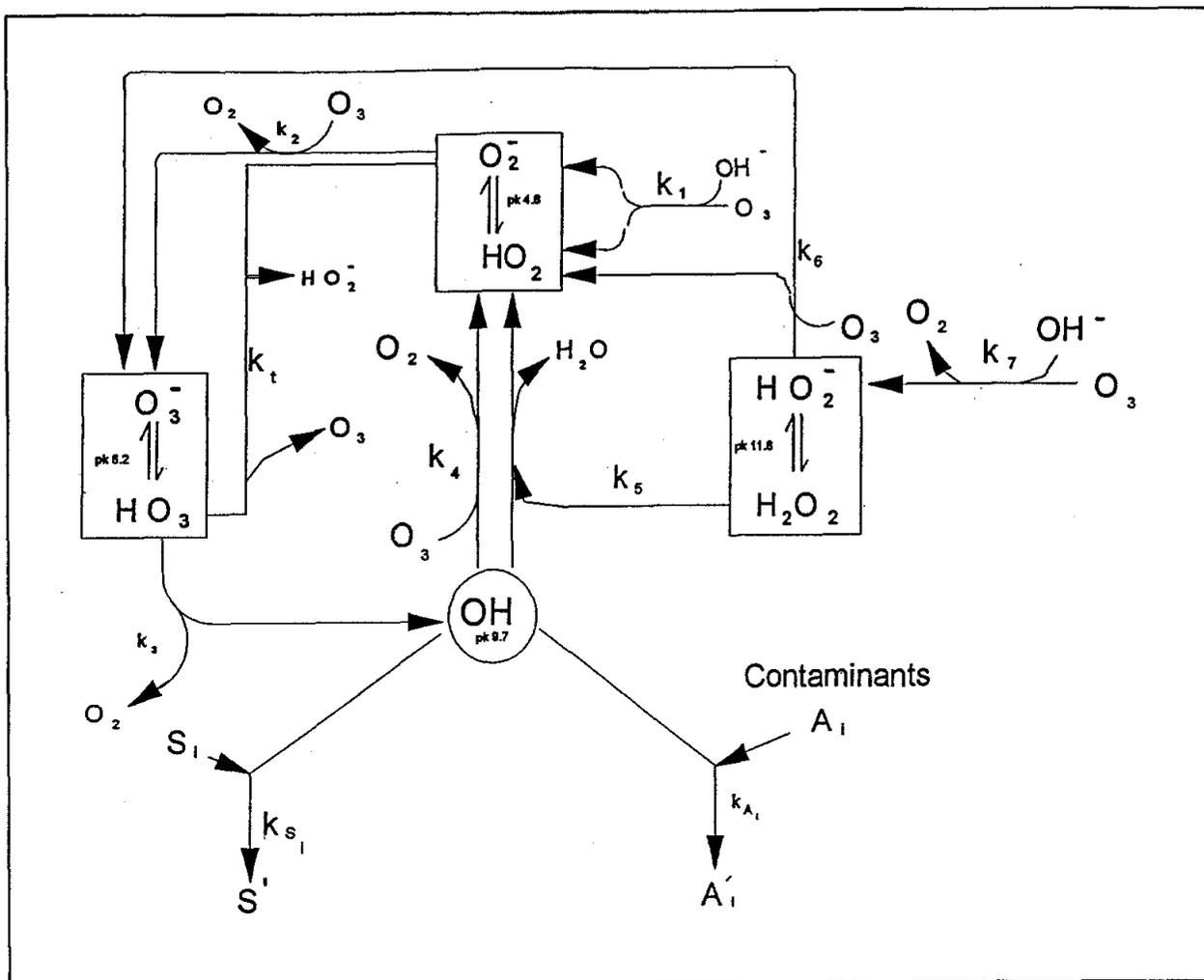
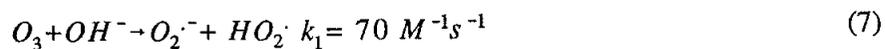
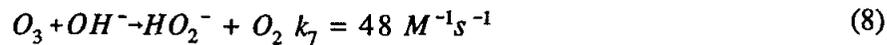


Figure 4. Hydroxyl radical formation/scavenging mechanisms during AOP treatment (Hong et al. 1994)

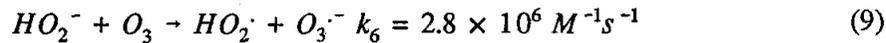
Dark Ozone Reactions

It is widely known that ozone reacts with the hydroxide ion at high pHs to decompose ozone (Buhler et al. 1984). As illustrated in Figure 4, ozone reacts readily with hydroxide ion at high pH to produce superoxide (HO_2^- and O_2^-) and/or peroxide (HO_2^-) (Bahnemann and Hart 1982). The stoichiometric mechanisms responsible for superoxide and peroxide production due to alkalinity are presented below:

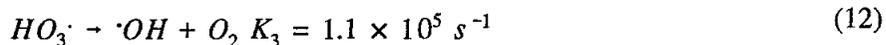




The latter product further reacts with ozone to form a hydroxylperoxide (HO_2) and an ozonide ion (O_3^-) as described by Stachelin and Hoigne (1982):

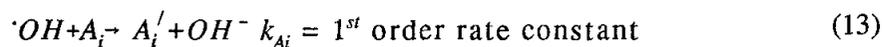


Once superoxide ions ($O_2^{\cdot-}$) are formed, they react with ozone to produce an ozonide, O_3^- . The ozonide ion then releases an oxygen to produce the hydroxyl radical as illustrated below (Buhler et al. 1984):

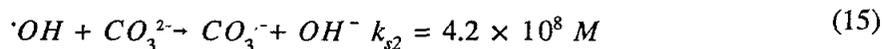
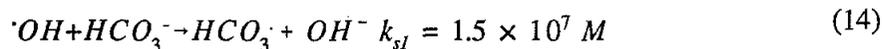


As previously stated, the radical is a very powerful oxidant and, once it is formed, will attack and oxidize most organic compounds (for example, Contaminant A). Unfortunately, the hydroxyl radical is not very selective in terms of reactants. Radicals will also react with nonregulated compounds referred to as scavengers (Stachelin and Hoigne 1985). Examples of scavenger species (S) include bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). Key hydroxyl radical reactions are summarized below:

- a. Reaction with a regulated contaminant (Contaminant A (i.e., DIMP)):

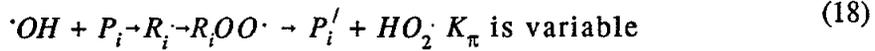
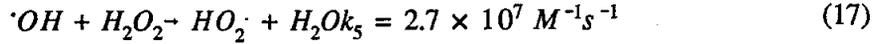
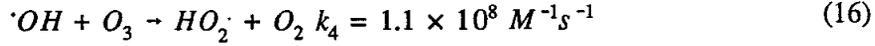


- b. Reactions with scavengers (S (i.e., bicarbonates and carbonates)):



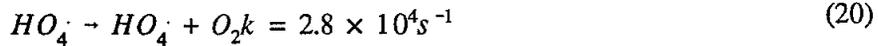
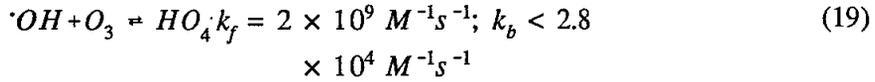
The hydroxyl radical may also be converted to superoxide (HO_2^{\cdot}) by reacting with ozone (Sehested et al. 1984), hydrogen peroxide (Christensen et al. 1982), or a chain promotor (P_i) such as t-butyl alcohol, which is referred to as a tertiary alcohol (Stachelin and Hoigne 1985). It should be noted that t-butyl alcohol was used by Zappi (1995) to segregate ozonation and/or hydrogen peroxide reactions from radical-based reactions during treatment of TNT-contaminated waters. His results indicated that TNT removal during peroxone oxidation was indeed hydroxyl radical

based and not due to primary oxidation. Mechanisms of the above discussed hydroxyl radical scavenging reactions are listed below:

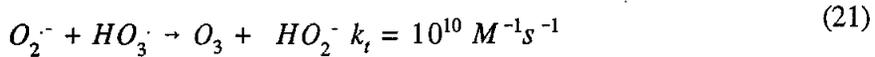


where k_{pi} is variable and is based on the alcohol species selected.

It has been suggested that the intermediate, $HO_4\cdot$, may also form during the k_4 step listed above (Stahelin et al. 1984). The proposed reactions are presented below:



Since $O_2\cdot^-$ and $HO_3\cdot$ may accumulate to significant concentrations, they may be involved in the termination of free radicals via the following termination reactions (Stahelin et al. 1984):



The reaction pathway described above occurs readily during ozonation of an aqueous solution (i.e., when ozone is introduced to water). During peroxone oxidation, the addition of hydrogen peroxide to an ozonated system will facilitate the same pathway, but enhance the k_6 step to become the predominant mechanism for radical production. It should be noted that when hydrogen peroxide is added via dosing, the k_7 step that produces $HO_2\cdot$ likely becomes negligible as the produced amount will be small compared with the added amount.

By comparing kinetic rate coefficients of Reactions 2.1, 2.6, and 2.7, it is apparent that when a hydrogen peroxide dose typical of most AOPs is used (10-200 mg/l), the k_6 step becomes more important than the k_7 step or the original k_7 route in the formation of $HO_2/O_2\cdot^-$. For example, for applied ozone and hydrogen peroxide concentrations of $[O_3] = 2 \times 10^{-5} \text{ M}$ (1 mg/l) and $[H_2O_2] = 1.5 \times 10^{-3} \text{ M}$ (50 mg/l) at neutral pH (pH = 7):

$$k_6 [O_3] [HO_2^-] = (2.8 \times 10^6) (2 \times 10^{-5}) (1.5 \times 10^{-3}) \\ (2.5 \times 10^{-5}) = 2.1 \times 10^{-6} M s^{-1} \quad (22)$$

$$k_1 [O_3] [OH^-] = 70 (2 \times 10^{-5}) (10^{-7}) \\ = 1.4 \times 10^{-10} M s^{-1} \quad (23)$$

Therefore, the enhancement of peroxone system over ozone alone in treatment may be due to the faster chain initiation by the k_6 step within peroxone systems. In addition, when large doses of hydrogen peroxide are added with respect to ozone, the scavenging of hydroxyl radicals by the excessive amount of added hydrogen peroxide (k_5 step) may overtake that by ozonation (k_4 step). For example, for applied doses of 1 mg/l soluble ozone and 50 mg/l hydrogen peroxide, the resulting kinetics listed below clearly highlight the scavenging impact of overdosing of oxidizers within AOP systems:

$$k_4 [O_3] [^{\bullet}OH] = (1.1 \times 10^8) (2 \times 10^{-5}) [^{\bullet}OH] \\ = 2.2 \times 10^3 [^{\bullet}OH] M s^{-1} \quad (24)$$

$$k_5 [H_2O_2] [^{\bullet}OH] = (2.7 \times 10^7) (1.5 \times 10^{-3}) [^{\bullet}OH] \\ = 4.0 \times 10^4 [^{\bullet}OH] M s^{-1} \quad (25)$$

Steady-State Hydroxyl Radical Concentration Model

It is useful for the dark hydroxyl radical fate mechanisms presented in Figure 4 to be incorporated into a model that will estimate the steady-state levels of radicals present in a given AOP system. This model was proposed by Hong et al. (1994) for use in comparing $[^{\bullet}OH]_{ss}$ levels in various test peroxone systems under consideration by design engineers. The model as proposed by Hong et al. is presented below:

$$[^{\bullet}OH]_{ss} = \frac{2k_6 [O_3] [H_2O_2]_T K_{H_2O_2} [H^+]^{-1}}{k_4 [O_3] + k_5 [H_2O_2]_T + k_A [A] + k_s [S]} \quad (26)$$

This equation reveals a complex dependence of $[^{\bullet}OH]_{ss}$ on $[O_3]$, $[H_2O_2]_T$, $[A]$, $[S]$, and pH. The degradation rate is expected to increase and then level off as hydrogen peroxide and/or ozone concentrations are increased from very low to high values.

The steady-state expression for $[^{\bullet}OH]_{ss}$ is useful for explaining the complex kinetics often observed in AOPs. It is also useful as a guide in optimizing treatment conditions and selecting an appropriate treatability test matrix based on influent

chemistry. For example, the rate of degradation for a Contaminant A under attack by the $\cdot OH$ can be written as:

$$-\frac{d[A]}{dt} = k[\cdot OH]_{ss}[A] = k_p[A] \quad (27)$$

where

k_p (s^{-1}) = a pseudo first-order rate constant

Supply of Oxidizers

The final expression useful for engineering desired operating conditions is design of ozone transfer into peroxone reactors. One approach is described here. In anticipated treatment applications, hydrogen peroxide can be added continuously within the contents of a reactor or in a single batch dose added at the head of the reactor. This study focused primarily on batch dosing at the head of a system because of the relative ease of system design and operation. However, ozone must be continuously sparged into a reactor to maintain a steady-state concentration during treatment due to the limited steady-state concentration of ozone that can be added using a 2- to 10- percent ozonated air feed. The difference between the equilibrium concentration of aqueous ozone subject to its vapor pressure in the gas phase and the actual steady-state ozone concentration can be termed ozone deficit (i.e., $[O_3]^* - [O_3]_{ss}$). The rate of supply of a dilute ozone gas, Q_{O_3} , (Ls^{-1}) required to maintain a desired $[O_3]_{ss}$ can then be determined according to:

$$Q_{O_3} \frac{P_{in, O_3} - P_{out, O_3}}{RT} = k_L a V_L ([O_3]^* - [O_3]_{ss}) \quad (28)$$

where

Q_{O_3} = rate of supply of dilute O_3 /air gas mixture, (Ls^{-1})

P_{in, O_3} ; P_{out, O_3} = partial pressure of O_3 at entrance and exit, respectively
15(atm), (e.g., 1 percent O_3 gas = 10^{-2} atm)

R = universal gas constant ($0.082 \text{ L atm deg}^{-1} \text{ mol}^{-1}$)

T = temperature, K

$k_L a$ = mass transfer coefficient of O_3 (s^{-1})

V_L = volume of liquid being treated (L)

$[O_3]^*$ = equilibrium concentration of O_3 (M)

$[O_3]_{ss}$ = desired steady-state concentration of O_3 (M)

It should be stressed that the derived expression of $[^{\cdot}OH]$ has been based on instantaneous concentrations of ozone and hydrogen peroxide (i.e., residual concentrations at the moment) in the system. The actual (or residual) value of $[O_3]_{ss}$ being maintained for a particular Q_{O_3} should be monitored, then the Q_{O_3} can be adjusted to meet a target $[O_3]_{ss}$ value. Glaze and Kang (1988) reported an increase in pseudo-first-order rate constants for TCE degradation when hydrogen peroxide and ozone were continuously supplied at rate ratios >0.8 (up to 2.0) mol H_2O_2 /mol O_3 . They point out that this ratio should not be interpreted as the optimal residual mole ratio of hydrogen peroxide and ozone affecting contaminant degradation, because the residual ozone in the liquid phase varied for systems of different reaction rates. However, Zappi (1995) concluded that molar stoichiometric ratios between 1 and 1.5 were optimal for peroxone systems that employed batch adding of hydrogen peroxide for removing TNT from contaminated waters.

Model Predictions for Various Peroxone Systems

To better understand potential differences in peroxone system performance, the above proposed steady-state hydroxyl radical concentration model (26) was evaluated using a variety of peroxone systems (i.e., ozone and hydrogen peroxide-dosing combinations under a variety of buffered pH ranges). The systems modeled were selected to determine an appropriate range of oxidizer concentrations that may be evaluated during laboratory experimentation. Emphasis was placed on oxidizer concentrations without extreme pH effects (i.e., $3 < \text{pH} < 9$).

Table 2 lists the first series of model runs that evaluated a constant hydrogen peroxide dose of 10 mg/l and various residual ozone concentrations ranging from 0 to 25 mg/l. The table also presents runs that evaluated the impact of pH on hydroxyl radical concentration. These data clearly indicate that increasing pH should also increase steady-state hydroxyl radical concentration and conversely reaction rate. Increasing pH from 3 to 7 generally increased hydroxyl radical concentrations by 4 orders of magnitude (for $[O_3] = 1$ mg/l, EE-15 to EE-11 mg/l). Increasing from pH = 7 to 9 results in an approximate 2 order of magnitude increase (for $[O_3] = 1$ mg/l, EE-11 to EE-9 mg/l). Although increasing pH beyond pH = 9 is feasible, this practice is generally not considered viable for design of groundwater treatment systems; therefore, pHs in excess of 9 were not evaluated during this study. In the case of all pHs evaluated, increasing ozone concentration resulted in increased radical concentrations. However, beyond an ozone concentration of 6 mg/l, a point of vastly diminishing returns appears because of minimum net increase in steady-state hydroxyl radical concentrations. This indicates that for the 10-mg/l hydrogen peroxide-dosed system, ozone concentrations beyond 6 mg/l would provide little benefit in terms of TNT removal (assuming all TNT removal was due to radical oxidation and not primary oxidation). These predictions do present some shortfalls in terms of the model performance because overdosing with ozone does not yield an adverse effect on steady-state hydroxyl radical concentration. However, the results of the experiments performed during this study indicate that a scavenging effect due to excessive oxidizer presence does occur as witnessed by reduced contaminant removal rate (see Chapter 4).

Table 3 presents model runs that evaluated the same range of ozone concentrations evaluated in the runs listed in Table 1, except that a 100-mg/l hydrogen peroxide dose was for system pHs of 3, 7, and 9. Comparing these results to the 10-mg/l hydrogen peroxide-dose runs (Table 2) indicates that little benefit is gained by adding higher hydrogen peroxide concentrations until applied residual ozone levels in excess of 2 mg/l are achieved. At this point, the steady-state hydroxyl radical concentration predicted for the 100-mg/l hydrogen peroxide dose (2.052EE-10 mg/l) is approximately 30 percent more than the concentration predicted for the 10-mg/l hydrogen peroxide dose (1.37EE-10 mg/l). The difference in performance increases with increasing ozone dose, while the point of diminishing returns appears to be an ozone dose of 25 mg/l.

Table 4 lists the results of model runs using a 1-mg/l hydrogen peroxide dose for the same ozone doses and pH values evaluated above. These data indicate the point of diminishing returns to be approximately at an ozone dose of 4 mg/l. These data indicate very similar results as observed with the 10-mg/l hydrogen peroxide-dosed systems.

The results of the various model runs indicate that the model appears to be incapable of predicting scavenging reactions by the parent oxidizers (i.e., hydrogen peroxide and ozone). The results of Glaze and Kang (1988) clearly support that these scavenging or termination reactions do occur. The lack of a predictive capability for termination reactions indicate that a key termination step may have been overlooked within the development of the model or that the reaction rates reported by the various research groups are in error. In either case, the model does indicate an upper ceiling of residual ozone concentration beyond which little benefit is gained in increasing ozone concentrations beyond that point (i.e., point of diminishing returns).

Table 2 Model Approximations for SS Hydroxyl Radical Concentrations Maintained Within a 10-mg/l Hydrogen Peroxide-Dosed Peroxone System With Varying Ozone Doses			
[Ozone] [OH] mg/l	pH3 [OH] _{ss} mol/l	pH7 [OH] _{ss} mol/l	pH9 mol/l
0	0	0	0
0.1	1.05EE-16	1.05EE-11	1.05EE-9
0.25	2.53EE-16	2.53EE-11	2.53EE-9
0.5	4.74EE-16	4.74EE-11	4.74EE-9
1	8.42EE-15	8.42EE-11	8.42EE-9
2	1.38EE-14	1.38EE-10	1.38EE-8
4	2.01EE-14	2.01EE-10	2.01EE-8
6	2.38EE-14	2.38EE-10	2.38EE-8
8	2.62EE-14	2.62EE-10	2.62EE-8
10	2.79EE-14	2.79EE-10	2.79EE-8
25	3.30EE-14	3.30EE-10	2.30EE-8

Table 3
Model Approximations for SS Hydroxyl Radical Concentrations
Maintained Within a 100-mg/l Hydrogen Peroxide-Dosed Peroxone
System With Varying Ozone Doses

[Ozone] mg/l	pH3 [OH].. mol/l	pH7 [OH].. mol/l	pH9 [OH].. mol/l
0	0	0	0
0.1	1.08EE-15	1.08EE-11	1.08EE-9
0.25	2.69EE-15	2.69EE-11	2.69EE-9
0.5	5.35EE-14	5.35EE-10	5.35EE-8
1	1.06EE-14	1.06EE-10	1.06EE-8
2	2.05EE-14	2.05EE-10	2.05EE-8
4	3.89EE-14	3.89EE-10	3.89EE-8
6	5.55EE-14	5.55EE-10	5.55EE-8
8	7.05EE-14	7.05EE-10	7.05EE-8
10	8.42EE-14	8.42EE-10	8.42EE-8
25	1.58EE-13	1.58EE-9	1.58EE-7

Table 4
Model Approximations for SS Hydroxyl Radical Concentrations
Maintained Within a 1-mg/l Hydrogen Peroxide-Dosed Peroxone
System With Varying Ozone Doses

[Ozone] mg/l	pH3 [OH].. mol/l	pH7 [OH].. mol/l	pH9 [OH].. mol/l
0	0	0	0
0.1	3.64EE-16	3.64EE-12	3.64EE-10
0.2	7.03EE-16	7.03EE-12	7.03EE-10
0.5	1.60EE-15	1.60EE-11	1.60EE-9
1	2.79EE-15	2.79EE-11	2.79EE-9
2	4.44EE-15	4.44EE-11	4.44EE-9
5	6.88EE-15	6.88EE-11	6.88EE-9
10	8.42EE-15	8.42EE-11	8.42EE-9
50	1.03EE-14	1.03EE-10	1.03EE-8

The impact of increasing pH is also observed upon review of the model runs (Tables 1 through 3). These results indicate that experiments evaluating peroxone's ability to remove TNT should generally be focused toward pHs within the neutral to basic range with pH = 9 considered a practical upper limit.

The model runs clearly indicate the value of supplying adequate amounts of ozone into the peroxone system. However, ozone generators currently available typically are only capable of producing ozone gas phase percentages within the 1- to 10- percent range with most systems producing 2- to 5- percent ozone. Therefore, steady-state (SS) residual ozone concentrations in excess of 20 mg/l are generally not possible using the generators of today. Recent advances in generator technology indicate that ozone percentages in excess of 30 percent may one day be obtainable, which will vastly improve a given reactors capability.

Summary

According to the proposed mechanisms and model runs, the following predictions with respect to peroxone performance using typical reactor conditions are predicted:

- a. The model did not account for termination (scavenging) reactions observed by others during their experiments. This indicates that either an important termination mechanism was overlooked or that the rate constants reported by some for key peroxone-related reactions are inaccurate (it is very likely that both scenarios have occurred).
- b. During peroxone or ozonation, pH becomes an important factor, with faster degradation at higher pH. The pH dependence is primarily because the reaction of $\cdot OH$ with HO_2^- (the k_6 step) is many orders of magnitude faster than with its conjugate acid H_2O_2 .
- c. With peroxone, higher SS residual ozone concentrations should be maximized to yield fast rates. However, appropriate respective hydrogen doses should be added to prevent possible radical scavenging from occurring.
- d. With peroxone, the reaction is likely, as evident in the data table, to show a first-order dependence on ozone over a wide range of hydrogen peroxide doses (i.e., increasing ozone dose will result in a proportional increase in radical concentrations, and in turn, reaction rate).
- e. The peroxone experiments performed within this study should focus on a neutral to basic pH range (within practical limits) and hydrogen peroxide doses ranging between 1 and 100 mg/l since SS residual ozone concentrations beyond 8 mg/l were beyond the capability of the ozone generator used in this study and also those typically found within the marketplace.

3 Materials and Methods

Peroxone Oxidation Pilot System

The POPS used in this study was funded by the DoD Strategic Environmental Research and Development Program and was constructed and assembled by the WES Environmental Restoration Branch and the WES Public Works Division. A schematic diagram of the system is presented in Figure 5. The general construction of the unit consisted of four glass columns plumbed in series, a holding tank for influent water supply, two 3-lb per day ozone generators, a microcomputer for data logging system control, and oxidizer monitors for vapor and aqueous phase concentrations of hydrogen peroxide and ozone. The POPS unit is discussed in more detail below.

Influent holding tank

The influent holding tank was a 500-gal stainless steel tank equipped with an automated level control sensor used to maintain a minimum volume or greater for supply of influent to the POPS unit.

Hydrogen peroxide injection system

Before explosives-contaminated influent entered the POPS columns, a metering pump delivered concentrated hydrogen peroxide to the influent of Column 1 or to the influent of all columns. An in-line vortex mixer was used to mix the hydrogen peroxide and contaminated water. Based upon the required dosage, the metering pump delivery rate was established and the pump set to deliver the required volume of hydrogen peroxide.

Ozone generators

Two 3-lb per day Orec™ generators were used to supply a maximum of 2.2 percent ozone (wt/wt) in the vapor-phase feed stream. Ozone was sparged into the base of the column via rectangular ceramic spargers measuring 6 in. in height, 1.5 in. in width, and 1.5 in. in depth.

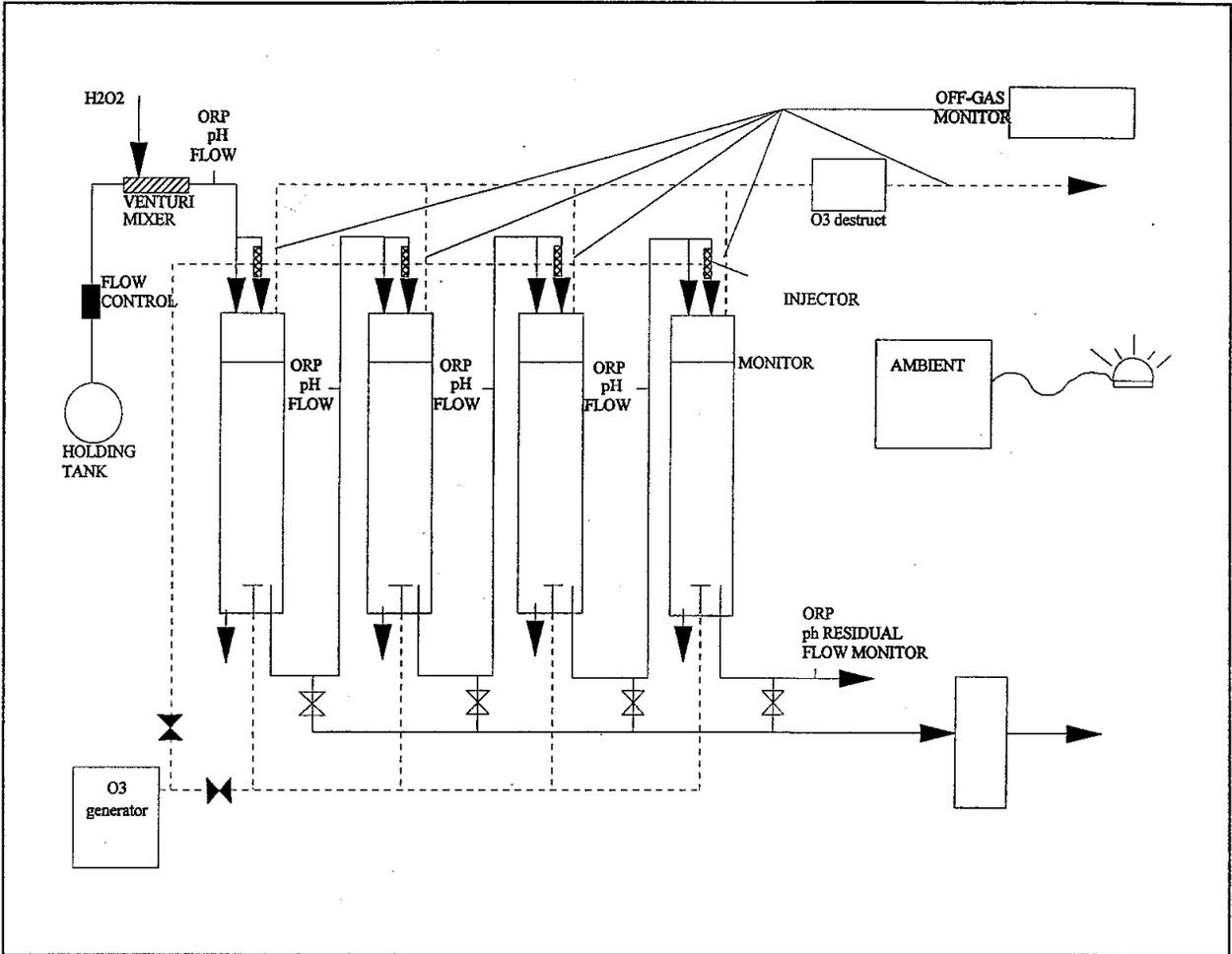


Figure 5. Schematic of POPS unit

Four glass reaction columns

Four columns were constructed of glass and plumbed in series and were 6 in. in diam and 14 ft in height (two 7-ft sections). The columns were operated at a liquid level of 12.5 ft, with 1.5 ft of freeboard to allow for pressure buildup relief and foaming.

Ozone decomposition unit

An ozone decomposition unit containing Hopkolite was used to decompose unreacted ozone exiting the vapor-phase of the four columns to prevent release of ozone into the ambient air. A GAC unit was placed in-line after the ozone decomposition unit to capture undecomposed ozone or volatile organics (CAAP waters did not contain volatiles, but the POPS unit is equipped to treat them if necessary).

Ozone monitors

PCI Ozone and Control Systems, Inc., monitors were used to detect ozone in the vapor-phase immediately on-line after the ozone generator, pre- and post- the ozone decomposition unit, and in the ambient air. CHEMetrics test kits were used to monitor ozone in the aqueous phase.

Hydrogen peroxide analyses

A Rqflex colorimeter manufactured by EM Sci., Inc., was used to monitor hydrogen peroxide dosage being delivered to the POPS unit and residual hydrogen peroxide remaining in the column effluents.

Oxidation reduction potential, pH, and flowmeters

Probes for measuring oxidation reduction potential, pH probes, and flowmeters were in-line after the hydrogen peroxide vortex mixer and in the effluents from each column.

The POPS unit was operated in a countercurrent flow mode. Ozone was sparged into the base of the reactor, flowing upward in an attempt to obtain maximum contact with CAAP water, while hydrogen peroxide-dosed CAAP water flowed downward. The ozone-sparged bubbles were approximately 2 mm in diameter and mass transfer efficiencies (MTE, further information provided under the following sections describing Pretest 3) were generally greater than 80 percent.

The POPS unit was shipped to the CAAP by truck and assembled onsite. Pretest runs were conducted to assess the system's ability to obtain the required concentrations of oxidizers in the CAAP waters and to test for leaks. The following pretests and system checks were conducted in order as described below:

- a. Check for leaks of ozone or water after assembling the POPS unit.
- b. Calibration of in-line pH probes and pump settings required to obtain selected hydrogen peroxide concentrations (a more detailed description of the procedures is provided below).
- c. Preliminary determination of system ozone MTE in tap water.

Pretest 1 involved observation of the system after setup to determine whether there were water leaks and observance of ozone monitors to determine whether there were ozone leaks. Pretest 2 involved calibration of the in-line probes for monitoring pH according to manufacturer's instructions. Pretest 2 also involved calibration of pumps to attain the settings required to reach the required hydrogen peroxide concentration. A stroke length of 70 (equating to 0.0135 gal per min (gpm)) was used on the hydrogen peroxide injection metering pump. The concentration of hydrogen peroxide in the delivery solution was determined based upon the

approximate CAAP influent water flow rate. The flow rate (i.e., stroke length) of the metering pumps was adjusted to achieve higher or lower concentrations of hydrogen peroxide in the influent to each reaction column, depending on the test conditions. Calculations of the required hydrogen peroxide concentration in the makeup solution provided an approximation for influent flow rate of hydrogen peroxide.

Pretest 3 involved evaluation of MTE for ozone in tap water. MTE was determined by monitoring the residual aqueous-phase ozone concentration and the concentration of ozone in the exhaust vapor-phase. The equations for calculation of MTE are presented below:

$$\text{Transfer efficiency (TE, \%)} = [(O_3 \text{ feed}) - (O_3 \text{ out})] / (O_3 \text{ feed}) \times 100 \quad (29)$$

$$\text{Transferred mass (TM, mg } O_3/\text{min)} = \text{TE} \times O_3 \text{ feed (mg/l)} \times \text{Q/min} \quad (30)$$

$$\text{Transferred dose (mg/l)} = [TM] / \text{flow rate in Q/min} \quad (31)$$

Among the 21 treatment scenarios evaluated (specific runs are listed later in this section) the concentration of ozone exiting the generator was varied from 1.0 to 2.2 percent (wt/wt). Upon initiating water flow, two hydraulic retention times (HRTs) were allowed to flow through the reactor before initiation of testing and collection of off-gas and residual ozone measurements to reach steady-state conditions. Concentrations of ozone in the vapor-phase were measured every 3 min, and residual ozone measurements in the aqueous phase were measured after one, two, three, and four HRTs for Columns 1, 2, 3, and 4, respectively. Aqueous-phase ozone and aqueous-phase hydrogen peroxide were measured using CHEMetrics test kits and Merckoquant peroxide tests, respectively. The ozone concentration in the vapor-phase was analyzed using a PCI Ozone and Control Systems, Inc., monitor.

After completion of the pretests, test runs on the CAAP waters were initiated. Three wells were tested (66, 22, and the New Well) and included 21 treatment scenarios, which are presented in Table 5. Well 66 waters were tested first and were evaluated the most comprehensively. Minimum dosages of oxidizers were added to Well 66 waters, i.e., no ozone with 25-ppm hydrogen peroxide and 2-percent ozone with no hydrogen peroxide to tests how well less aggressive techniques would work (in addition to evaluation of peroxone and as a basis of comparison to peroxone, which was expected to be more aggressive). In the first column of Table 5, a series of numbers follow the run number in parentheses. These numbers describe the run conditions and will be used heretofore in discussions of the results and are explained below:

Table 5
Summary of Treatment Scenarios Evaluated During Peroxone
Treatment at CAAP^a

Run No. (Run Description)	Well No.	Hydraulic Flow rate gpm	H ₂ O ₂ Conc., mg/l	Percent Ozone by Weight (Avg. MTE)
1 (2OZNHP)	66	0.96	--	2.3 (46%)
2 (2OZC25HP)		0.88	25 ^b (1-4)	2.2 (89%)
3 (NOZC25HP)		0.92	25 ^b (1-4)	--
4 (2OZC100HP)		0.90	100 ^b (1-4)	2.3 (77%)
5 (2OZ100HP)		0.91	100 ^c (1)	2.3 (90%)
6 (1OZC10HP)		0.87	10 ^b (1-4)	1.0 (86%)
7 (2OZC10HP)		0.88	10 ^b (1-4)	2.2 (65%)
8 (2OZC12HP40)		1.88	12 ^b (1-4)	2.2
9 (1OZC25HP)		0.91	25 ^b (1-4)	1.0 (80%)
10 (2OZ1000HP)		0.90	1,000 ^c (1)	2.2 (68%)
11 (2OZC12HP40) ^d	22	1.8	12 ^b (1-4)	2.2
12 (1OZC10HP)		0.89	10 ^b (1-4)	1.0 (80%)
13 (2OZC10HP)		0.90	10 ^b (1-4)	2.2 (57%)
14 (2OZC25HP)		0.86	25 ^b (1-4)	2.2 (86%)
15 (2OZ100HP)		0.86	100 ^c (1)	2.2 (85%)
16 (2OZC5HP40)		1.8	5 ^b (1-4)	2.2 (62%)
17 (2OZC2HPO120)	New Well	0.6	2 mg/l ^b (1-4) effluent	2.0 (88%)
18 (2OZ100HP)		0.87	100 ^b (1-4)	2.2 (85%)
19 (2OZC10HP)		0.87	10 ^b (1-4)	2.2 (64%)
20 (2OZC25HP)		0.86	25 ^b (1-4)	2.2 (87%)
21 (2OZC2HPO120)	66	0.58	2 mg/l ^b (1-4) effluent	2.3 (89%)

^a Samples were collected in triplicate.
^b Indicates dosage was applied to Columns 1 through 4, i.e., continuous dosing.
^c Indicates dosage was applied to Column 1 only, i.e., batch dosing.
^d Samples were discarded since problems with hydrogen peroxide dosing system were discovered.

For example, setting

$$2OZC2HPO120 = 2OZ/X/2HPO/120$$

$$1 / 2 / 3 / 4$$

where

1 = 2OZ - 2 percent ozone concentration, other possible - 1 percent -
 1OZ, or NOZ - no ozone

- 2 = Continuous dosing of hydrogen peroxide to Columns 1 through 4, other possible, no entry indicating batch addition of hydrogen peroxide in Column 1 only
- 3 = 2HPO - 2 ppm hydrogen peroxide in Columns 1-4 effluents, other possible - 5 ppm, 10 ppm, 12 ppm, 100 ppm, or 1,000 ppm
- 4 = 120 - "low flow" (120-min HRT), 40 - "high flow" (40-min HRT), no entry indicates 80-min HRT

Before each run, two hydraulic retention times were processed in the reactor before collection of oxidizer or explosives samples in an attempt to reach steady-state conditions. It should be noted that immediately after ozonation sparging was initiated, Well 66 water was observed to turn a pinkish color. Although the source of discoloration was unknown, it may have been due to an ozone-phosphate base reaction with the explosives in the water. After allowing two HRTs to pass through the four columns, each test run was conducted for one HRT. Samples for explosives, influent oxidizer concentration (aqueous phase), and residual oxidizers (aqueous phase) were collected after 10, 20, 30, and 40 min (40-min total HRT), or 20, 40, 60, and 80 min of treatment (80-min total HRT), or 30, 60, 90, and 120 (120-min total HRT) by sampling the effluents of Columns 1, 2, 3, and 4. The only exceptions were samples collected for Runs 1 (ozone only) and 3 (hydrogen peroxide only) at the 80-min hydraulic retention time using Well 66 waters. The retention times for the "high flow" runs were 10, 20, 30, and 40 min for Columns 1, 2, 3, and 4, respectively, at a flow rate of ≈ 1.8 gpm. "Low flow" runs were conducted at $\approx 0.50 - 0.60$ gpm with an HRT of 30, 60, 90, and 120 min for Columns 1, 2, 3, and 4, respectively. One "low flow" run was conducted each on Well 66 (Run 21) and the New Well (Run 17); one "high flow" run was conducted on Well 22 (Runs 11 and 16 in Table 5, but Run 11 was discarded due to problems with the hydrogen peroxide-dosing system); and one "high flow" run was conducted on Well 66 (Run 8). Explosives samples were collected in triplicate in 1-l precleaned amber bottles. Residual ozone in the vapor phase was recorded at 3-min intervals.

Treatment Conditions for Wells 66, 22, and the New Well

Well 66 was tested using 11 different treatment scenarios (see Table 5). Two air-stream ozone concentrations, 2.3 percent (128.608 mg/min) \approx 2.2 percent (123.017 mg/min) \approx 2.0 percent (111.833 mg/min), and 1.0 percent (55.917 mg/min), and six hydrogen peroxide concentrations, 10 ppm (influent), 12 ppm (influent), 25 ppm (influent), 100 ppm (influent), 1,000 ppm (influent), and 2 ppm (effluent), were evaluated. For reporting purposes, 2.3-percent and 2.2-percent ozone will be referred to as 2-percent ozone since system variabilities lead to the slight decrease in ozone concentration in the air phase. The 2-ppm (effluent) hydrogen peroxide dosage was evaluated in order to test maintaining a minimum effluent hydrogen peroxide concentration, avoiding limiting hydrogen

peroxide concentration to the system, since excess hydrogen peroxide dosing can act as a hydroxyl radical scavenger. Two methods of dosing the system with hydrogen peroxide were evaluated: batch and continuous. Batch addition of hydrogen peroxide involved addition of hydrogen peroxide to the first column only, and continuous operation involved addition of hydrogen peroxide to Columns 1 through 4. Two runs were operated using batch addition of hydrogen peroxide (100 ppm and 1,000 ppm influent), one run involved ozonation only, and the remaining runs were continuously dosed with hydrogen peroxide.

Well 22 was tested using six treatment scenarios. Concentrations of 2-percent and 1.0-percent ozone were varied with five hydrogen peroxide concentrations: 5 ppm (influent), 10 ppm (influent), 12 ppm (influent), 25 ppm (influent), and 100 ppm (influent). One run was evaluated with hydrogen peroxide-dosage addition in batch (100 ppm influent), and the remaining five runs were operated using continuous hydrogen peroxide addition.

The New Well was tested under four treatment conditions. Influent ozone concentrations of 2 percent were varied with four hydrogen peroxide concentrations: 10 ppm (influent), 25 ppm (influent), 100 ppm (influent), and 2 ppm (effluent). One run evaluated batch addition of hydrogen peroxide (100 ppm influent), and the remaining three runs were operated with continuous hydrogen peroxide addition.

4 Discussion of Results

The results of the ozone MTE in Runs 1 through 21 are presented in Table 6 and are based on the results of ozone measurements in the influent and effluent vapor and effluent aqueous phases. The ozone MTE was calculated according to Equations 21 through 31, and the average results of ozone

MTE obtained during Runs 1 through 21 ranged from 59 to 96 percent. Although the results of MTE on the pilot-scale level are not generally used to estimate full-scale efficiency, the results of pilot-scale MTE can be related to full-scale applications. One objective of the peroxone evaluations was to identify the optimal treatment scenario combined with the optimal hydrogen peroxide-to-ozone ratio to obtain the highest percent removal of explosives. The results of comparison of optimal MTE and optimal treatments for each well are presented later in this report.

The results of the peroxone runs are presented in Figures 6 through 27 for Wells 66, 22, and the New Well for HMX, RDX, TNB, TNT, 4A-DNT, 2A-DNT, and 2,4-DNT, respectively. The percent removal of each explosive is presented in Tables 7 through 9, and a composite of the percent removals of all explosives in Wells 66, 22,

Table 6 Results of Mass Transfer Efficiency Calculations for Wells 66, 22, and the New Well (Highest to Lowest)	
Well 66	2MTE, percent
2OZC25HP	96
2OZ100HP	94
2OZ1000HP	94
2OZC2HPO120	90
2OZC12HP40	90
1OZC10HP	87
1OZC25HP	86
2OZC100HP	85
2OZC10HP	75
2OZNHP	59
NOZC25HP	NA
Well 22	
2OZ100HP	92
2OZC25HP	88
1OZC10HP	80
2OZC10HP	71
2OZC5HP40	67
New Well	
2OZC2HPO120	89
2OZC25HP	89
2OZ100HP	88
2OZC10HP	73
NA: Not applicable.	

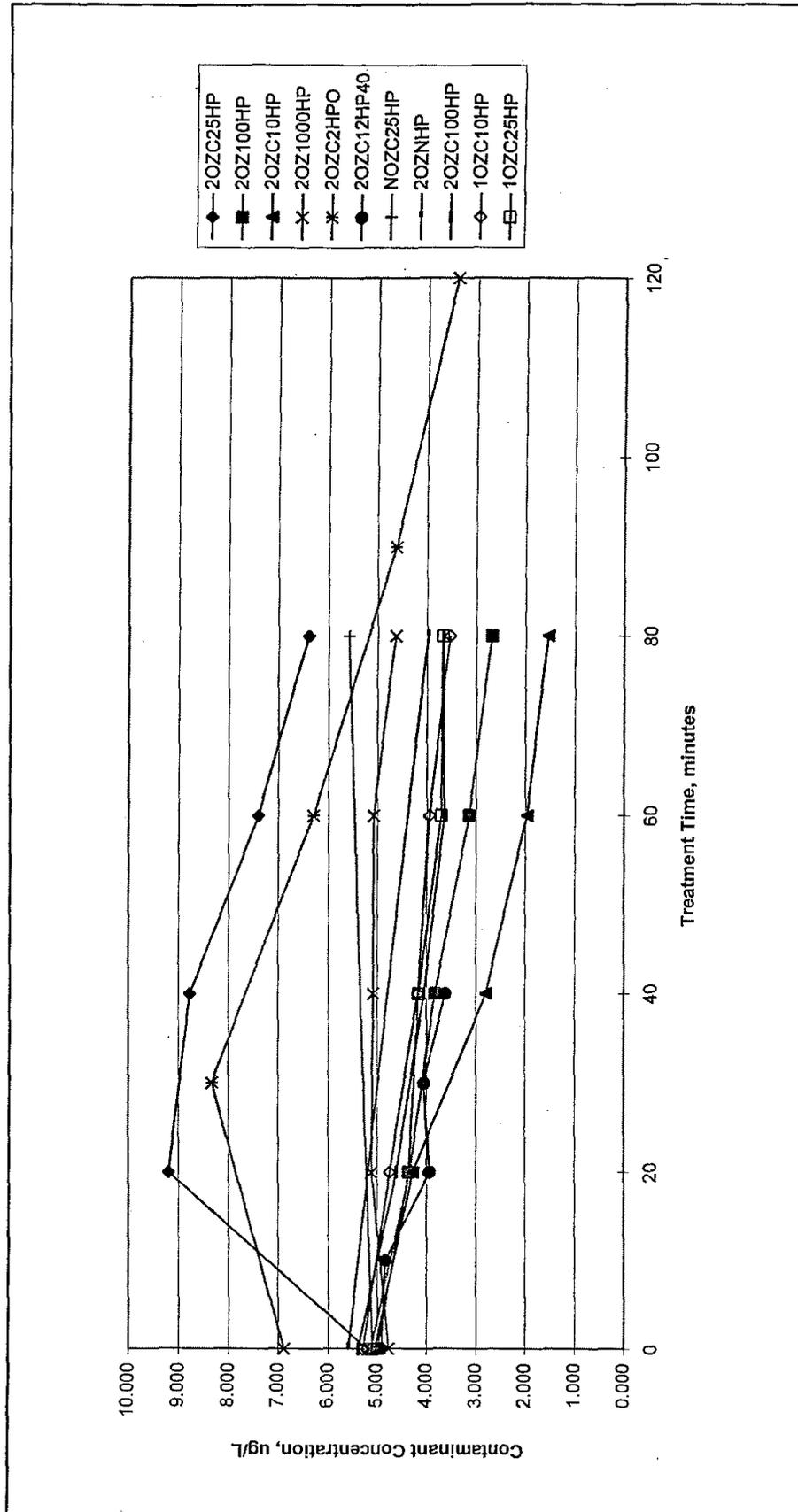


Figure 6. Well 66 HMX removal

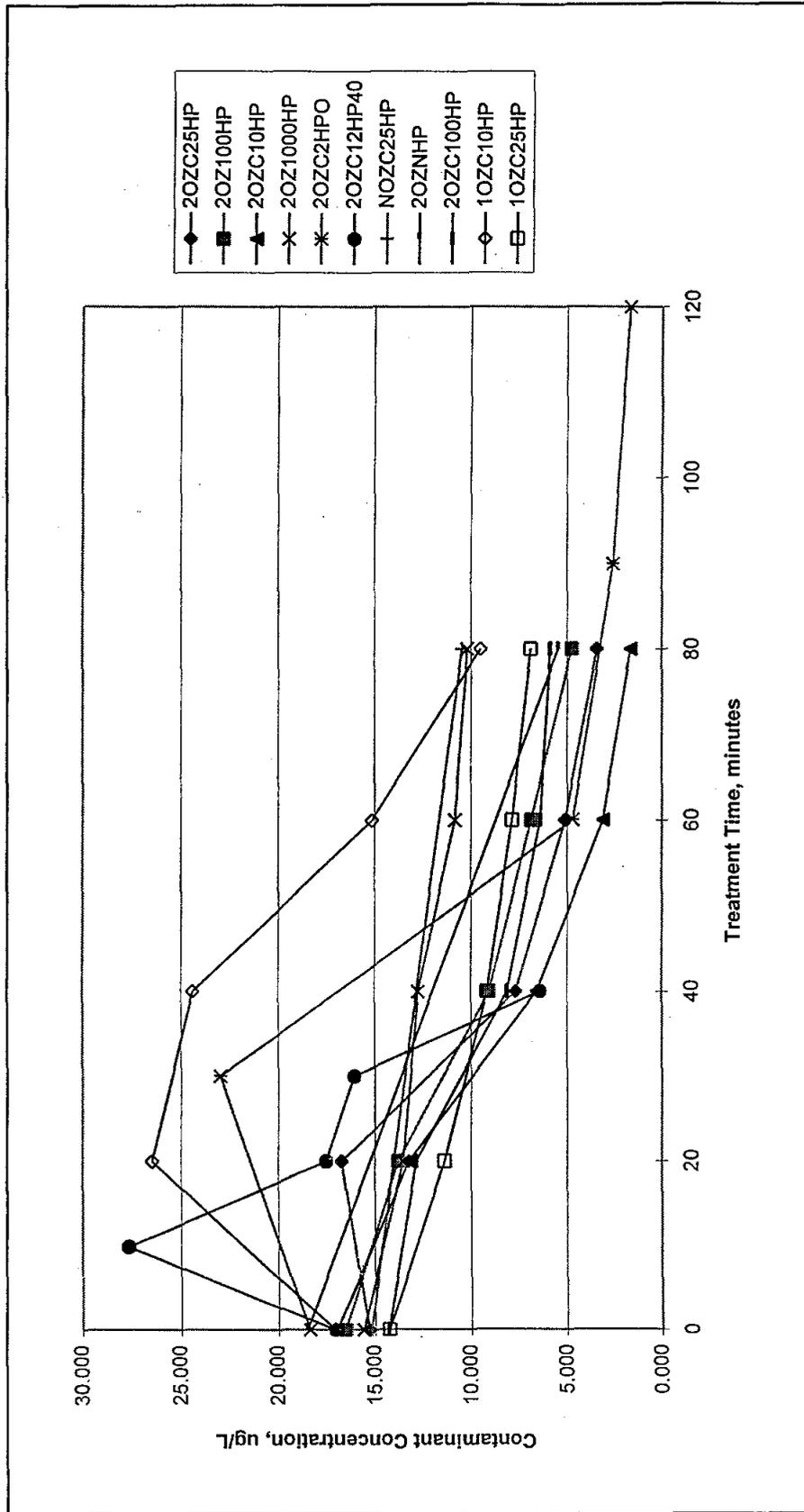


Figure 7. Well 66 RDX removal

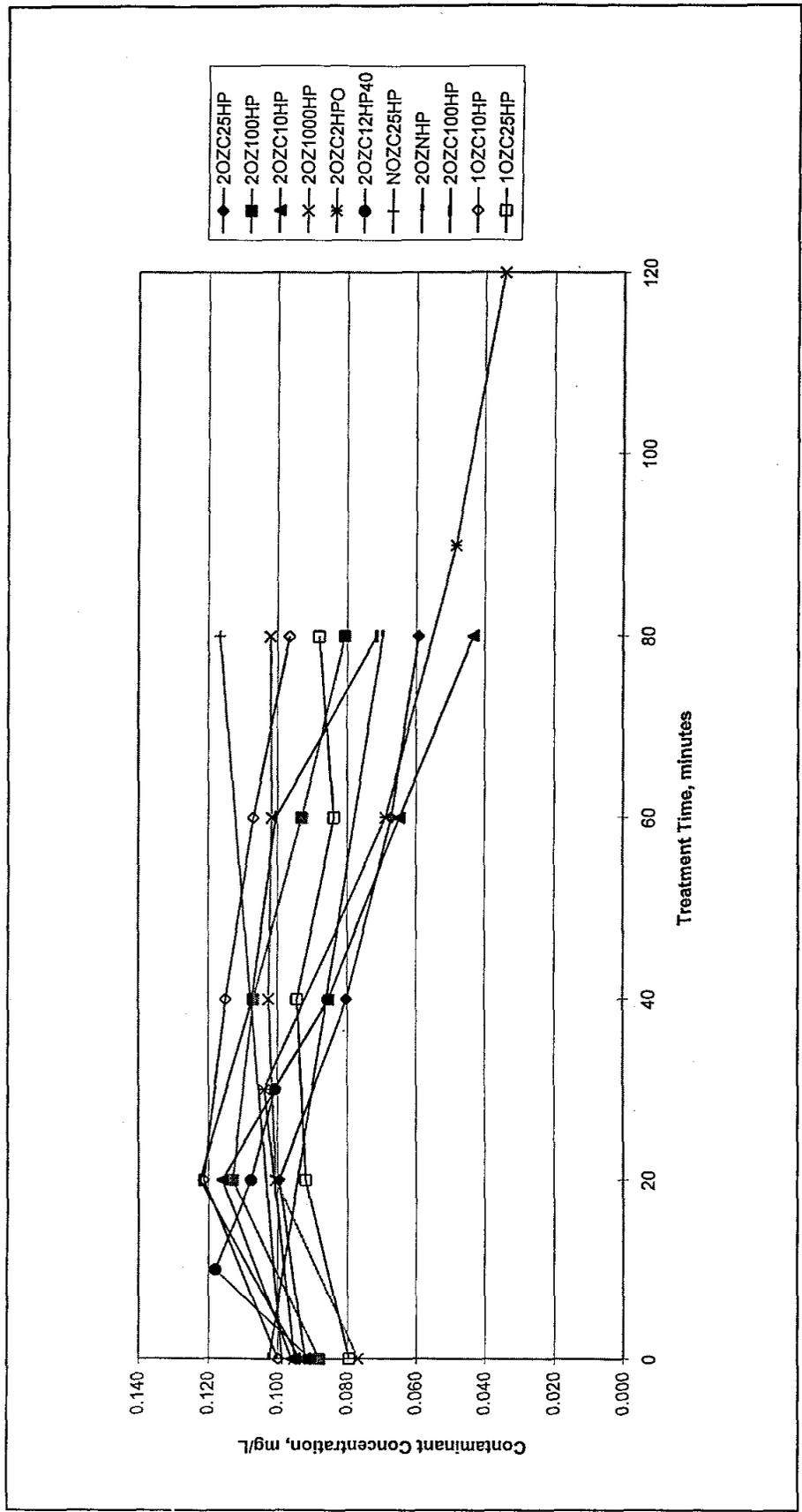


Figure 8. Well 66 TNB removal

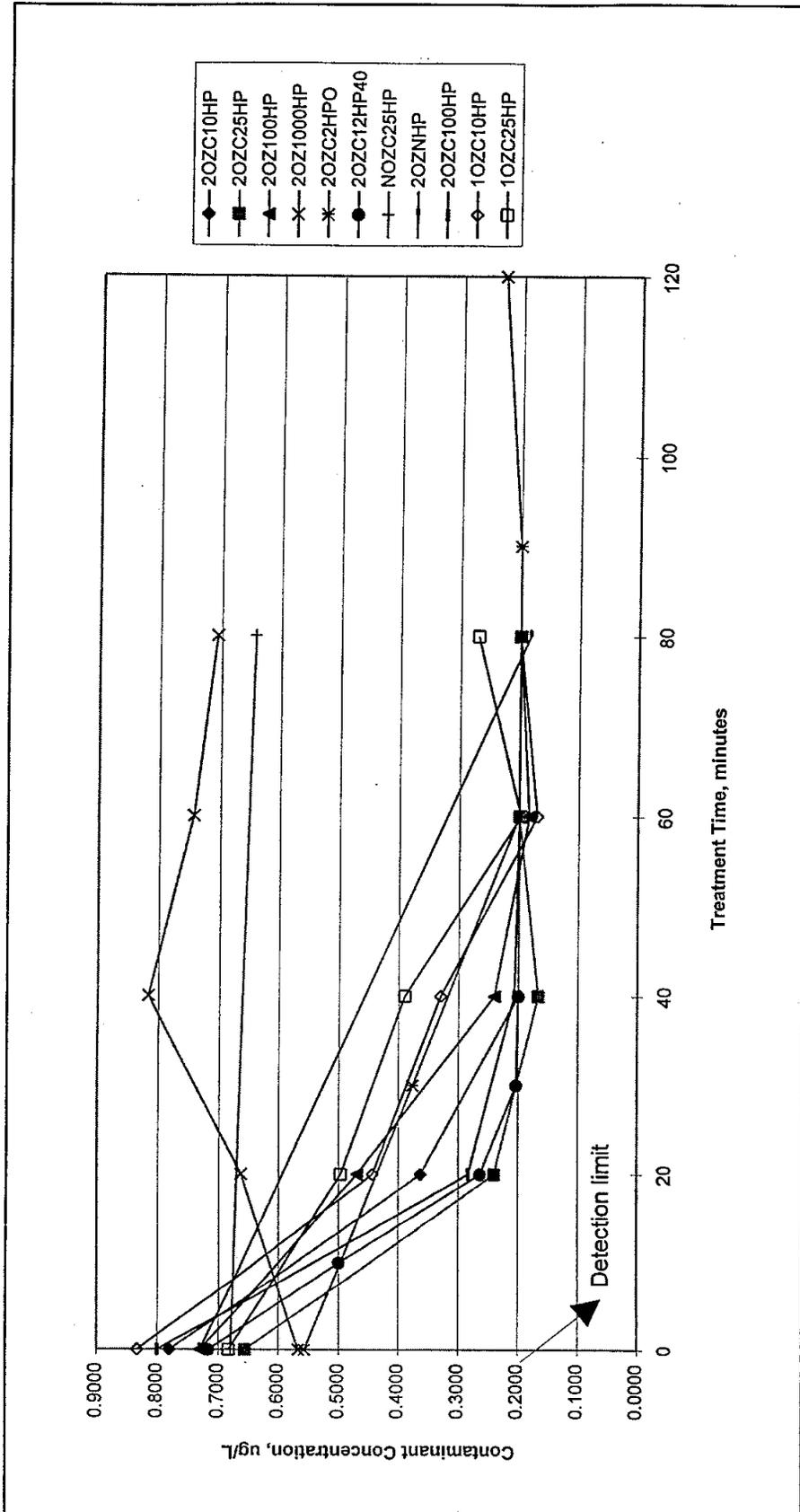


Figure 9. Well 66 DNB removal

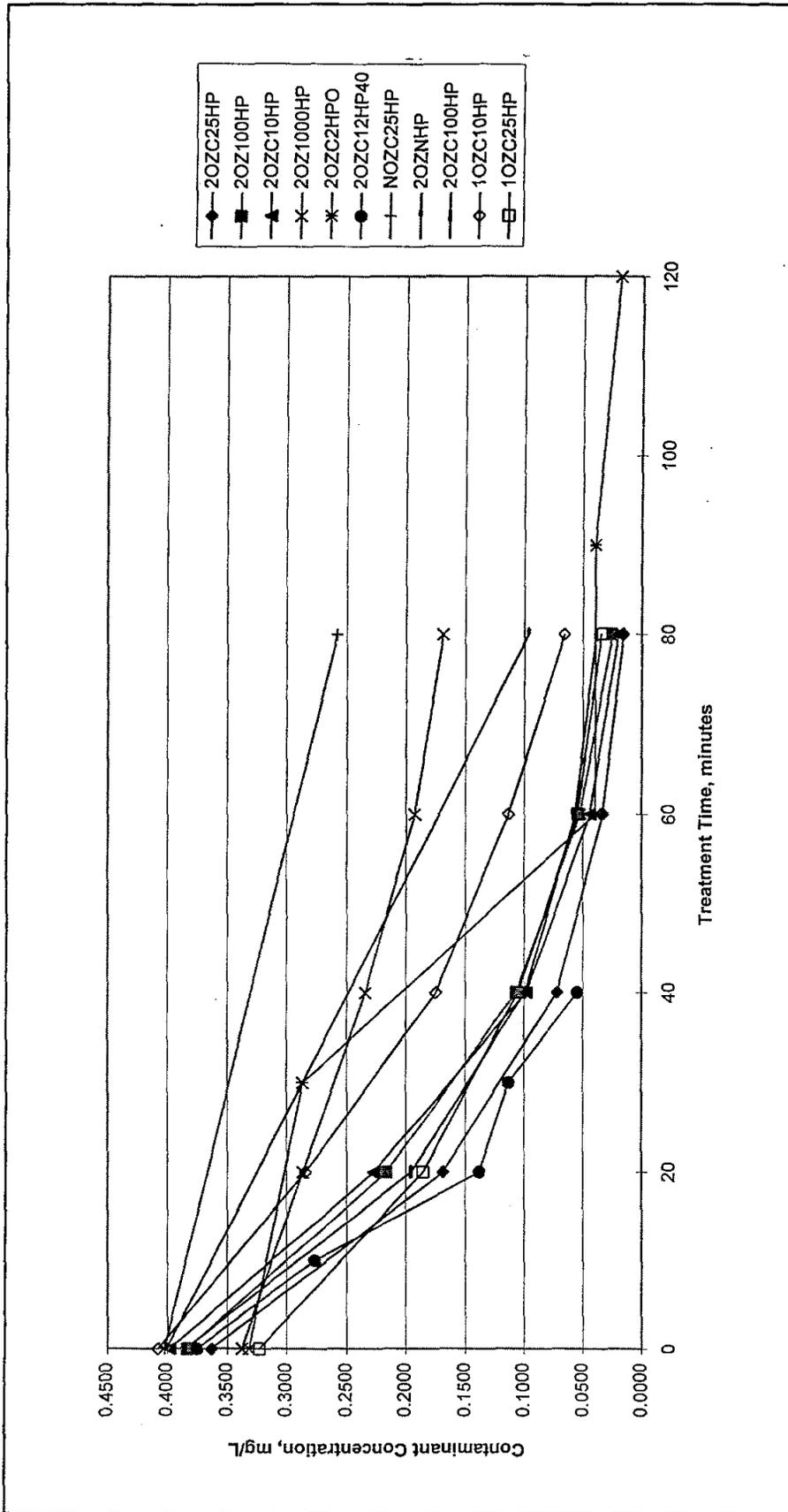


Figure 10. Well 66 TNT removal

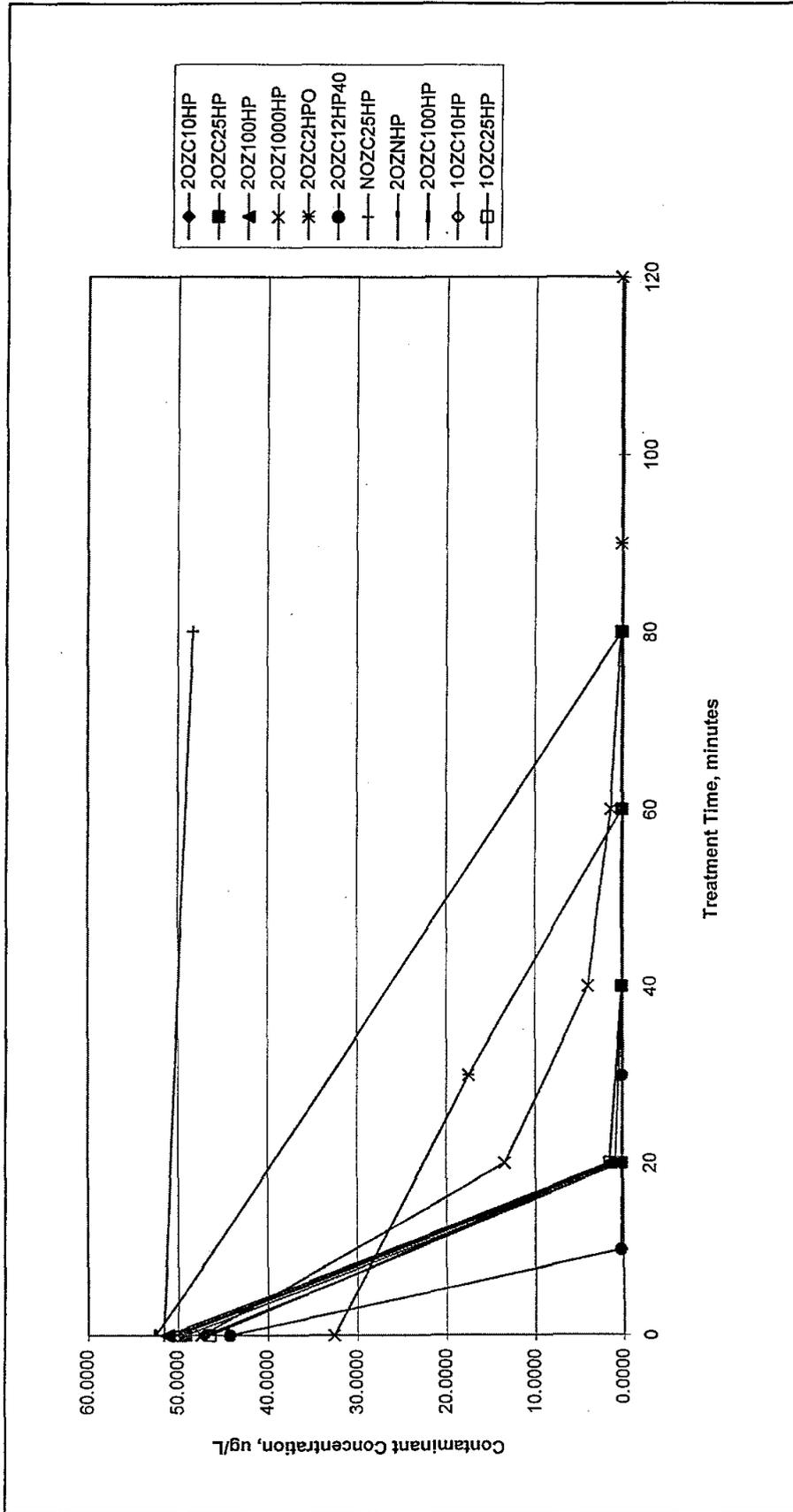


Figure 11. Well 66 4A-DNT results

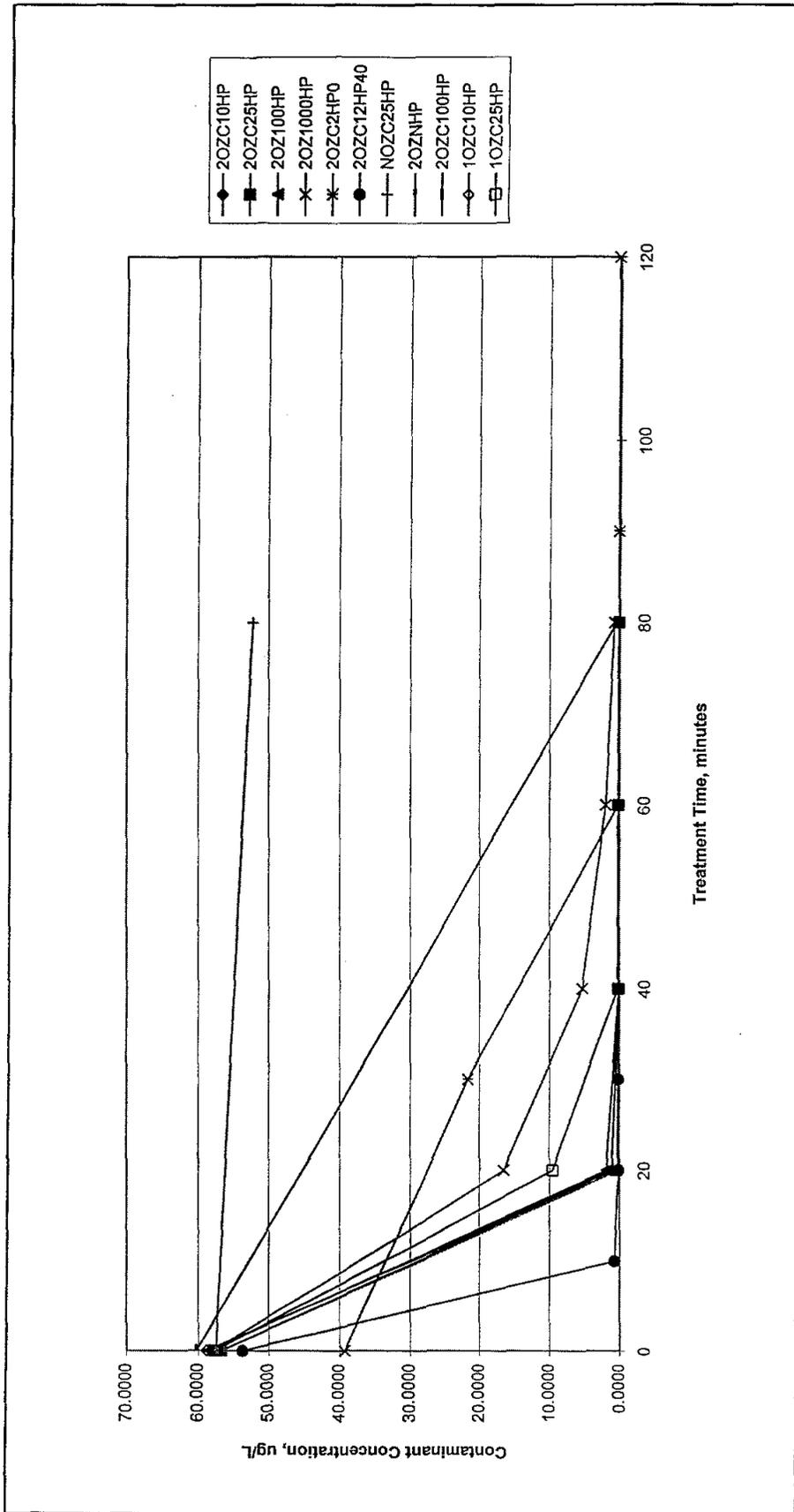


Figure 12. Well 66 2A-DNT results

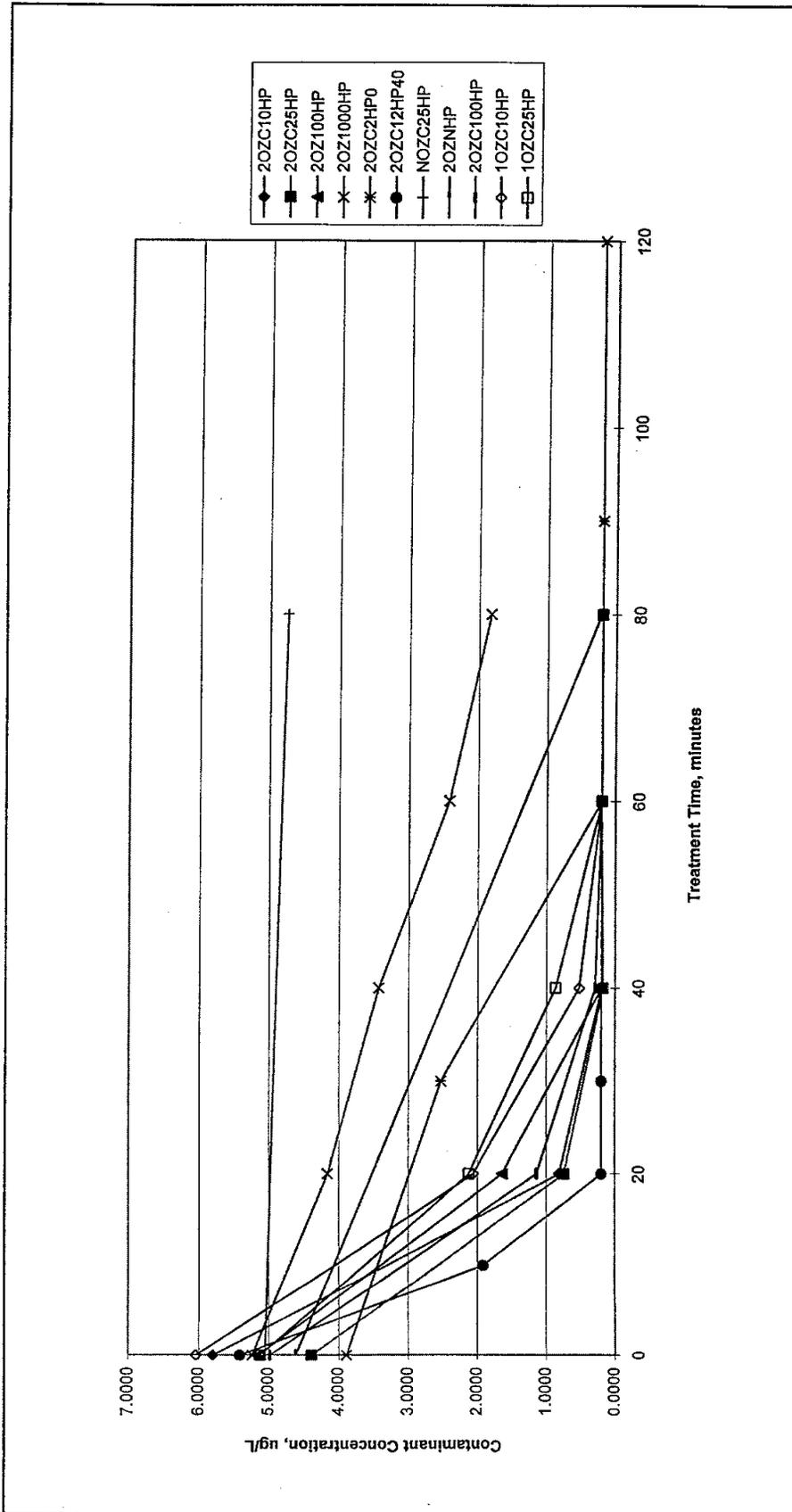


Figure 13. Well 66 2,4-DNT results

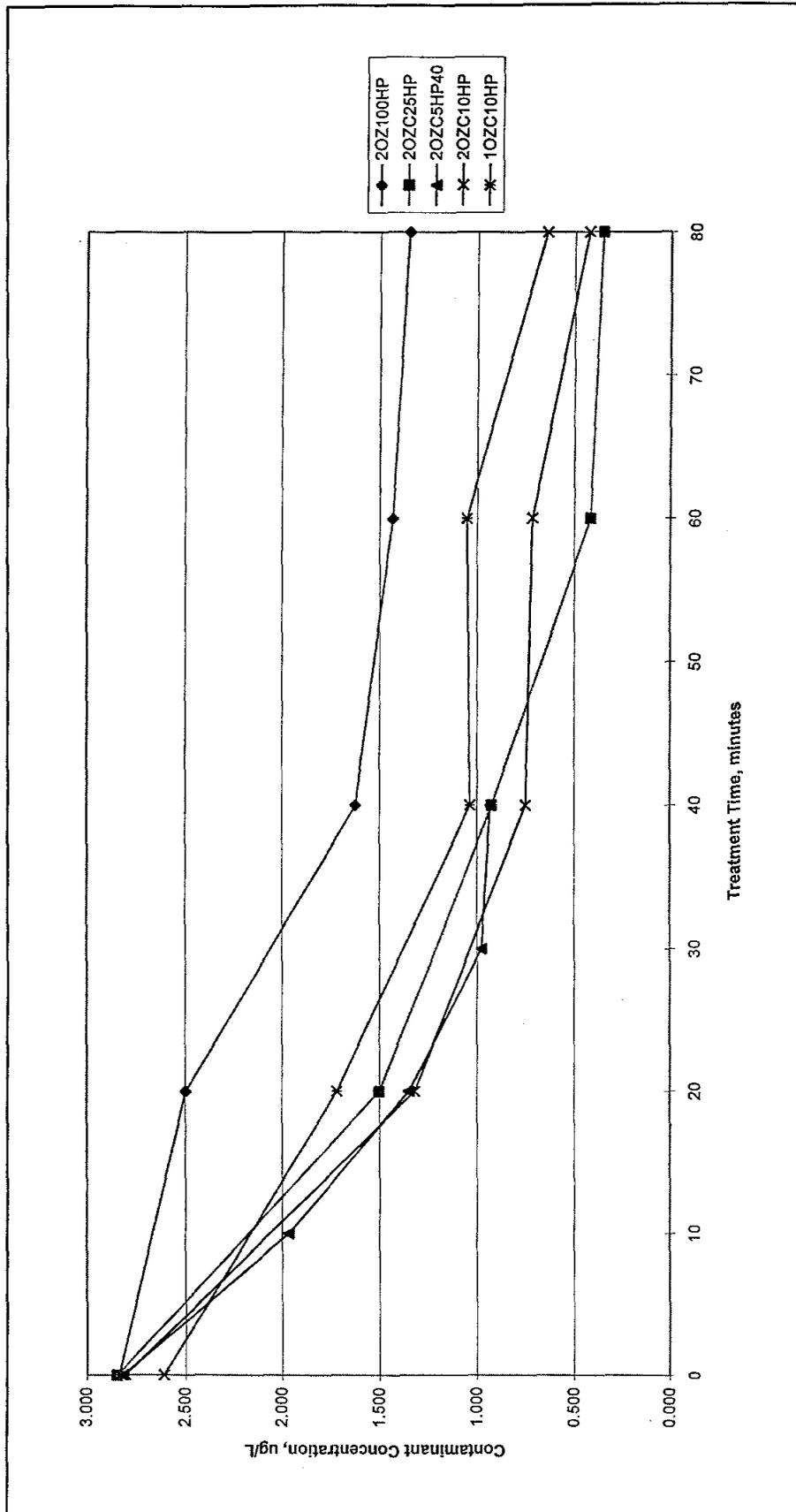


Figure 14. Well 22 HMX removal

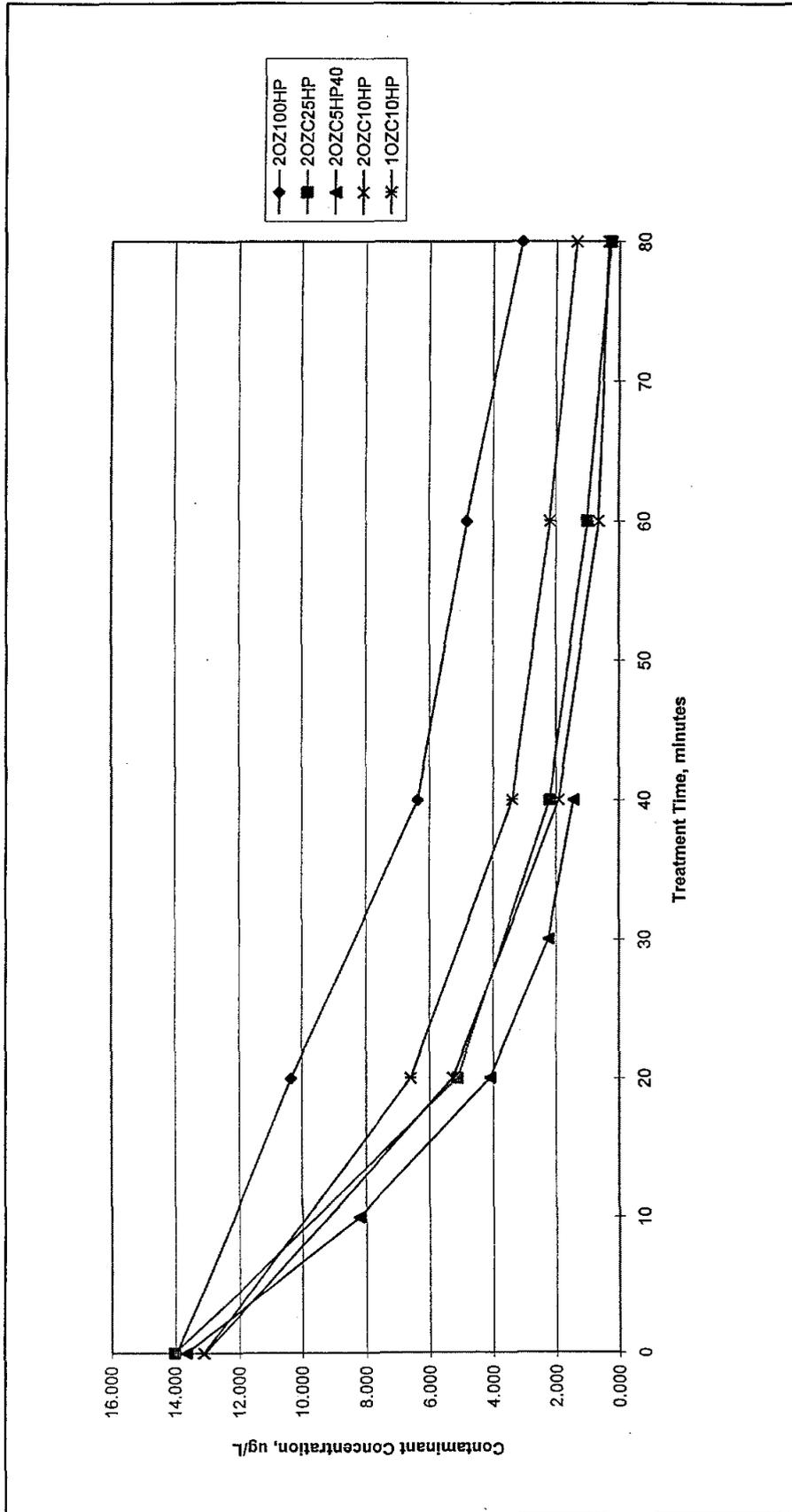


Figure 15. Well 22 RDX removal

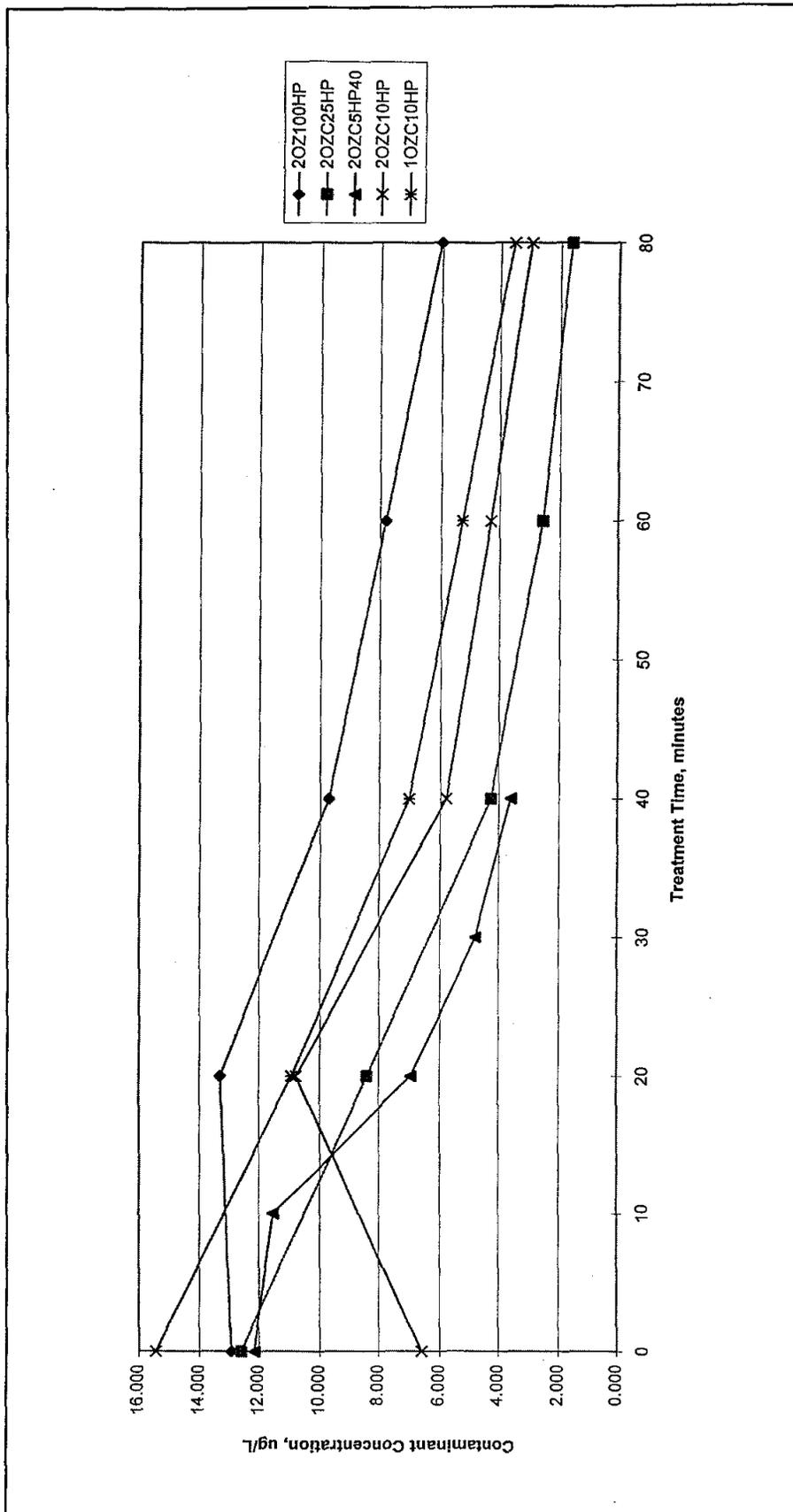


Figure 16. Well 22 TNB removal

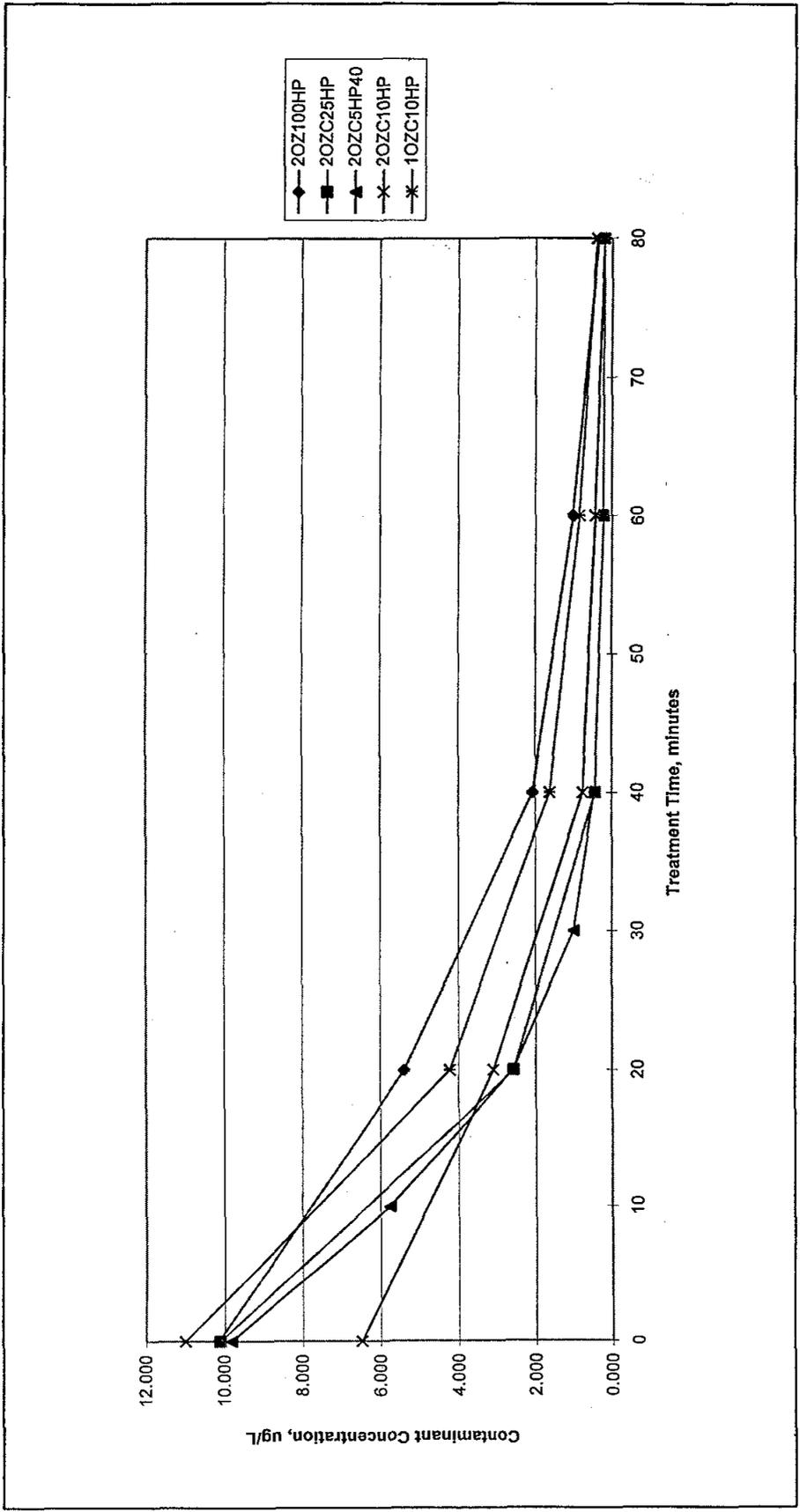


Figure 17. Well 22 TNT removal

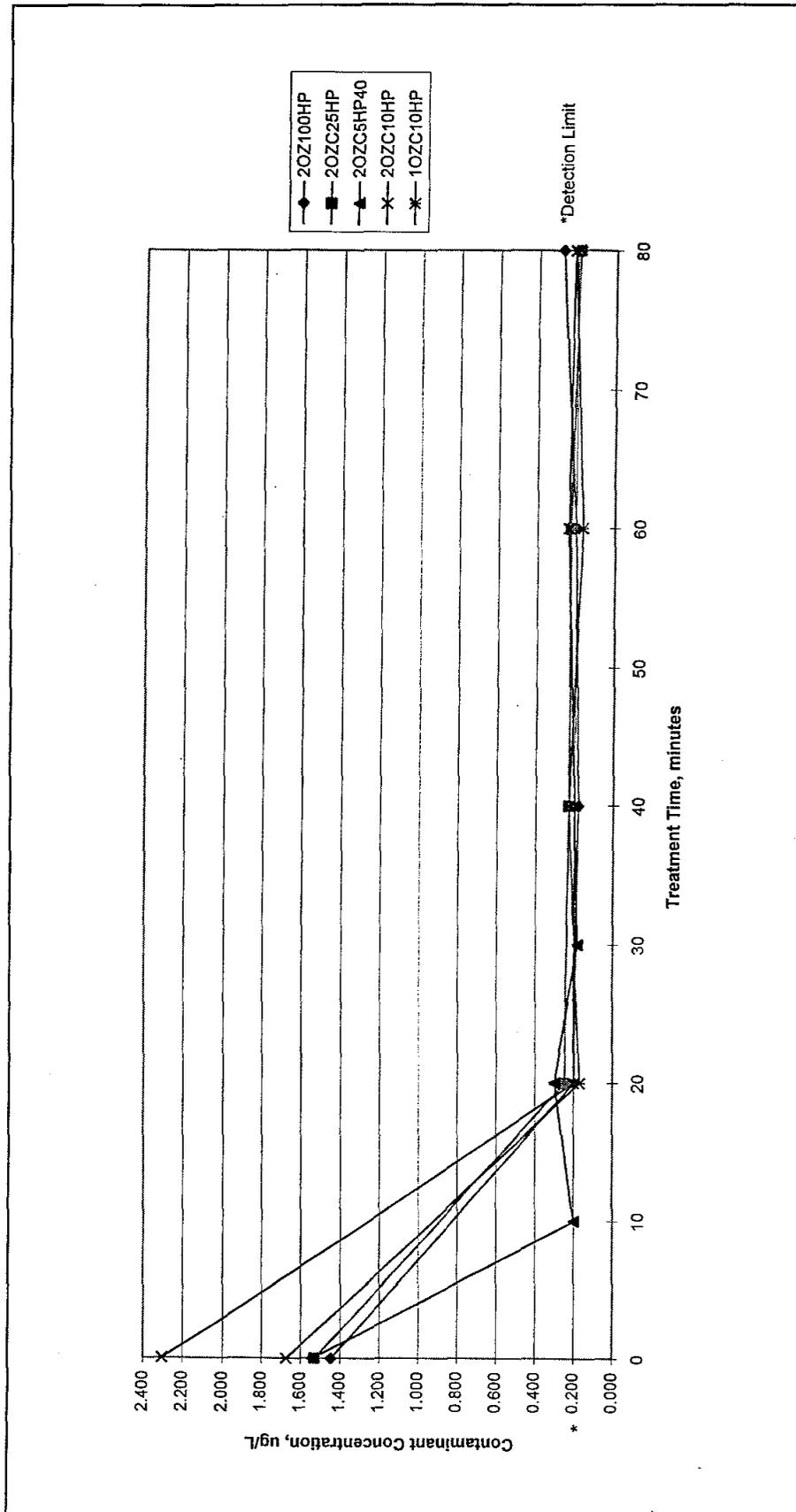


Figure 18. Well 22 4A-DNT removal

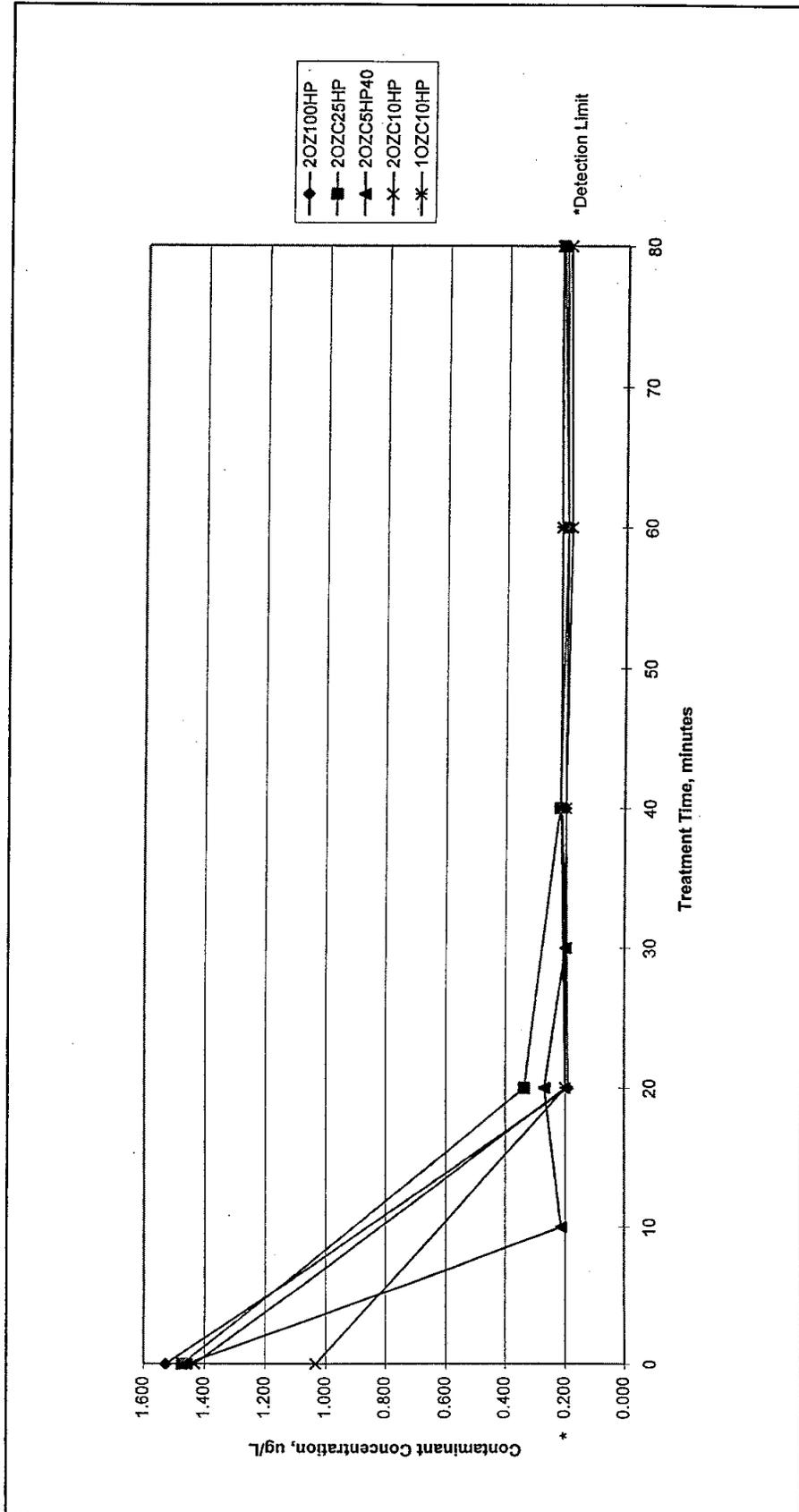


Figure 19. Well 22 2A-DNT removal

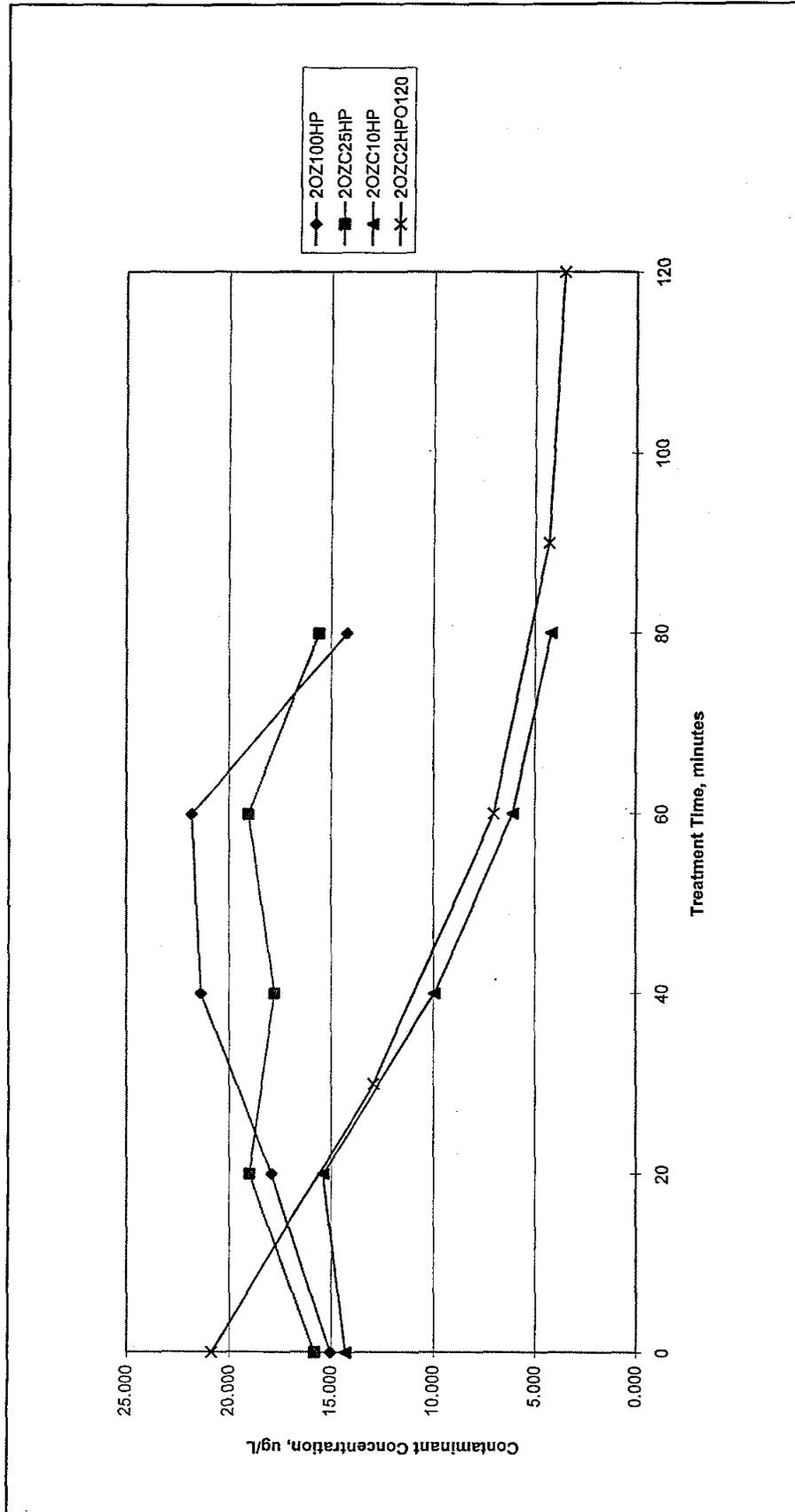


Figure 20. New Well HMX removal

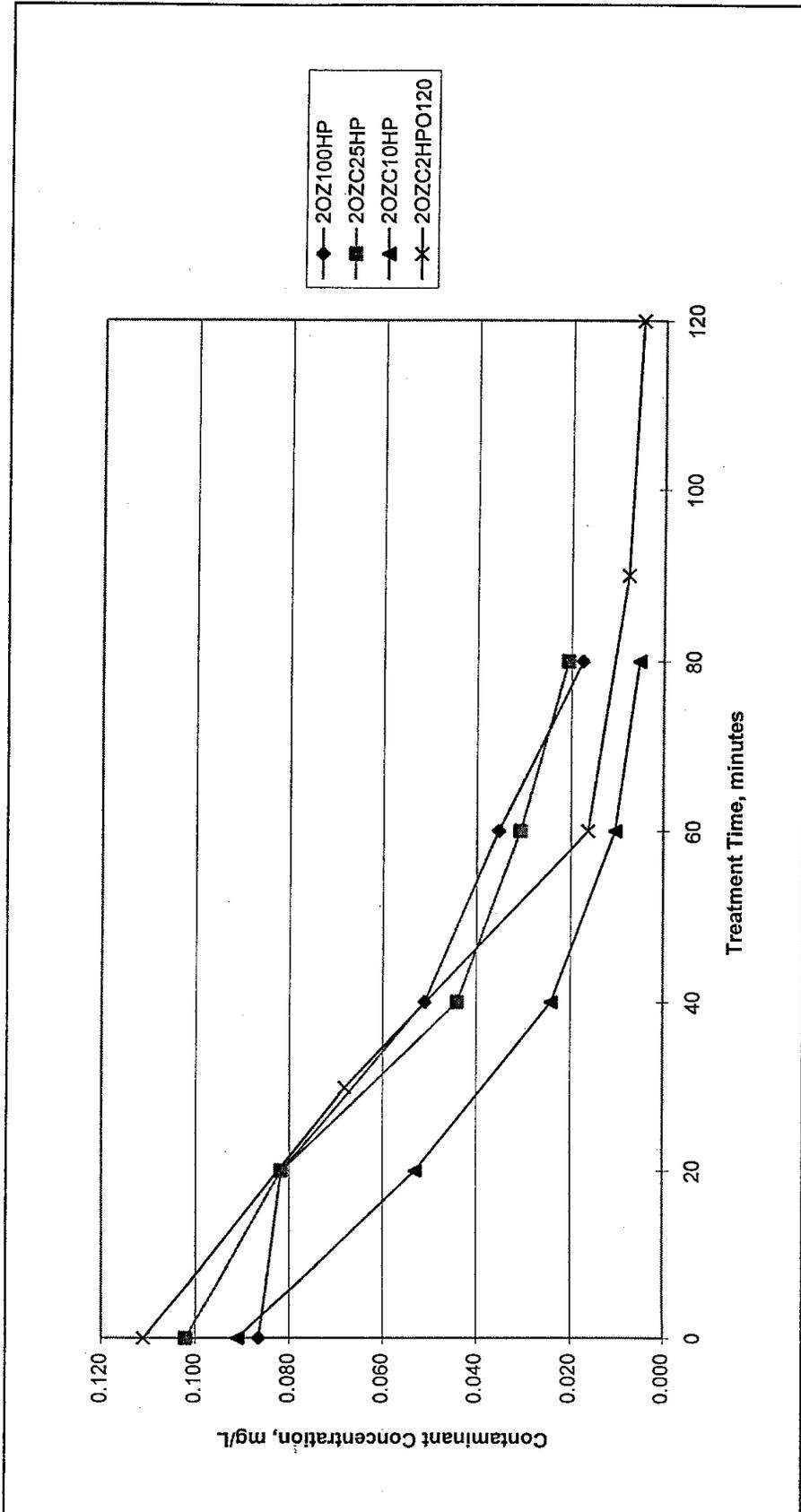


Figure 21. New Well RDX removal

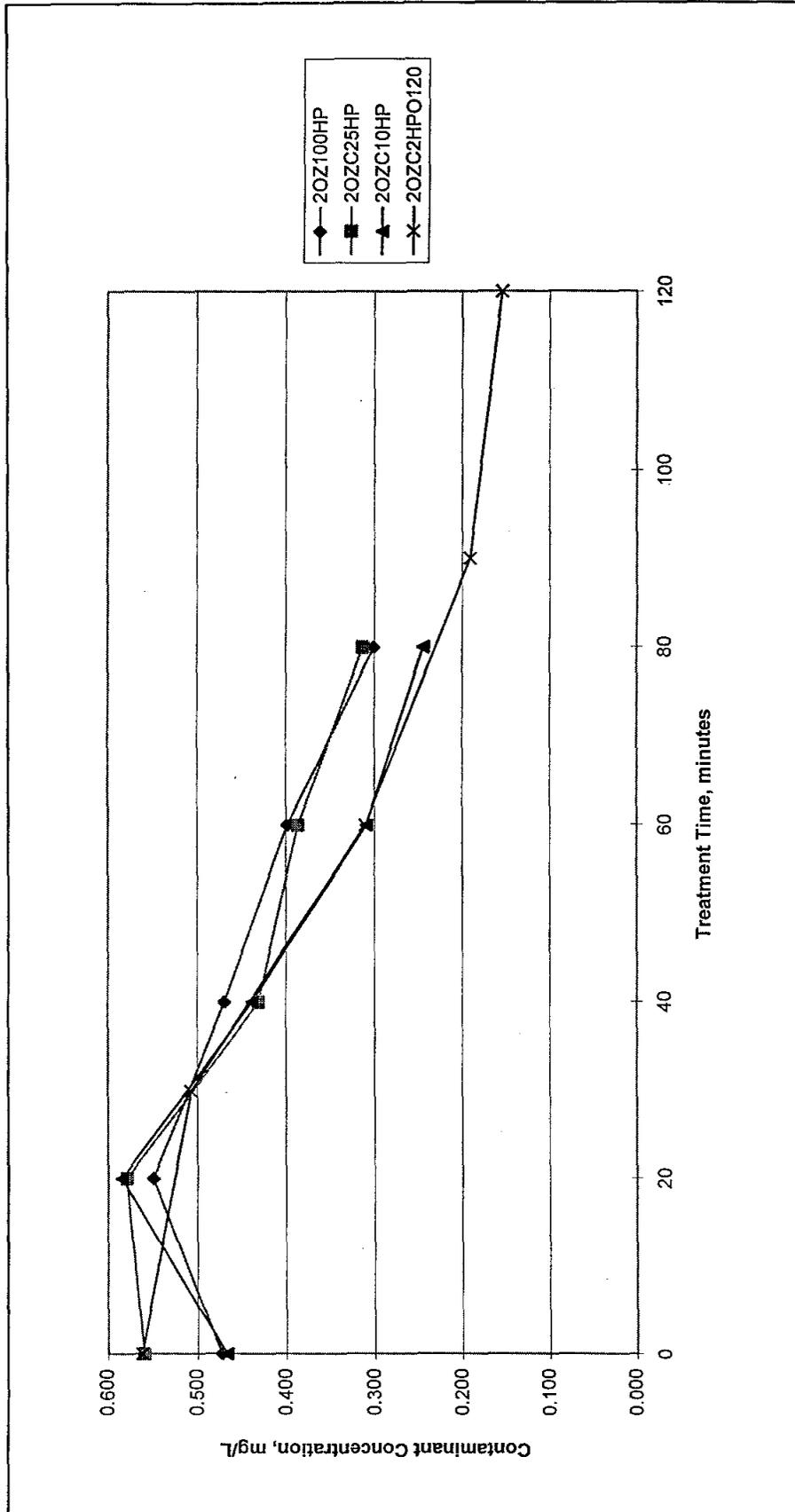


Figure 22. New Well TNB removal

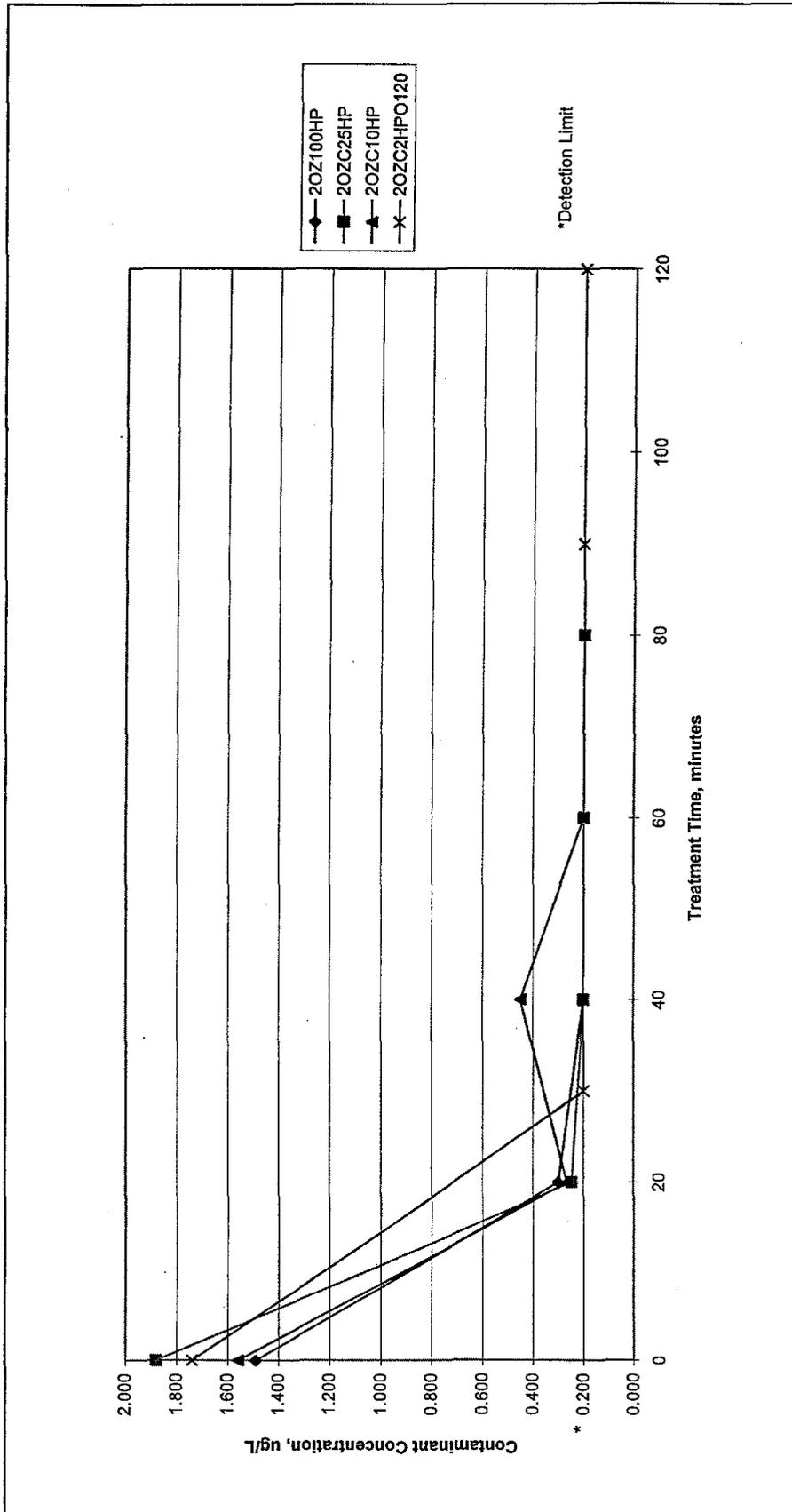


Figure 23. New Well DNB removal

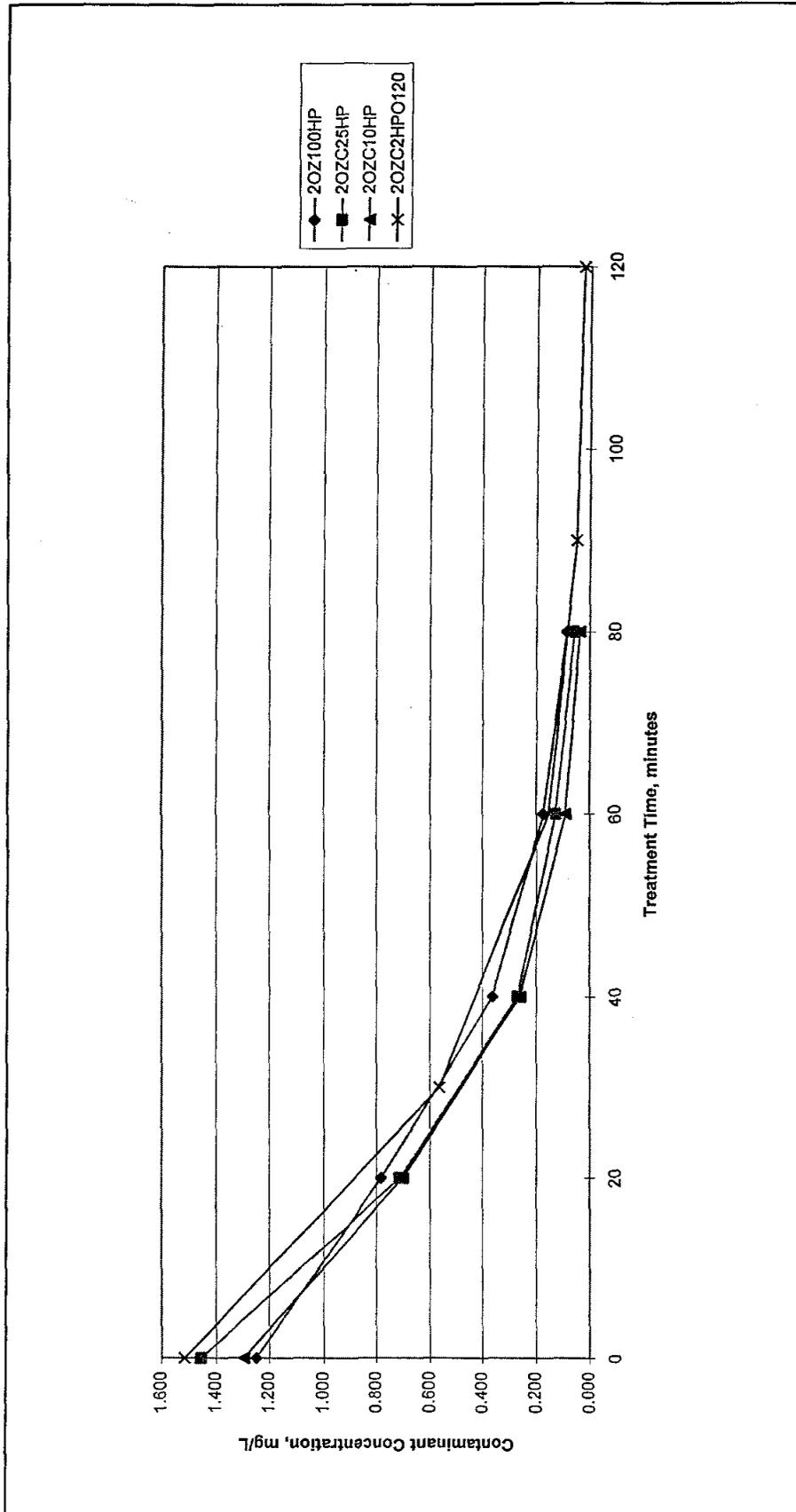


Figure 24. New Well TNT removal

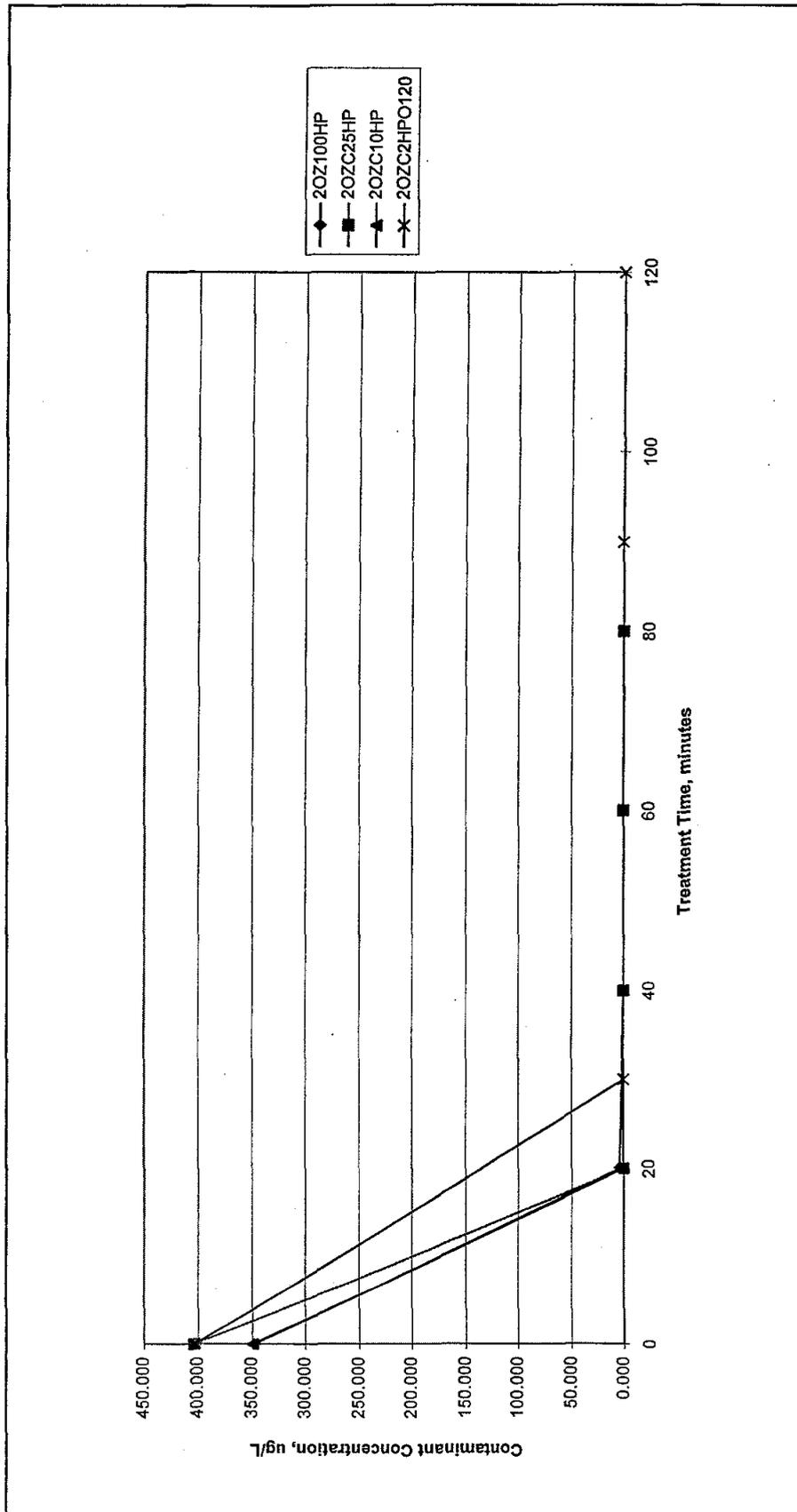


Figure 25. New Well 4A-DNT removal

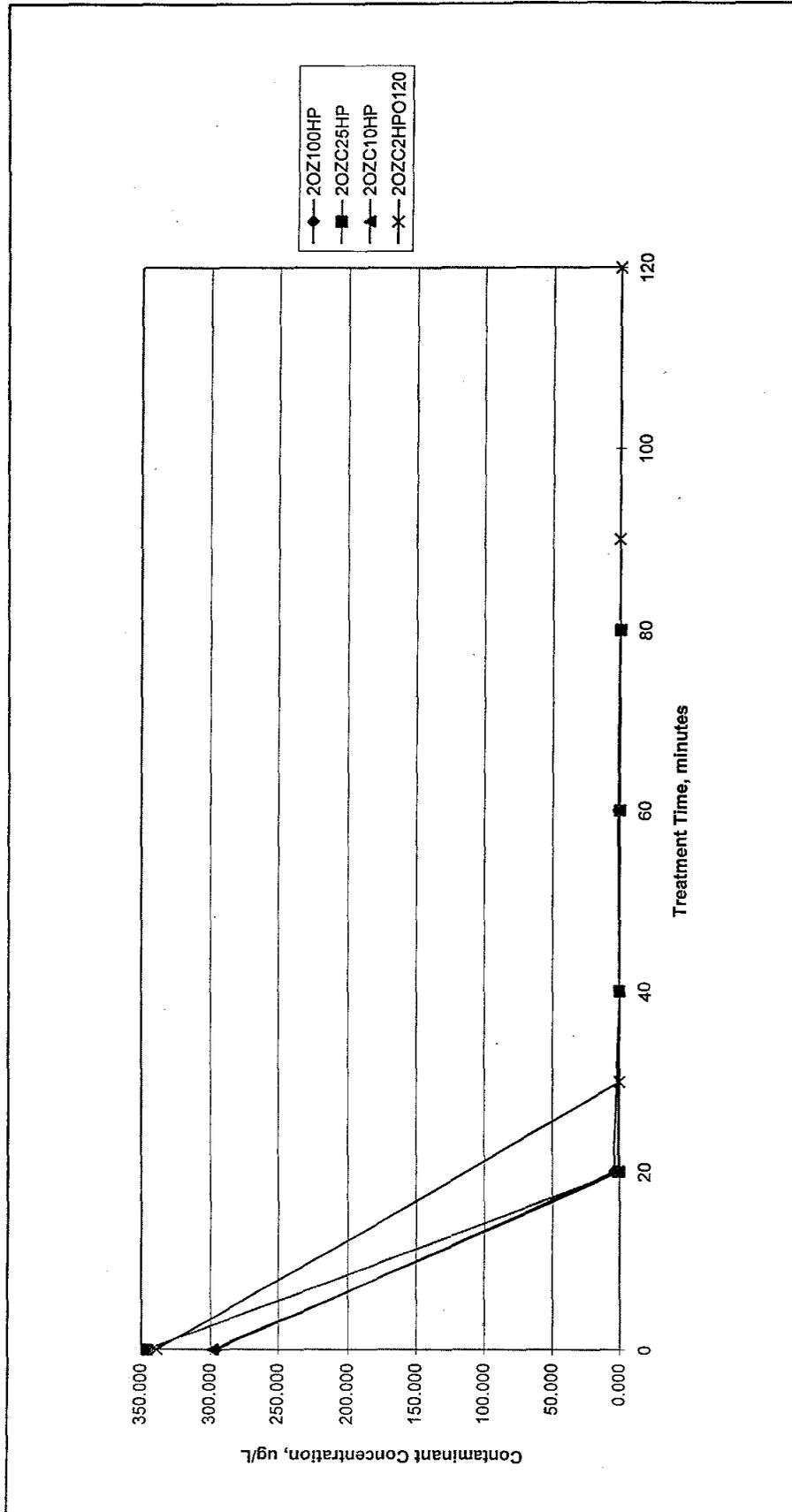


Figure 26. New Well 2A-DNT removal

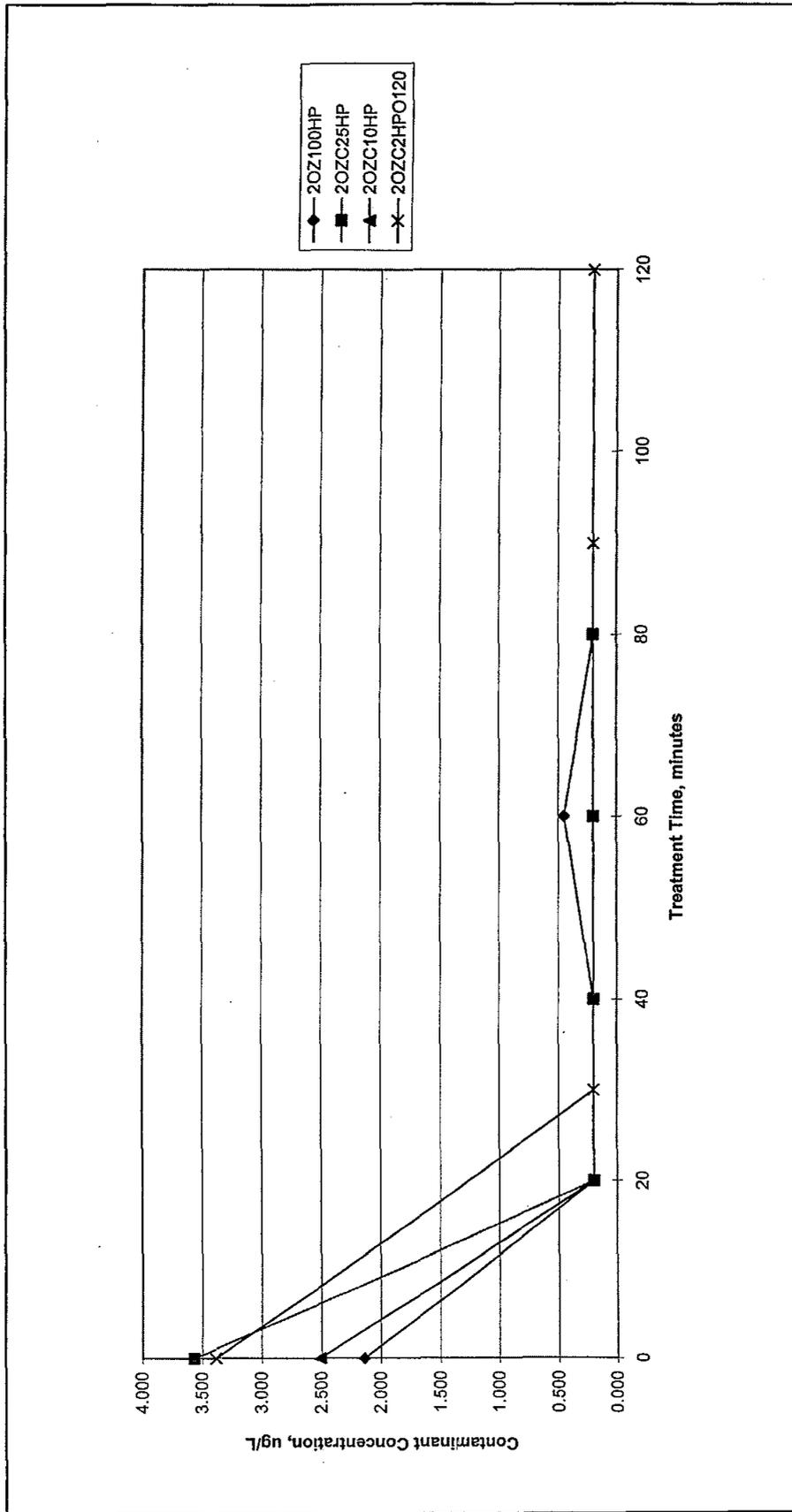


Figure 27. New Well 2,4-DNT removal

**Table 7
Summary of Treatment Effectiveness for Well 66 Waters**

	HMX (Percent Removal)	RDX (Percent Removal)	TNB (Percent Removal)	DNB (Percent Removal)	TNT (Percent Removal)	4A-DNT	2A-DNT ¹	2,4-DNT ²
Most	2OZC10HP (59%)	2OZC10HP (90.3%)	2OZC2HP0120 (64%)	1OZC10HP (76%)	2OZC25HP (96%)	NA	NA	NA
I	2OZC2HP0120 (51%)	2OZC2HP0120 (90.0%)	2OZC10HP (55%)	2OZC100HP (75%)	2OZC10HP (95%)	NA	NA	NA
	2OZ100HP (48%)	2OZC25HP (78%)	2OZC25HP (36%)	2OZ10HP (74.9%)	2OZC2HP0120 (94%)	NA	NA	NA
	1OZC10HP (33%)	2OZ100HP (71%)	2OZ10HP (32%)	2OZC25HP (74.4%)	2OZ100HP (93%)	NA	NA	NA
I	2OZC100HP (32%)	2OZ100HP (70%)	2OZ100HP (9%)	2OZC10HP (72.6%)	2OZC100HP (90%)	NA	NA	NA
	2OZ10HP (29%)	2OZC12HP40 (62%)	2OZC12HP40 (6%)	2OZC12HP40 (72.1%)	1OZC25HP (89%)	NA	NA	NA
	2OZC12HP40 (26.3%)	2OZC100HP (59%)	1OZC10HP (3%)	2OZ100HP (70%)	2OZC12HP40 (85%)	NA	NA	NA
I	1OZC25HP (26.2%)	1OZC25HP (52%)	2OZC100HP (-5%)	2OZC2HP0120 (64%)	1OZC10HP (84%)	NA	NA	NA
	2OZ1000HP (3%)	1OZC10HP (44%)	1OZC25HP (-11%)	1OZC25HP (60%)	2OZ10HP (76%)	NA	NA	NA
I	NOZC25HP (-10%)	2OZ1000HP (35%)	NOZC25HP (-18%)	NOZC25HP (5%)	2OZ1000HP (50%)	NA	NA	2OZ1000HP (65%)
Least	2OZC25HP (-23%)	NOZC25HP (31%)	2OZ1000HP (-33%)	2OZ1000HP (-25%)	NOZC25HP (36%)	NOZC25HP (6%)	NOZC25HP (11%)	NOZC25HP (6%)

Note: NA = Indicates analysis are at the analytical detection limit, and optimal technology could not be determined.

¹ Indicates NA results were >99-percent removal.

² Indicates NA results were >95-percent removal.

Table 8							
Summary of Treatment Effectiveness and Percent Removal for Well 22 Waters¹							
	HMX (Percent Removal)	RDX (Percent Removal)	TNB (Percent Removal)	TNT (Percent Removal)	4A-DNT	2A-DNT	2,4-DNT
Most	2OZC25HP (88%)	2OZC25HP (98%)	2OZC25HP (87%)	2OZC25HP (98%)	NA	NA	NA
I	2OZC10HP (85%)	2OZC10HP (97.8%)	1OZC10HP (77%)	2OZC10HP (96.9%)	NA	NA	NA
I	1OZC10HP (75%)	1OZC10HP (90%)	2OZC5HP40 (70%) High Flow	2OZC100HP (96.7%)	NA	NA	NA
I	2OZC5HP40 (53%) High Flow	2OZC5HP40 (89%) High Flow	2OZC10HP (55%)	1OZC10HP (96.5%)	NA	NA	NA
Least	2OZ100HP (52%)	2OZ100HP (78%)	2OZ100HP (53%)	2OZC5HP40 (95%) High Flow	NA	NA	NA

Note: NA indicates sample results were at or near the detection limit and optimal technology could not be determined.
¹ When results were equal, preceding sample point was evaluated. When percent removal values were the same, the tenths digit was evaluated.

Table 9							
Summary of Treatment Effectiveness and Percent Removal for New Well Waters¹							
	HMX	RDX	TNB	TNT	4A-DNT	2A-DNT	2,4-DNT
Most	2OZC2HPO120 (83%) Low Flow	2OZC2HPO120 (96%) Low Flow	2OZC2HPO120 (72%) Low Flow	2OZC2HPO120 (98%) Low Flow	NA	NA	NA
I	2OZC10HP (71%)	2OZC10HP (94%)	2OZC10HP (48%)	2OZC10HP (97%)	NA	NA	NA
I	2OZ100HP (5%)	2OZ100HP (79.8%)	2OZC25HP (44%)	2OZC25HP (96%)	NA	NA	NA
Least	2OZC25HP (2%)	2OZC25HP (79.8%)	2OZ100HP (36%)	2OZ100HP (93%)	NA	NA	NA

Note: NA indicates sample results were at or near the analytical detection limit and optimal technology could not be determined.
¹ When results were equal, preceding sample point was evaluated. When percent removals were equal, the tenths digit was evaluated.

and the New Well are presented in Figures 28 through 33, respectively. The extensive data collected in this study were evaluated by a number of means:

- a. Figures 6 through 27 representing concentration versus treatment time.
- b. The treatment technique with highest percent removal for each individual explosive in each water (Tables 7, 8, and 9 for Wells 66, 22, and the New Well).

- c. The overall optimal treatment technique based upon evaluation of the total removal of explosives from Wells 66, 22, and the New Well (Figures 28 through 33, respectively).
- d. A summary of treatment effectiveness when some explosives compounds were treated to site criteria and some were not (i.e., RDX may be below the 2- $\mu\text{g}/\ell$ criteria, while TNT is not—TNT is then an indicator compound).

In averaging triplicate analysis, where samples were less than the analytical detection limit, the detection limit was averaged (i.e., if the detection limit was $<0.002 \mu\text{g}/\ell$, $0.002 \mu\text{g}/\ell$ was averaged with the other two replicates). The average results are discussed below. For comparison purposes, “high flow” (40-min system retention time) runs and “low flow” runs (120 min of treatment) will be directly compared with 80-min retention time runs. Optimal treatment of the individual explosive compounds was that treatment with the highest percent removal based upon initial and final concentrations.

Well 66 Results

The results of the most and least effective treatments of Well 66 waters based upon percent removal efficiency are presented in Table 7 and Figures 28 and 29.

Well 66 HMX results

The results of Runs of 1 through 10 and 21 for removal of HMX are presented in Figure 6. HMX was not of regulatory concern for Well 66 water since initial concentrations were well below the $400\text{-}\mu\text{g}/\ell$ criteria. The optimal treatment scenario for HMX in Well 66 water was 2-percent ozone with continuous dosing of 10-ppm hydrogen peroxide (2OZC10HP). Percent removal of HMX using 2OZC10HP conditions was 69 percent. Concentrations of HMX were reduced from approximately 5.3 to $1.5 \mu\text{g}/\ell$ after 80 min of treatment. Neither increasing (120 min of treatment) or decreasing (40 min of treatment) the hydraulic retention time improved the removal of HMX over the 2OZC10HP treatment. Although it was beyond the scope of this study to determine the cause, two runs, no ozone with 25-ppm hydrogen peroxide (NOZ25HP) and 2-percent ozone with continuous dosing of 25-ppm hydrogen peroxide (2OZC25HP), resulted in increases in HMX concentrations. Conversely, the 2OZC25HP treatment was effective for the other explosives present in Well 66 waters as is discussed below.

Well 66 RDX results

The results of RDX removal from Well 66 waters are presented in Figure 7. The concentration of RDX was reduced from approximately 16.3 to $1.6 \mu\text{g}/\ell$, below the $2\text{-}\mu\text{g}/\ell$ drinking water criteria, in 80 min using a 2-percent ozone, continuous dosing of 10-ppm hydrogen peroxide (2OZC10HP) treatment scenario. The percent

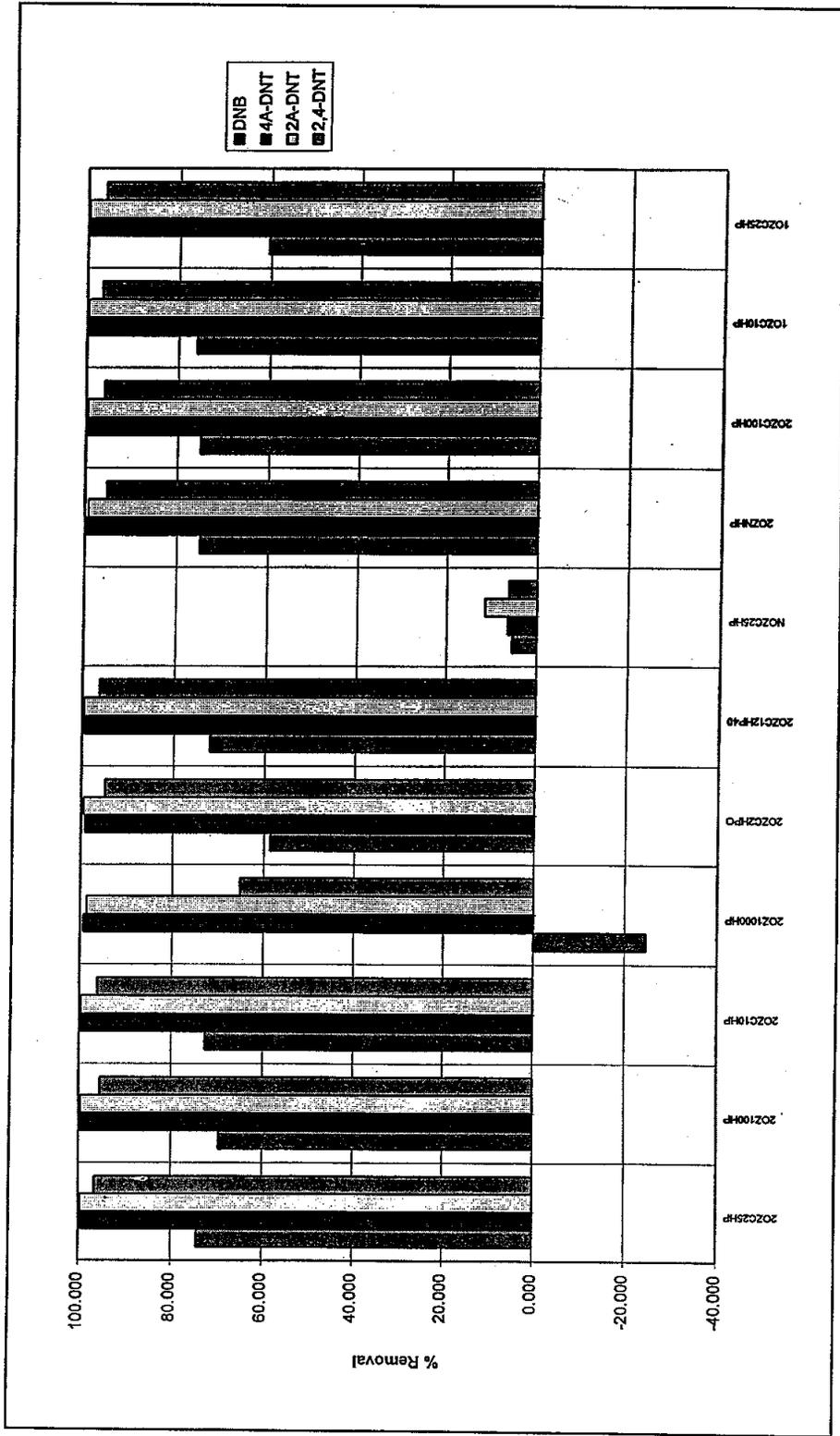


Figure 29. Percent removal of aminodinitrotoluenes for Well 66

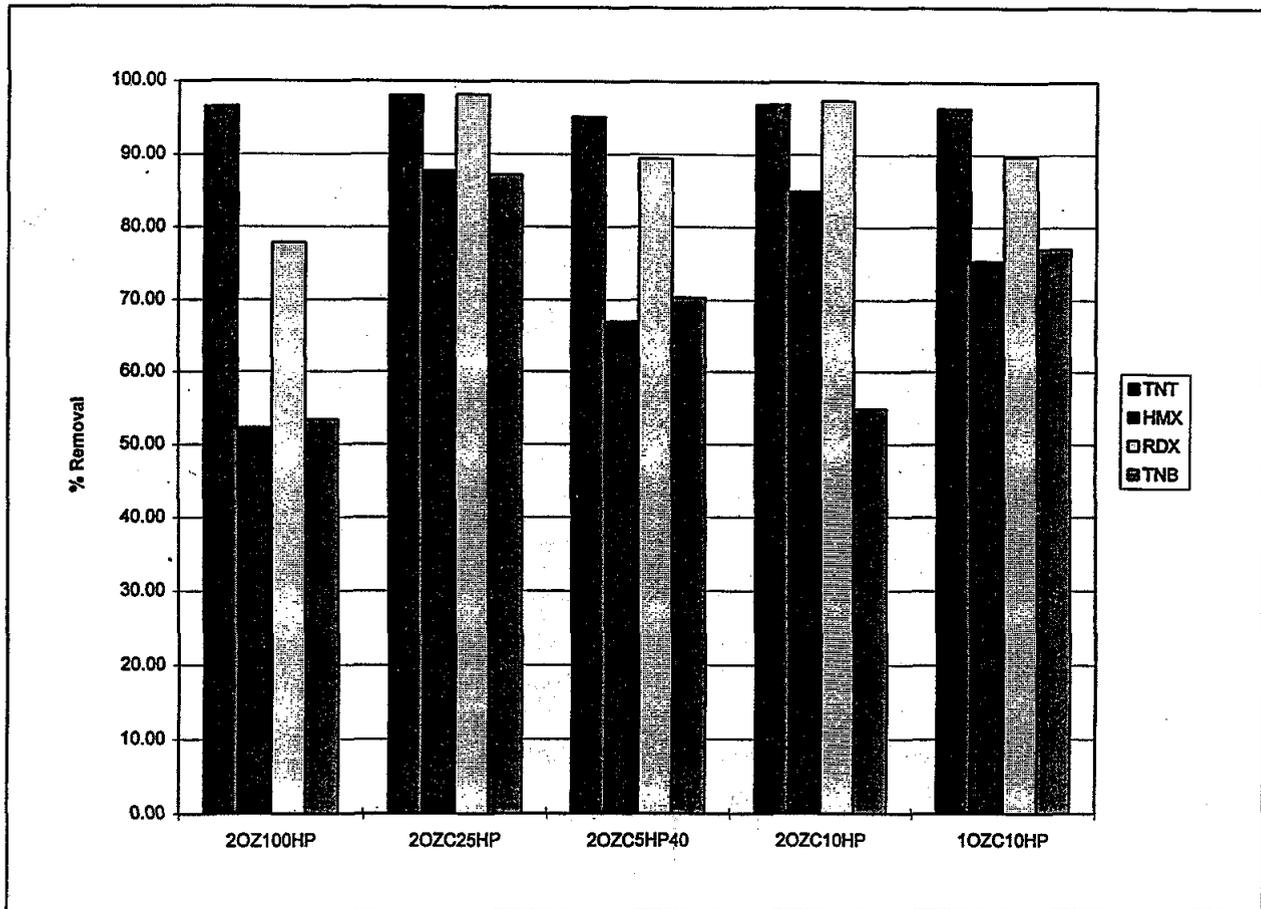


Figure 30. Percent removal of HMX, RDX, TNT, and TNB for Well 22

removal using 2OZC10HP was 90.3 percent. Based upon a comparison of the data at the 40-min retention time, the “high flow” run (2OZC12HP40) was effective, but RDX was not reduced to below the 2- $\mu\text{g}/\text{l}$ criteria within the 40-min treatment time. Trends in the data indicate that 2-percent ozone treatment is generally optimal for RDX removal, with the exception of the 1,000-ppm hydrogen peroxide run (2OZ1000HP). In general, the optimal runs based on hydrogen peroxide dosage were those with approximately 10 ppm hydrogen peroxide, and treatment effectiveness decreased as hydrogen peroxide concentration increased (with the exception of the “high flow” run (12-ppm hydrogen peroxide), which had a shorter HRT), and treatment effectiveness also decreased as ozone concentration decreased to 1 percent or no ozone (see 1OZC25HP, 1OZC10HP, NOZC25HP, 2OZC100HP, and 2OZ1000HP).

Well 66 TNB results

The results of TNB treatment are presented in Figure 8. The optimal treatment conditions for removal of TNB from Well 66 waters were using 2-percent ozone with approximately 12 ppm continuous dosing of hydrogen peroxide to obtain

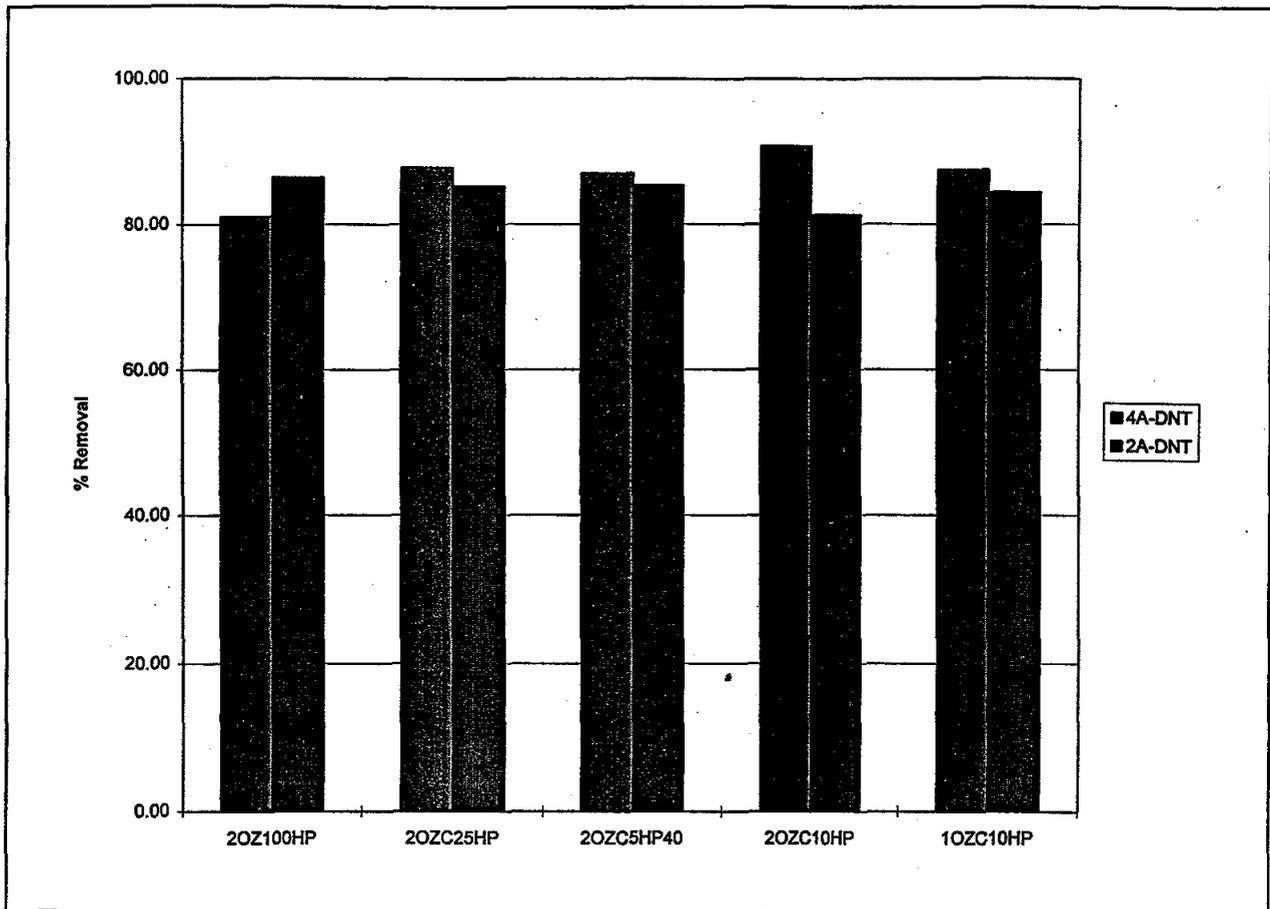


Figure 31. Percent removal of aminodinitrotoluenes for Well 22

2-ppm hydrogen peroxide (2OZC2HPO120) in the effluent. The percent removal of TNB using 2OZC2HPO120 was 64 percent. The concentration of TNB in 2OZC2HPO120 was reduced from an approximate initial concentration of 95.1 to 34 $\mu\text{g}/\ell$ after 120 min of treatment. During the first retention time through Column 1, after 20-30 min of treatment, concentrations of TNB increased for all treatment scenarios. As a part of this project, researchers from the U.S. Army Cold Regions Engineering Laboratory (CRREL) and Stanford Research Institute (SRI) evaluated the peroxone oxidation by-products of TNT oxidation and found TNB to be an intermediate in the ultimate degradation of TNT. Their report is presented in Appendix A. According to SRI and CRREL research, during degradation of TNT, TNB is formed, resulting in increased concentrations of TNB, until TNB is degraded to aldehydes as referenced by the WES and SRI research. As was the case for RDX, the optimal hydrogen peroxide ratios were at or those closest to 10 ppm combined with 2-percent ozone. The run utilizing 2-percent ozone with no hydrogen peroxide (2OZNHP) was more effective than those runs utilizing high hydrogen peroxide (≥ 100 ppm) with 2-percent ozone (2OZ100HP, 2OZC100HP, and 2OZ1000HP), no ozone (NOZC25HP), or those runs utilizing 1-percent ozone (1OZC10HP, 1OZC25HP). Hence, the results indicate the importance of determining the appropriate dosages and combination of oxidizers to obtain the desired effect.

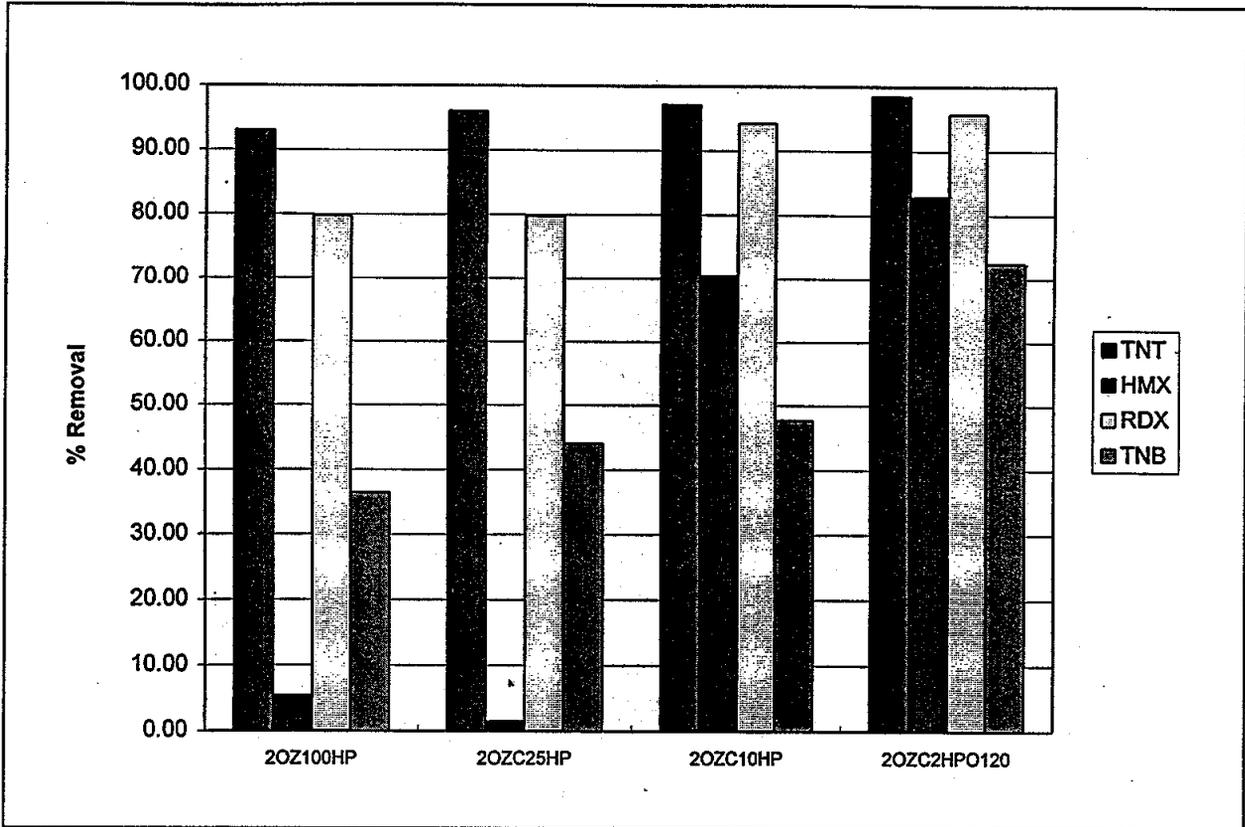


Figure 32. Percent removal of HMX, RDX, TNT, and TNB for the New Well

Well 66 DNB results

The results of DNB removal are presented in Figure 9. The optimal treatment was 1-percent ozone dosed continuously with 10-ppm hydrogen peroxide (1OZC10HP) with a percent removal of 76 percent. The three optimal treatments for DNB were 1-percent ozone with continuous dosing of 10-ppm hydrogen peroxide (1OZC10HP, 76-percent removal), 2-percent ozone dosed continuously with 100-ppm hydrogen peroxide (2OZC100HP, 75-percent removal), and 2-percent ozone with no addition of hydrogen peroxide (2OZNHP, 74.9-percent removal). None of the aforementioned treatments were in the top three most effective treatments for HMX, RDX, or TNB, illustrating the point that individual explosives may be more susceptible to treatment by different treatment conditions. However, in Well 66 waters, DNB was not an explosive of concern since initial concentrations were well below the 2 µg/l at an average of 0.7 µg/l (an average of the initial concentrations in the 11 runs).

Well 66 TNT results

The results of TNT removal from Well 66 water are presented in Figure 10. The optimal treatment scenario was 2-percent ozone with continuous dosing of 25-ppm

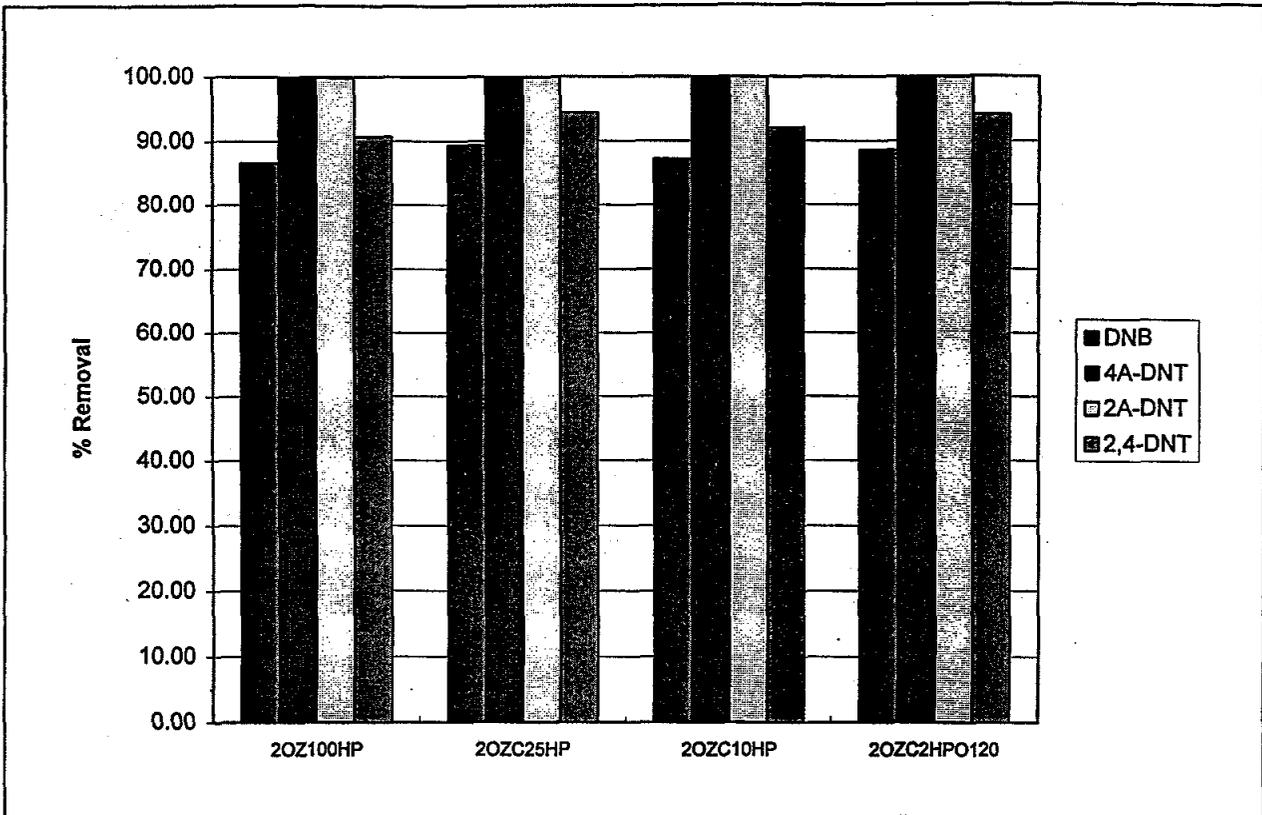


Figure 33. Percent removal of aminodinitrotoluenes for the New Well

hydrogen peroxide (2OZC25HP) with 96-percent removal of TNT. Despite 96-percent removal of TNT, concentrations were not below the 2- $\mu\text{g}/\ell$ site criteria for TNT. The 2OZC25HP treatment reduced concentrations from an average initial TNT concentration of 363 to 15.2 $\mu\text{g}/\ell$ in 80 min. Similar to the HMX, RDX, and TNB results, removal of TNT was generally more effective using 2-percent ozone in combination with hydrogen peroxide dosages ranging from 10 to 25 ppm (2OZC25HP, 2OZC10HP, and 2OZC2HPO120 (approximately 12 ppm influent hydrogen peroxide)). The lesser effective treatments involved 1-percent ozone, no ozone, or concentrations of hydrogen peroxide ≥ 100 ppm. However, the 2-percent ozone with continuous dosing of 12 ppm hydrogen peroxide using “high flow” (2OZC12HP40) is the exception, being less effective than the 1-percent ozone with 25 ppm continuous dosing of hydrogen peroxide. But this treatment was retained in the POPS for a shorter treatment period, one-half to one-third the retention time of the other treatments. It should be noted that, in Figure 9 at the 40-min retention time, 2OZC12HP40 was the most effective treatment at that sampling period but was not evaluated beyond that treatment period.

Well 66 aminodinitrotoluene results

The results of aminodinitrotoluene removal are presented in Figures 11 through 13 for 4A-DNT, 2A-DNT, and 2,4-DNT, respectively. Average initial

concentrations of 4A-DNT, 2A-DNT, and 2,4-DNT were 45.8, 57.6, and 5.2 $\mu\text{g}/\ell$, respectively (an average of initial concentrations of the 11 runs). In general, concentrations of aminodinitrotoluene compounds were reduced very effectively. Concentrations of 4A-DNT were reduced to below the 2- $\mu\text{g}/\ell$ criteria in 20-30 min using all treatments with the exception of two: 2-percent ozone with continuous dosing of hydrogen peroxide and maintaining 2-ppm hydrogen peroxide in the column effluent (2OZC2HPO, 30 min of treatment) and 2-percent ozone with 1,000-ppm hydrogen peroxide (2OZ1000HP, 20 min of treatment). No 20-min data were collected for 2-percent ozone with no hydrogen peroxide (2OZNHP, 80-min sample was below 2 $\mu\text{g}/\ell$) and no ozone dosed continuously with 25-ppm hydrogen peroxide (NOZC25HP, 80-min sample showed little treatment). Similarly, results of 2A-DNT were below the 2- $\mu\text{g}/\ell$ criteria in 20-30 min using every treatment technique with the exception of 2-percent ozone with 1,000-ppm hydrogen peroxide (2OZ1000HP). Again, no 20-min sample was collected for the 2OZNHP and NOZC25HP treatments, but 2OZNHP treatment resulted in reduction of 2A-DNT to below the 2- $\mu\text{g}/\ell$ criteria in 80 min. Concentrations of 2,4-DNT were reduced to below the 2- $\mu\text{g}/\ell$ criteria in 20-30 min by all treatment techniques with the exception of 1-percent ozone with continuous dosing of 25-ppm hydrogen peroxide (1OZC25HP), 1-percent ozone with continuous dosing of 10-ppm hydrogen peroxide (1OZC10HP), 2-percent ozone with 1,000-ppm hydrogen peroxide (2OZ1000HP), and 2-percent ozone with continuous dosing of approximately 12-ppm hydrogen peroxide and 2-ppm hydrogen peroxide in the effluent of each column (2OZC2HPO120). Samples were not collected at the 20-min sampling period for 2-percent ozone with no hydrogen peroxide (2OZNHP) or no ozone with continuous dosing of hydrogen peroxide (NOZC25HP), but concentrations were reduced to below 2 $\mu\text{g}/\ell$ using 2OZNHP at the 80-min sampling period. An evaluation of NOZC25HP and 2OZNHP results for the aminodinitrotoluene compounds indicates they are reactive towards ozone alone as well as peroxone techniques (this will be discussed further based upon results of studies by SRI presented in a later section), but the aminodinitrotoluene compounds are not as effectively degraded by application of hydrogen peroxide alone (NOZC25HP) as the other techniques evaluated. Because several of the technologies were equally effective at removal of aminodinitrotoluenes based on the samples collected in this study, selection of the optimal techniques were based upon HMX, RDX, TNB, DNB, and TNT results.

Summary of Well 66 Results

Figures 28 and 29 summarize the results of percent removal using peroxone evaluations, ozone alone, and hydrogen peroxide treatment alone of Well 66 waters for removal of explosives. Based upon the composite evaluation of the percent removals, the 2-percent ozone run combined with a dosage of 10-ppm hydrogen peroxide, dosed continuously (2OZC10HP), was optimal for treatment of Well 66 waters based upon a cumulative evaluation of explosives removal. However, the selection of the optimal treatment for Well 66 waters is not simple since two compounds, TNT and TNB, were not treated to the site criteria.

The most difficult compounds in Well 66 waters for peroxone techniques to treat were TNT and TNB. Although TNT was reduced by 96 percent, a factor of twenty-four, from approximately 363 to 15.2 $\mu\text{g}/\ell$, and TNB was reduced from approximately 95.1 to 34 $\mu\text{g}/\ell$, a factor of three, using 2OZC25HP and 2OZC2HPO, respectively, concentrations were not below the site criteria of 2 $\mu\text{g}/\ell$.

Among the aminodinitrotoluene compounds, optimal treatment conditions were difficult to determine because several of the treatments resulted in concentrations of aminodinitrotoluenes being reduced below the analytical detection limit of 0.2 $\mu\text{g}/\ell$. Overall, aminodinitrotoluenes were easily reduced by peroxone techniques and by the 2-percent ozone treatment with no hydrogen peroxide (2OZNHP). Concentrations of RDX and HMX were reduced below the required criteria of 2 $\mu\text{g}/\ell$ using 2 percent-ozone with 10-ppm and 25-ppm hydrogen peroxide, respectively.

Trends in Well 66 data indicate that, in general, those runs involving 2-percent ozone with hydrogen peroxide concentrations 100 ppm or less were the most effective. Exceptions were the 1OZC10HP run for HMX and 1OZC10HP for DNB. The 2OZC12HP40 run was also an exception, but the HRT was much shorter using this treatment. Another trend is the general higher effectiveness of continuous versus batch addition of hydrogen peroxide, when using 2-percent ozone with less than 100-ppm hydrogen peroxide added continuously, i.e., 10- and 25-ppm hydrogen peroxide.

Although peroxone was highly effective for removal of explosives, longer retention times would be required to meet the site criteria. Since TNT and TNB are the limiting compounds, three treatment conditions are recommended for further evaluation/consideration and were selected because they were optimal for removal of HMX and RDX (2OZC10HP), optimal for removal of TNT (2OZC25HP), and optimal for removal of TNB (2OZC2HPO120). Note 2OZC2HPO120 is the second most optimal treatment for HMX and RDX, with 51- and 90-percent removal, respectively. However, concentrations of HMX increased by 23 percent using 2OZC25HP. But it is unlikely that 2OZC25HP treatment of HMX in Well 66 waters will be limiting since average initial concentrations are well below the 400- $\mu\text{g}/\ell$ site criteria for HMX. It should also be noted that the 2-percent ozone with continuous dosing of 12-ppm hydrogen peroxide "high flow" (2OZC12HP40) run was the most effective treatment of TNT and RDX at the 40-min retention time, the final sampling for that run. Further evaluations of this treatment may also be warranted. A suggestion for further evaluation of the high flow includes longer retention times. However, this would require a larger reaction vessel than the POPS, or in the case of the POPS unit, addition of a contact chamber or recirculation of the treated water through the system. The possible cause and effect of the good results using "high flow" treatment may be more dissolution of ozone due to a higher flow rate since the water is not as solubility limited at a higher flow rate.

Well 22 Results

The results of the five treatment techniques evaluated for removal of explosives from Well 22 waters are presented in Figures 14 through 19 and in order in Table 8 from most to least effective technique for each explosive. Percent removal is also presented and the results discussed below.

Well 22 HMX results

Initial concentrations of approximately 2.81- $\mu\text{g}/\ell$ HMX (well below the criteria of 400 $\mu\text{g}/\ell$) were reduced to approximately 0.25 $\mu\text{g}/\ell$, 88-percent removal, in 80 min by 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) as illustrated in Figure 14. The least effective treatment of HMX in Well 22 waters was using 2-percent ozone dosed by batch with 100-ppm hydrogen peroxide (2OZ100HP), which may be due to overdosing of the system with hydrogen peroxide. The trend of decreasing effectiveness being directly proportional to increasing hydrogen peroxide and decreasing ozone to 1 percent as seen in the Well 66 results was repeated in Well 22 results. The exception was the "high flow" 2-percent ozone with continuous dosing of 5-ppm hydrogen peroxide run (2OZC5HP40), which was the second most effective treatment at the 40-min retention time, but the run was not sampled further. A longer retention time would result in further treatment. The least effective treatment was 2-percent ozone with 100-ppm hydrogen peroxide (2OZ100HP), which contained the highest dosage of oxidizers, possibly resulting in overdosing.

Well 22 RDX results

Figure 15 presents the results of evaluations of removal of RDX from Well 22 runs. The most effective treatment, yielding the lowest concentration of RDX after 80 min of treatment, was 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP). However, it should be noted that initial concentrations of approximately 14 $\mu\text{g}/\ell$ were reduced to less than 2.0 $\mu\text{g}/\ell$ in less than 40 min using both "high flow" 2-percent ozone dosed continuously with 5-ppm hydrogen peroxide (2OZC5HP40) and 2-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP), although the percent removal based on initial and final concentrations was greatest using 2OZC25HP. At the 40-min HRT, the "high flow" run (2OZC5HP40) had a lower concentration of RDX than the 2-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP), but higher HRTs were not evaluated using the "high flow" (2OZC5HP40) treatment technique; it is not known whether further treatment would have yielded the lowest concentration using the "high flow" (2OZC5HP40) treatment scenario. The "high flow" (2OZC5HP40) system treated RDX to less than 2.0 $\mu\text{g}/\ell$ in approximately 33 min, more rapidly than any of the other treatment systems. But, based upon initial concentrations and percent removal, the most effective treatment was 2OZC25HP.

Well 22 TNB results

The results of TNB evaluations are presented in Figure 16. The most effective treatment for TNB was using 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) with a percent removal of 87 percent. At the 40-min HRT, the most effective treatment was 2-percent ozone dosed continuously with 5-ppm hydrogen peroxide (2OZC5HP40) with a concentration of approximately 3.6 $\mu\text{g}/\ell$. As previously discussed, it is not known whether further treatment would have yielded lower concentrations of TNB at an 80 minute retention time. The 2 percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) treated TNB concentrations to approximately 2 $\mu\text{g}/\ell$ in approximately 72 min.

Well 22 TNT results

Figure 17 presents the results of peroxone oxidation of Well 22 waters for removal of TNT. Based upon percent removal, the optimal treatment of TNT in Well 22 waters was 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP). Based upon attainment of the 2- $\mu\text{g}/\ell$ criteria for TNT, the "high flow" 2-percent ozone dosed continuously with 5-ppm hydrogen peroxide (2OZC5HP40) attained that treatment level in approximately 24 min, while the optimal treatment based upon percent removal met the 2- $\mu\text{g}/\ell$ criteria in approximately 38 min. Further treatment for an HRT of 80 min resulted in reduction of TNT to the analytical detection limit of 0.2 $\mu\text{g}/\ell$ using 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) and 2-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP). In general, all treatments evaluated were effective at removal of TNT based upon a percent removal from least to most effective of 95-98 percent.

Well 22 aminodinitrotoluene results

The results of removal of 4A-DNT and 2A-DNT are presented in Figures 18 and 19, respectively. The remaining aminodinitrotoluene compounds and DNB were below the analytical detection limit of 0.2 $\mu\text{g}/\ell$ in the influent and effluent samples. The concentrations of 4A-DNT were below the 2- $\mu\text{g}/\ell$ criteria for all influent and effluent samples with the exception of one influent sample collected for the 2-percent ozone with continuous dosing of 10-ppm hydrogen peroxide (2OZC10HP), which was reduced to below the 2- $\mu\text{g}/\ell$ criteria at the 20 min sample period. All concentrations of 2A-DNT, including all influent and effluent samples, were below the 2- $\mu\text{g}/\ell$ criteria. The 4A-DNT and 2A-DNT figures illustrate the effectiveness of peroxone in reducing aminodinitrotoluene compounds as was discussed for Well 66 results. It is not known whether oxidation was due to peroxone or ozonation alone in Well 22 waters since no ozonation alone evaluation was performed for Well 22.

Summary of Well 22 Results

Figures 30 and 31 present a summary of the percent removal for each explosive using the five treatments evaluated for Well 22. Based upon review of the overall removal of HMX, RDX, TNB, and TNT, the optimal treatment was using 2-percent ozone with continuous dosing of 25-ppm hydrogen peroxide (2OZC25HP). The 2OZC25HP treatment reached the 2- $\mu\text{g}/\ell$ requirement for RDX, TNB, and TNT, and the initial HMX concentration was well below the criteria of 400 $\mu\text{g}/\ell$ for HMX.

The least effective treatment for HMX, RDX, and TNB was 2-percent ozone dosed in batch with 100-ppm hydrogen peroxide (2OZ100HP). A possible reason for less effective treatment could be due to overdosing of the system with hydrogen peroxide, resulting in scavenging of the hydroxyl radicals as discussed in Chapter 2: Technology Description.

Aminodinitrotoluene compounds were easily removed by all five of the treatments tested. Review of Figures 15 through 19 shows TNB to be the indicator compound, requiring approximately 72 min of treatment to reach the 2- $\mu\text{g}/\ell$ criteria using 2OZC25HP. However, as was recommended for further evaluation for Well 66 waters, the "high flow" 2-percent ozone dosed continuously with 5-ppm hydrogen peroxide (2OZC5HP40) may warrant further evaluation for Well 22 waters. At the final sampling event for the 2OZC5HP40 run, after 40 min of treatment, 2OZC5HP40 was the most effective treatment for RDX and TNB (the limiting compound).

As was discussed in Well 66 results, continuous addition of hydrogen peroxide to each of the four columns performs more effectively than batch addition of hydrogen peroxide at the influent to Column 1. The 2-percent ozone with 100-ppm hydrogen peroxide (2OZ100HP) run was the least effective treatment for HMX, RDX, and TNB.

New Well Results

The results of the optimal treatment for each explosive from most to least effective and percent removal are presented in Table 9.

New Well HMX results

The results of HMX treatment are presented in Figure 20. The optimal treatment conditions were "low flow" 2-percent ozone with continuous dosing of hydrogen peroxide, measuring 2-ppm hydrogen peroxide in the effluent from each column (2OZC2HPO120). Percent removal was approximately 83 percent, based upon reducing HMX in the 2OZC2HPO120 run from an average of 20.9 to 3.6 $\mu\text{g}/\ell$. However, concentrations of HMX were well below the 400- $\mu\text{g}/\ell$ criteria, so HMX would not have been a regulated compound. Hence, HMX would not be the basis for selection of the optimal treatment. A noticeable trend in the New Well

HMX results is the difference in effectiveness between “low flow” 2-percent ozone dosed with approximately 10- to 12-ppm hydrogen peroxide continuously (dosage required to obtain 2-ppm hydrogen peroxide in the effluent of each column, 2OZC2HPO120) and 10-ppm hydrogen peroxide continuously (2OZC10HP) versus 2-percent ozone dosed continuously with 25 ppm and batch dosing of 100-ppm hydrogen peroxide (2OZC25HP and 2OZ100HP, respectively). The 2OZC25HP and 2OZ100HP treatments were considerably less effective as is illustrated in Figure 20 and in the percent removals in Table 9. A possible explanation of this phenomenon is overdosing of the hydrogen peroxide oxidizer, resulting in hydrogen peroxide being a OH[·] or scavenger.

New Well RDX results

The results of RDX treatment in the New Well are presented in Figure 21. The optimal treatment method was using “low flow” 2-ppm hydrogen peroxide in the effluent of each column with 2-percent ozone to treat RDX to an average of 5.2 µg/l after 120 min (2OZC2HPO120) of treatment with a percent removal of 96 percent. The 2-percent ozone with a continuous dosage of 10-ppm hydrogen peroxide (2OZC10HP) treated RDX to 5.3 µg/l in 80 min and may have proven to be a more effective treatment than the “low flow” 2-ppm hydrogen peroxide in the effluent, 2-percent ozone run (2OZC2HPO120) if treated for a longer HRT as was the case of the “low flow” 120-min run previously described. As was the case with HMX, the 2-percent ozone runs dosed with 25-ppm and 100-ppm hydrogen peroxide (2OZC25HP (continuous dosing) and 2OZ100HP (batch dosing), respectively) were less effective than the approximately 10-ppm hydrogen peroxide-dosed runs, (i.e., 2OZC2HPO120 and 2OZC10HP) by approximately 16 percent. Again, this could be due to inappropriate dosing of hydrogen peroxide, resulting in OH[·] scavenging effects.

New Well TNB results

The results of TNB removal for the New Well are presented in Figure 22 and indicate the “low flow” run with 2-ppm hydrogen peroxide in the column effluents and 2-percent ozone in the column influent gas (2OZC2HPO120) removed the most TNB. As was the case in TNB removal from Well 66 waters, concentrations of TNB increased at the 20-min HRT for the 2-percent ozone with continuous hydrogen peroxide dosages of 10 and 25 ppm (2OZC10HP and 2OZC25HP, respectively) and for the 2-percent ozone with 100-ppm hydrogen peroxide added in batch before the influent to Column 1 (2OZ100HP). A possible reason for increases in TNB concentrations is the intermediate formation of TNB in the degradation of TNT as was previously discussed and as is presented in a report by CRREL and SRI in Appendix A. The concentration of TNB did not increase after one HRT in the “low flow” 2-percent ozone, 2-ppm hydrogen peroxide in the effluent run (2OZC2HPO120); concentrations continually decreased from an average initial concentration of approximately 562 µg/l to a concentration of 155 µg/l, an approximately 72-percent reduction in TNB.

New Well DNB results

The results of DNB removal from the New Well are presented in Figure 23. All concentrations in the influent and effluent samples were below the 2- $\mu\text{g}/\ell$ criteria, and concentrations were reduced to the analytical detection limit of 0.2 $\mu\text{g}/\ell$ in 40 min using all treatments with the exception of 2-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP, treated to 0.2 $\mu\text{g}/\ell$ in 60 min). DNB results were not used as a basis for selection of the optimal treatment.

New Well TNT results

The results of TNT destruction are presented in Figure 24. Again, the optimal treatment for the New Well waters was 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide to obtain 2-ppm hydrogen peroxide in the effluent of each column (2OZC2HPO120), also the optimal treatment for HMX, RDX, and TNB. The percent removal using 2OZC2HPO120 was 98 percent. However, all four treatments, including 2-percent ozone dosed continuously with 10 and 25 ppm (2OZC10HP and 2OZC25HP, respectively) and batch dosing of 100-ppm hydrogen peroxide (2OZ100HP) were in the range of 93- to 98-percent removal of TNT. But, none of the treatments reduced TNT to below the 2- $\mu\text{g}/\ell$ criteria. The 2OZC2HPO120 treatment reduced TNT from an average concentration of 1,510 to 24 $\mu\text{g}/\ell$, the lowest effluent concentration among the four treatments evaluated.

New Well aminodinitrotoluene results

The results of removal of 4A-DNT, 2A-DNT, and 2,4-DNT are presented in Figures 25 through 27, respectively. Concentrations of 4A-DNT and 2A-DNT were reduced to below the analytical detection limit of 0.2 $\mu\text{g}/\ell$ at the first sampling for each of the techniques evaluated (i.e., after 20 min for 2-percent ozone with 100-ppm hydrogen peroxide (2OZ100HP), 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP), and 2-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP), and after 30 min for 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide and 2-ppm hydrogen peroxide in the effluent of each column (2OZC2HPO120)). One concentration of 2,4-DNT was above the analytical detection limit of 0.2 $\mu\text{g}/\ell$ at the 60-min sampling period using 2-percent ozone with 100-ppm hydrogen peroxide (2OZ100HP) at approximately 0.5 $\mu\text{g}/\ell$, but all concentrations were below the 2- $\mu\text{g}/\ell$ after treatment was initiated.

Summary of New Well Results

Figures 32 and 33 present a summary of the percent removal for each explosive using the four treatments evaluated for the New Well. Based upon review of the

optimal treatments in Table 9 and Figures 32 and 33, the optimal treatment for all explosives in the New Well waters was the “low flow” 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide, with an effluent concentration of 2-ppm hydrogen peroxide from each column (2OZC2HPO120). But the 2- $\mu\text{g}/\ell$ criteria was not met for RDX, TNB, or TNT. Based upon residual concentrations, 5.2, 155, and 24 $\mu\text{g}/\ell$ for RDX, TNB, and TNT, respectively, TNB is the most recalcitrant compound and hence the most limiting compound, since it had the lowest percent removal efficiency of 72 percent and the highest residual concentration. Aminodinitrotoluene compounds were removed quickly using peroxone techniques and were not the basis for selection of optimal treatment.

Similar to trends observed for Wells 66 and 22, continuous dosing of hydrogen peroxide in Columns 1 through 4 was generally more effective than dosing of hydrogen peroxide in batch at the influent to Column 1, with the exception of HMX using 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP). As a reminder to the reader, the 2OZC25HP run for removal of HMX in Well 66 waters was also the least effective and actually appeared to cause HMX concentrations to increase. But 2OZC25HP was the most effective treatment for Well 22 waters. HMX is not a concern in the selection of optimal treatment of the New Well waters since initial concentrations were well below the site criteria of 400 $\mu\text{g}/\ell$.

A recommendation for further studies includes an evaluation of “high flow” treatment, which was not performed for New Well waters. However, longer treatment times will probably be required based upon the results of these studies. If further degradation of TNT, TNB, and RDX is not attained, some type of polishing or secondary treatment would be required to meet site criteria.

Intermediate Formation

Results of research into the intermediates and end products of RDX peroxone oxidation

Researchers at the University of North Carolina, Chapel Hill, NC, assisted WES with the evaluations presented in this report by investigating the intermediates and end products of RDX peroxone oxidation. This research was conducted on pure spiked solutions. Their research found that formamide (HCONH_2), urea ($\text{CH}_4\text{N}_2\text{O}$), and a third unidentified by-product were intermediates of RDX peroxone oxidation. N-hydroxyformamide ($\text{C}_3\text{H}_5\text{NO}_4$), nitro formaldehyde ($\text{C}_2\text{H}_3\text{NO}_2$), and two unknown compounds were the final products in the peroxone oxidation of RDX.

Results of research into the intermediates and end products of TNT peroxone oxidation

Researchers from SRI, Menlo Park, CA, evaluated intermediates and end products of TNT and aminodinitrotoluenes. Samples containing 1-mg/ ℓ TNT were

treated using varying concentrations of ozone and hydrogen peroxide and intermediates and end products evaluated according to methods described by Kieber and Mopper (1990). TNB was found to be an intermediate product in the degradation of TNT, and end products identified were formaldehyde, acetaldehyde, glyoxal, glyoxylic acid, and nitrates. Nitrite was analyzed but not detected. Hong, Zappi, and Kuo (1994) research supports the findings of SRI and CRREL. Hong, Zappi, and Kuo indicate the major degradation pathway of TNT consists of three parts: (a) a methyl side-chain oxidation of TNT to TNB, (b) hydroxylation of the aromatic ring or hydroxylation with removal of a nitro group from the ring, and (c) ring cleavage resulting in various organic acid derivatives that are eventually mineralized.

Results of research into the intermediates and end products of aminodinitrotoluene peroxone oxidation

Researchers from SRI also evaluated oxidation of aminodinitrotoluenes. Their results indicate that aminodinitrotoluenes are so reactive towards ozone alone that the hydroxyl radical is not crucial to their oxidation/destruction. Products of aminodinitrotoluene oxidation include nitrite ion and simple acids.

Table 10 presents a composite of the optimal treatment techniques for Wells 66, 22, and the New Well. The optimal treatments for Wells 22 and the New Well were clearly 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) and 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide with 2-ppm hydrogen peroxide in the effluent from each column (2OZC2HPO120), respectively. However, the optimal treatment for Well 66 is not as easily selected since the optimal treatments were variable among the explosives. Although percent removals were high (96 and 64 percent), two compounds did not meet the site criteria, TNT and TNB, respectively. The optimal treatments for TNT and TNB were 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP) and 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide to obtain 2-ppm hydrogen peroxide in the effluent from each column (2OZC2HPO120). Selection of the optimal treatment would require further evaluation of 2OZC25HP and 2OZC2HPO120 to determine whether the site criteria of 2 µg/l for TNT and TNB could be met.

In general, the optimal treatment conditions also had high ozone MTE. Comparison of the ozone transfer dose and ozone and hydrogen peroxide residuals for Wells 66, 22, and the New Well is presented in Figures 34 through 42. Analysis of Figures 34 through 36 for Well 66 shows that the 2OZ1000HP and 2OZC100HP runs were overdosed with hydrogen peroxide and ozone as was discussed previously in the results section. The effect of no hydrogen peroxide and overdosing of hydrogen peroxide on the ozone demand is illustrated in the 2OZNHP, 2OZ1000HP, and 2OZC100HP runs. Each of these runs had higher ozone residuals with respect to the other treatments. The three optimal treatments for removal of the explosives of concern were 2OZC10HP (HMX and RDX), 2OZC1HPO120 (TNB), and 2OZC25HP (TNT). The combination of ozone and hydrogen peroxide

Table 10 Summary of Optimal Treatment Scenarios for Wells 66, 22, and the New Well Based on Percent Removal ¹									
Well No.	HMX	RDX	TNB	DNB	TNT	4A-DNT	2A-DNT	2,4-DNT	
66	2OZC10HP (69%)	2OZC10HP (90.3%)	2OZC2HPO (64%)	1OZC10HP (76%)	2OZC25HP (96%)	NA	NA	NA	
22	2OZC25HP (88%)	2OZC25HP (98.2%)	2OZC25HP (87%)	NA	2OZC25HP (98%)	NA	NA	NA	
New Well	2OZC2HPO120 (83%)	2OZC2HPO120 (96%)	2OZC2HPO120 (72%)	NA	2OZC2HPO120 (98%)	NA	NA	NA	

Note: NA indicates optimal treatment scenario could not be determined due to analysis results less than detection limit (0.2 µg/l) after one HRT using each treatment or influent concentrations were less than detection limit.

¹ Based upon the treatment scenario that treats the explosive to below the 2-µg/l standard the most rapidly.

in those runs according to Figures 34 through 36 appears to be nicely matched based on the percent removals attained and the oxidizer usage required for treatment.

Figures 37 through 39 show the oxidizer usage for Well 22 waters. The optimal treatment was 2OZC25HP and, according to the figures, was a good combination of dosages for the oxidizers since minimal residuals of ozone and hydrogen peroxide were combined with the optimal treatment. This point is reinforced by consideration of the results of the 2OZC10HP residual oxidizers. Ozone residuals were high, while hydrogen peroxide residuals were negligible, indicating an excess of ozone. Another observation in analysis of the residuals is the possibility of hydrogen peroxide being limited in the 2OZC5HP40 run since there was approximately 2.5 ppm ozone residual in each column and very small to negligible concentrations of hydrogen peroxide residuals in the effluent of each column.

Results of residual oxidizers in the New Well waters are presented in Figures 40-42. Comparison of the optimal treatment, 2OZC2HPO120, to the other techniques based on oxidizer usage, indicates a good combination of oxidizers was used to obtain treatment, with minimal oxidizer residuals.

In general, Figures 34 through 42 for Wells 66, 22, and the New Well, respectively, illustrate the impact of overdosing peroxone systems, resulting in unused residual oxidizer, adding to the economics of implementation of peroxone techniques. Analysis of the results of Well 66 tests suggests that residual ozone or residual hydrogen peroxide alone does not result in significant further removal of HMX, RDX, TNB, and TNT, thus reinforcing the theory that oxidation of these explosives is probably due to indirect attack by the free radicals generated during peroxone treatment. However, the aminodinitrotoluene compounds were highly reactive toward ozonation alone, indicating they are oxidized by direct electrophilic addition of ozone.

The results of the minimum time required to reach treatment goals for each explosive in Wells 66, 22, and the New Well are presented in Table 11. In Well 22, the least contaminated well of the three evaluated, all explosive concentrations were reduced to regulatory levels in 80 min. In fact, concentrations of RDX, HMX, and TNT were reduced in less than 40 min, but TNB was the most limiting explosive. Concentrations of RDX in Well 66 were reduced to below 2 $\mu\text{g}/\ell$ in less than 80 min, but those levels were not reached for TNT and TNB and in the New Well; the site treatment criteria were not met for any of the explosives. However, the percent removals of the described peroxone treatment techniques for each of the explosives in Wells 66, 22, and the New Well should not be overlooked.

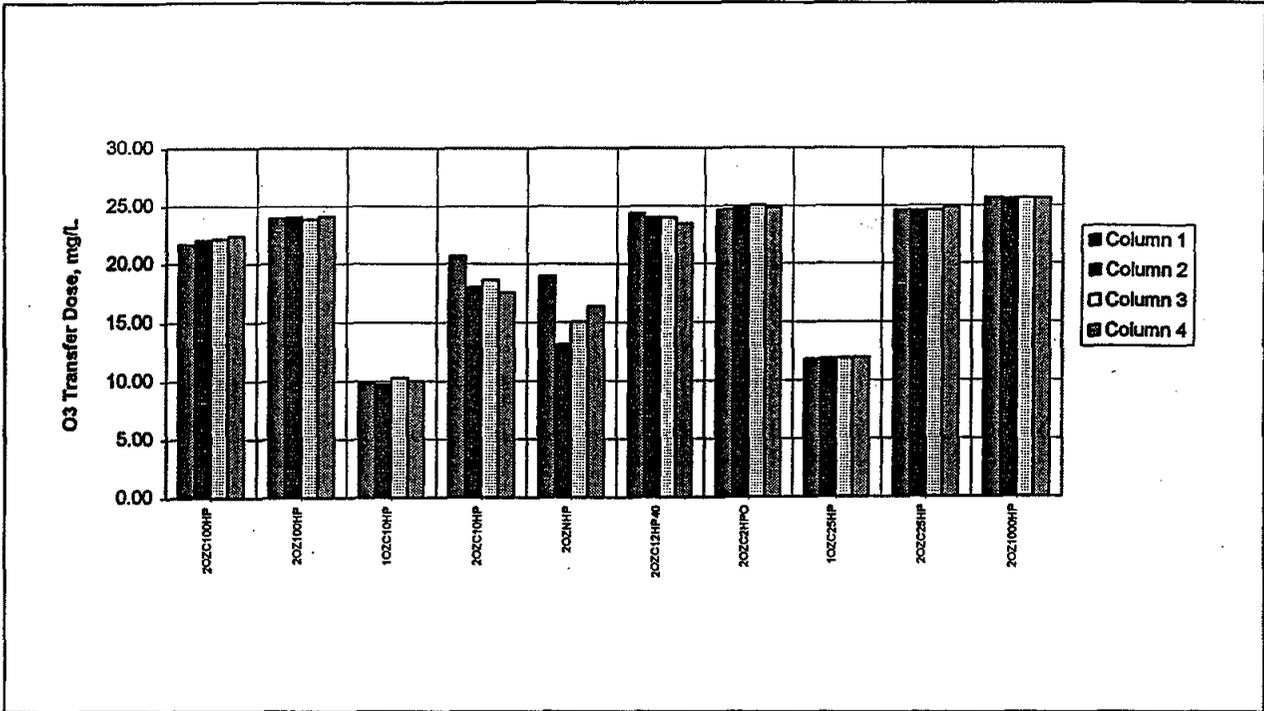


Figure 34. Well 66 ozone transfer dose

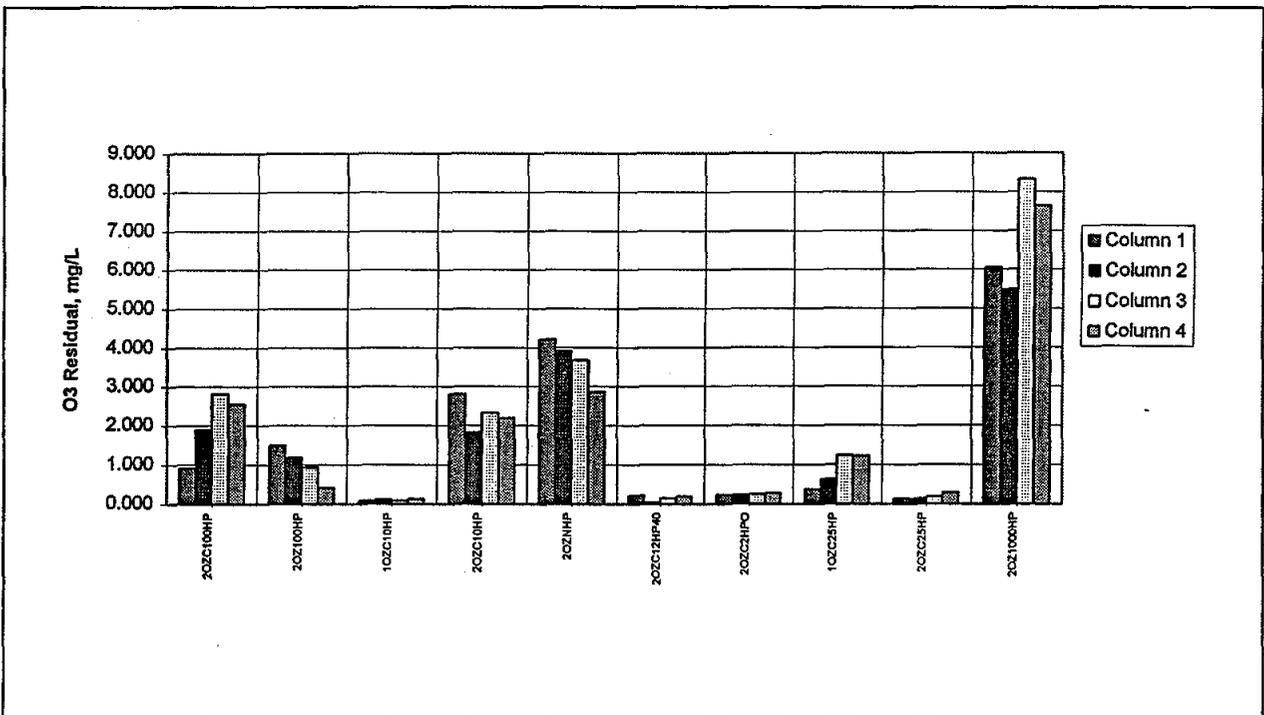


Figure 35. Well 66 residual ozone in Columns 1-4

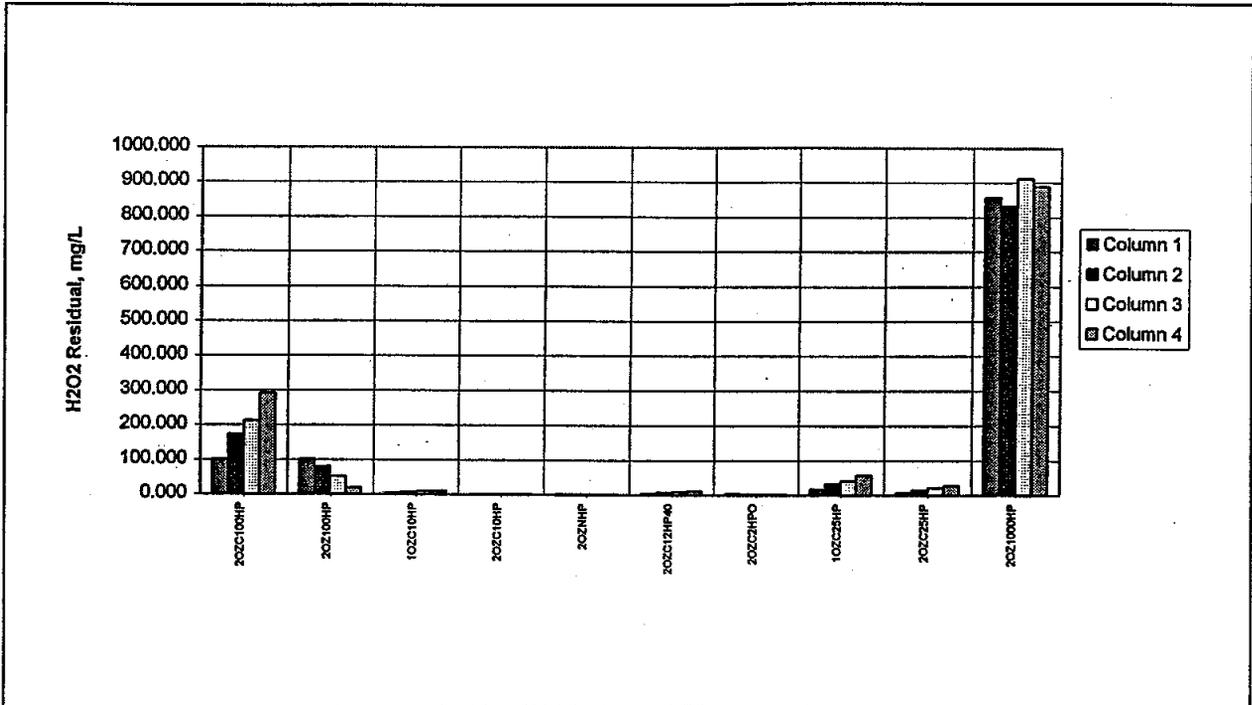


Figure 36. Well 66 residual hydrogen peroxide in Columns 1-4

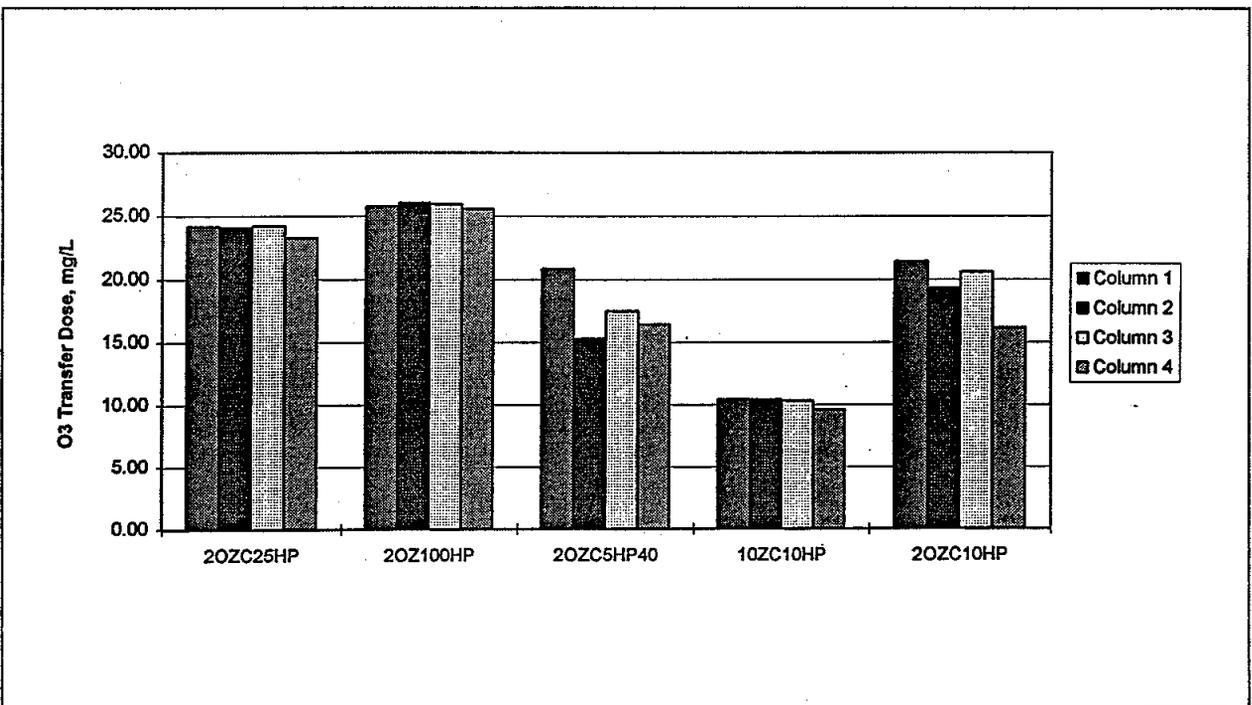


Figure 37. Well 22 ozone transfer dose

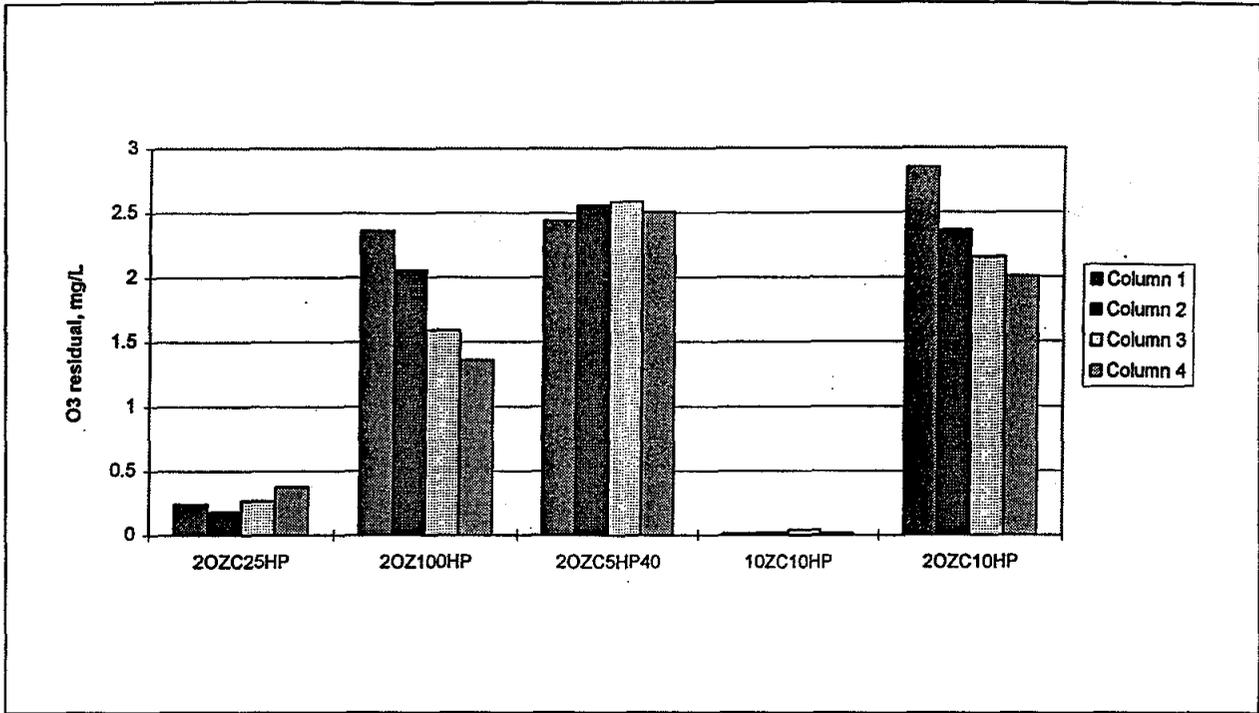


Figure 38. Well 22 residual ozone in Columns 1-4

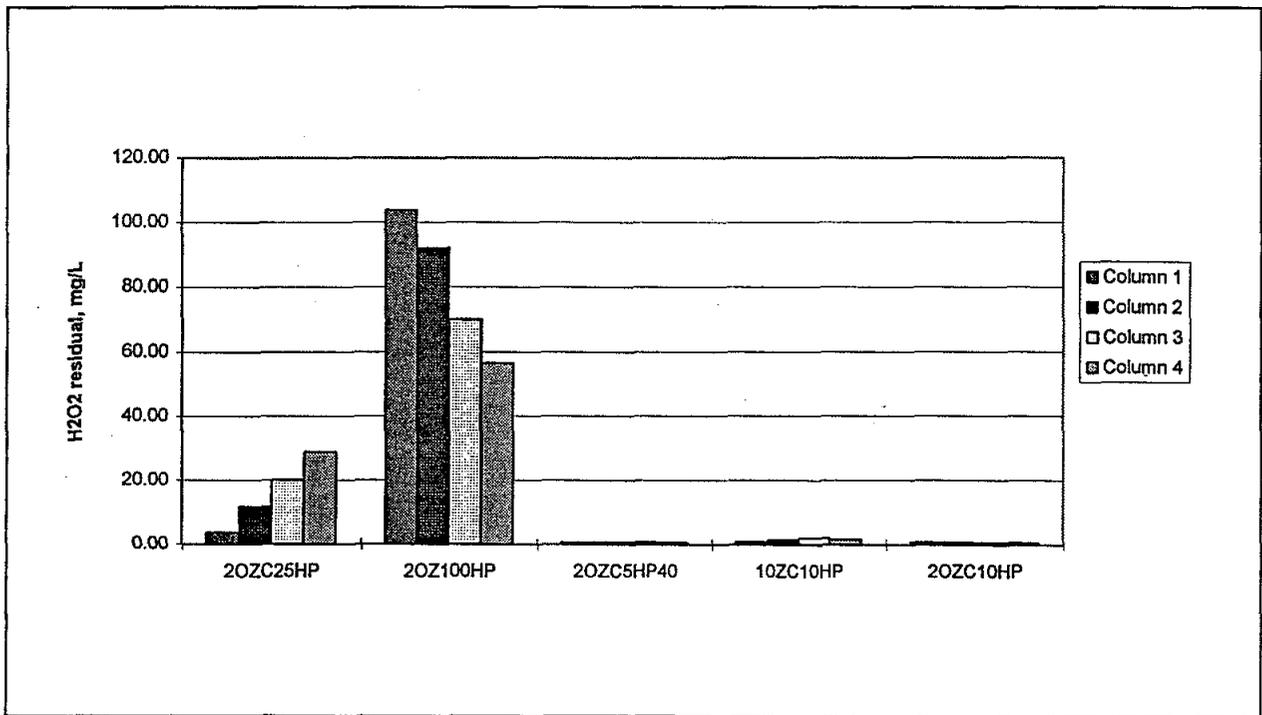


Figure 39. Well 22 residual hydrogen peroxide in Columns 1-4

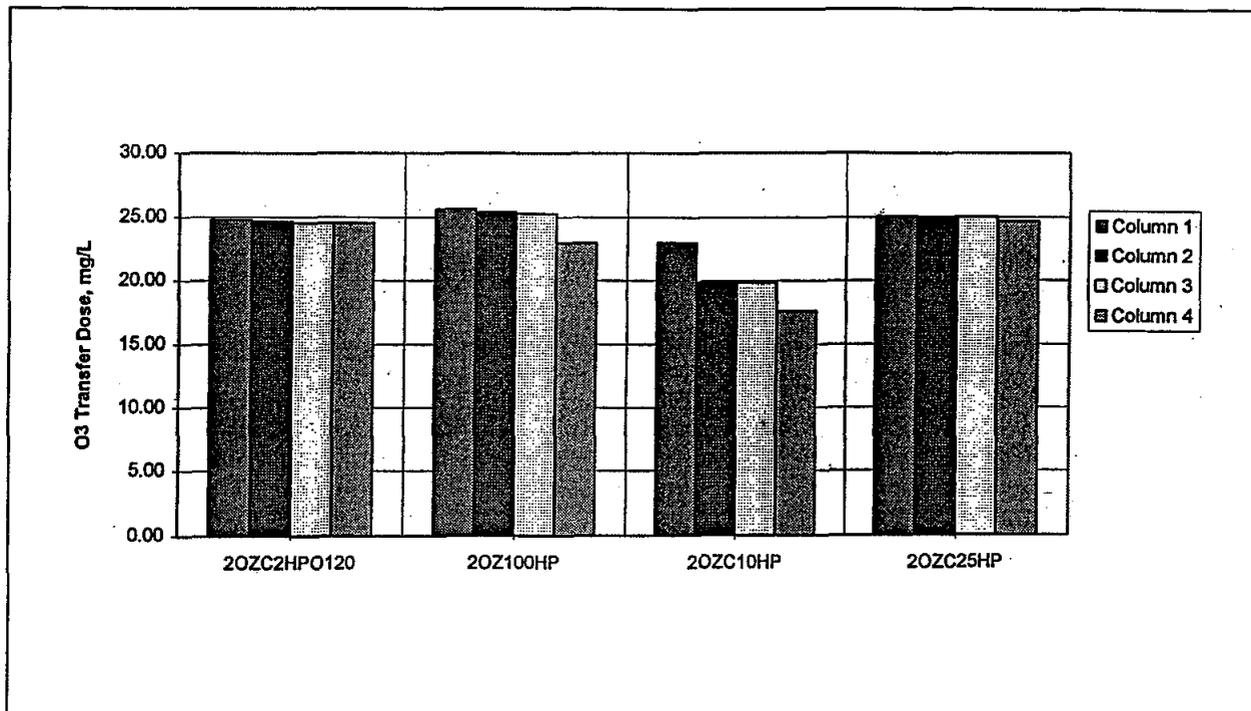


Figure 40. New Well ozone transfer dose

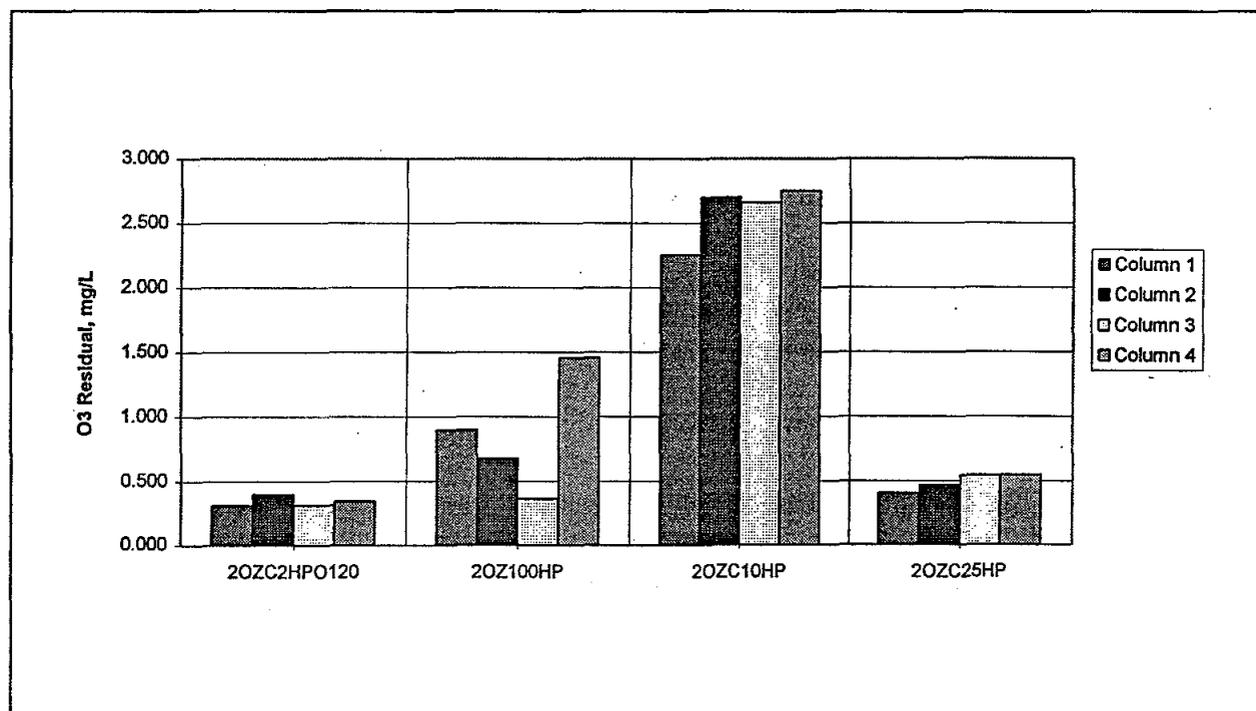


Figure 41. New Well residual ozone in Columns 1-4

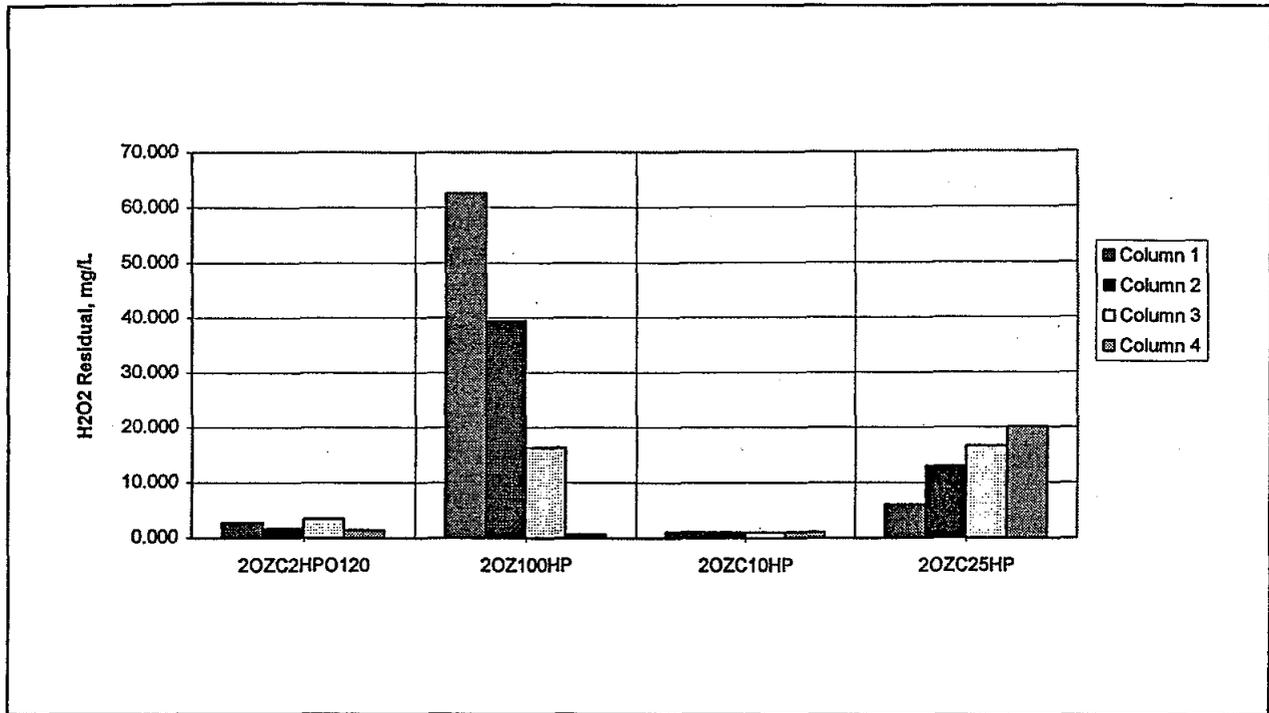


Figure 42. New Well residual hydrogen peroxide in Columns 1-4

Well No.	HMX	RDX	TNB	DNB	TNT	4A-DNT	2A-DNT	2,4-DNT
66	<60	<80	NR	NA	NR	<20	<20	<20
22	<20	<40	<80	NA	<30	NA	NA	NA
New Well	NA	NR	NR	NA	NR	<20	<20	<20

Note: NR indicates the 2- μ g/l standard was not reached. NA indicates the influent concentration was less than 2 μ g/l.

5 Conclusions

The main objective of studies of peroxone treatment of Wells 66, 22, and the New Well was to determine the feasibility of using peroxone treatment for remediation of explosives-contaminated waters using a pilot-scale system. Peroxone treatment is a viable treatment alternative for reducing explosives concentrations considerably and is capable of reducing low-level explosives concentrations to drinking water standards. More concentrated waters such as Well 66 and the New Well attained a high degree of destruction of the explosives—for example, up to 96 and 98 percent of TNT in Well 66 and the New Well, respectively. Hence, peroxone, a dark AOP, appears to be an alternative to UV-illuminated oxidation techniques, which are more costly.

The conclusions of this study based on specific objectives are presented separately below for Wells 66, 22, and the New Well.

Well 66

One optimal treatment was difficult to select since it was variable among the explosives. However, four treatments should be considered further.

- a. Two-percent ozone dosed continuously with 10-ppm hydrogen peroxide (2OZC10HP).
- b. Two-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP).
- c. “Low flow” 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide, with 2-ppm hydrogen peroxide in the effluent (2OZC2HPO120).
- d. “High flow” 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide (2OZC12HP40).

Removal efficiencies were 96, 90, 76, 69, and 64 percent for TNT, RDX, DNB, HMX, and TNB, respectively, based on the optimal treatment for each explosive.

The removal efficiencies presented above, resulting in attainment of the 2- $\mu\text{g}/\ell$ criteria for RDX, were reached in 80 min. Although high removal efficiencies were attained, the criteria were not met in the treatment times evaluated for TNB and TNT.

Well 22

The optimal treatment based on analysis of the results of removal of HMX, RDX, TNB, and TNT was 2-percent ozone dosed continuously with 25-ppm hydrogen peroxide (2OZC25HP).

Removal efficiencies were 98, 98, 88, and 87 percent for TNT, RDX, HMX, and TNB, respectively, using 2OZC25HP.

The drinking water criteria of 2 $\mu\text{g}/\ell$ for TNT, TNB, and RDX were met in less than 80 min, with TNB being the limiting compound. With exception of TNB, TNT and RDX were removed in less than 40 min.

New Well

The optimal treatment for all explosives in New Well waters was "low flow" 2-percent ozone dosed continuously with approximately 12-ppm hydrogen peroxide and containing 2-ppm hydrogen peroxide in the effluent (2OZC2HPO120).

Percent removal efficiencies using 2OZC2HPO120 were 98, 96, 83, and 72 percent for TNT, RDX, HMX, and TNB, respectively.

The drinking water criteria of 2 $\mu\text{g}/\ell$ were not met for RDX, TNB, or TNT after 120 min of treatment.

A recommendation for further studies for removal of the explosives to meet the drinking water criteria in the New Well would be evaluation of a "high flow" treatment.

A general observation in analysis of results of treatment of Wells 66 and 22 was that "high flow" treatment (specifically 2OZC12HP40 and 2OZC5HP40) was highly effective, although this treatment did not result in the highest removal efficiencies since retention times were lower. In those tests, it appears hydrogen peroxide was limited based upon Figures 34 and 37. Thus, "high flow" treatment combined with higher hydrogen peroxide dosages may be effective.

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**Appendix A
Stanford Research Institute
and U.S. Army Cold Regions
Research and Engineering
Laboratory Reports on
Explosives Intermediates**



Dr. Mark Zappi
U.S. Army Corps of Engineers
Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, MS 39180

March 7, 1996

Dear Dr. Zappi,

Enclosed herein, please find the results from our study regarding the Peroxone treatment of 2,4,6-trinitrotoluene (TNT) samples submitted to us in March, 1995. This work was performed under Contract No. DACA39-95-M-2183 (SRI Project 6348) to the U.S. Army Waterways Experiment Station.

SAMPLES

The first set of samples were received on March 15, 1995 in a cooled ice chest. The samples were identified as SRI 1-0, SRI 1-3, SRI 1-5, SRI 1-10, SRI 1-15, SRI 1-20, SRI 1-25, and SRI 1-60. The samples were stored at 4°C until analyzed. An additional four sets of samples were received on March 17, 1995. The samples were identified as SRI 2-0, SRI 2-3, SRI 2-5, SRI 2-10, SRI 2-15, SRI 2-20, SRI 2-25, SRI 2-60; SRI 3-0, SRI 3-3, SRI 3-5, SRI 3-10, SRI 3-15, SRI 3-20, SRI 3-25, SRI 3-60; SRI 4-0, SRI 4-3, SRI 4-5, SRI 4-10, SRI 4-15, SRI 4-20, SRI 4-25, SRI 4-60; and SRI 5-0, SRI 5-00, SRI 5-3, SRI 5-5, SRI 5-10, SRI 5-20, SRI 5-40, and SRI 5-60. All additional samples were stored at 4°C.

SAMPLE TREATMENT

Samples containing TNT were treated at WES with mixtures of ozone and hydrogen peroxide (Peroxone) or titanium dioxide (TiO₂). Table 1 describes the various reactant concentrations applied to the samples containing 1 ppm TNT. This Table is based on information sent to SRI by Ms Evelyn Toro in her letter of 3/8/95 (Appendix 1).

Table 1. Reaction Conditions For The Treatment of TNT Samples.

SAMPLE IDENTIFICATION	CONDITIONS
SRI-1-X	10 PPM H ₂ O ₂ / 8 PPM O ₃
SRI-2-X	10 PPM H ₂ O ₂ / 6 PPM O ₃
SRI-3-X	100 PPM H ₂ O ₂ / 8 PPM O ₃
SRI-4-X	100 PPM H ₂ O ₂ / 6 PPM O ₃
SRI-5-X	TiO ₂ with best decay rate

X = 0, 3, 5, 10, 15, 20, 25, 60 min

SRI International

333 Ravenswood Ave. • Menlo Park, CA 94025 • (415) 326-6200 • TWX: 910-373-2046 • Telex: 334486

Each sample was treated from 0 to 60 min. Thus, the sample identified as SRI 3-15 was treated with 100 PPM H₂O₂/ 8 PPM O₃ for 15 minutes.

ANALYTICAL METHODS

The samples were analyzed for TNT, aldehydes, nitrite, nitrate, and carboxylic acids using chromatographic methods. For TNT, the following conditions were employed:

Column: Altex Altima C18, 5 μ , (4.6 x 250 mm)
Solvent: Acetonitrile/ water (60/40)
Flow Rate: 1.2 mL/min
Detector: UV @ 254 nm
Injector: Waters WISP Model 712, 50 μ L
Integrator: HP 3390
Retention Time: 4.8 min

Aldehydes including formaldehyde, acetaldehyde, glyoxal, and glyoxylic acid were analyzed as their 2,4-dinitrophenylhydrazone derivatives according to the methods reported by Kieber and Mopper (1990). In this procedure, 2,4-dinitrophenylhydrazine (DNPH) was dissolved in 12M HCl, water, and acetonitrile (2:5:1, v:v:v) and repeatedly extracted with carbon tetrachloride. This procedure removes traces of low level carbonyl contamination. Then 50 μ L of the aqueous DNPH solution was added to 2.0 mL of test solution. The mixture was allowed to stand for 2 hr, then it was analyzed by HPLC using the following conditions:

Column: Altex Altima C18, 5 μ , (4.6 x 250 mm)
Solvent: A. 10% Acetonitrile/ water adjusted to pH 2.6 with
10 M H₂SO₄
B. 100% Acetonitrile
Program: 36% B in A for 2min
36% B ----> 45% B in 4 min. Hold 45% B for 8 min
45% B ----> 80% B in 10 min. Hold 80% B for 2min
80% B ----> 100% B in 2 min. Hold 100% B for 20 min
Flow Rate: 1.2 mL/min
Detector: UV @ 370 nm
Injector: Waters WISP Model 712, 200 μ L
Integrator: HP 3390
Retention Times: Glyoxylic acid - 3.79 min
Glyoxal monohydrazone - 5.78 min
Formaldehyde - 8.93 min
Acetaldehyde - 11.39 min
Glyoxal dihydrazone- 24.09 min

Nitrite and nitrate were analyzed directly by anion exchange HPLC according to the method of Thayer and Huffaker (1980). The following conditions were employed:

Column: Whatman Partisil SAX, 10 μ (4.6 x 250 mm)
Solvent: 50 mM NaH₂PO₄, pH 3.2
Flow Rate: 1.0 mL/min
Detector: UV @ 210 nm
Injector: Waters WISP Model 712, 50 μ L
Integrator: HP 3392
Retention Time: 6.7 min - nitrite
9.3 min - nitrate

Dicarboxylic acids were investigated by gas chromatography after conversion to their methyl esters. Detection was performed by mass spectrometry. In a typical example, a 100-ml sample was basified with KOH to pH 10.5 and lyophilized to dryness. The residue (10 mg) was acidified with 0.4 mL of 50% aqueous H₂SO₄ and 2 mL of methanol was added the mixture was heated at 60°C for 30 min. The solution was cooled, 1 mL of water was added and the solution was extracted with 0.5 mL of chloroform. A 2 µL aliquot was analyzed by GC/MS. This procedure is reported in Supelco Bulletin 748H (1985).

Methods were also attempted using derivatization with p-bromophenacyl bromide to form p-bromophenacyl esters that were analyzed by liquid chromatography according to the method of Durst et al. (1975). These derivatives gave strong UV chromophores at 250 nm, however, the method was not applicable to dicarboxylic acids such as oxalic and malonic acids. Also, inconsistencies in derivatization efficiencies were observed and interference from coeluting components made the methodology questionable for this application. We also attempted the preparation of the p-nitrobenzyl esters using O-(p-nitrobenzyl)-N,N'-(diisopropyl)isourea as the derivatizing reagent according to the methods reported by Knapp and Krueger (1975). While this methodology works well for fatty acids, it is not applicable to short chained carboxylic acids in water. Attempts to derivatize lyophilized residues were unsuccessful. Finally, the direct determination of short-chained acids was attempted using a Supelcogel resin column C-610H (H⁺ form) using the following conditions:

Column: Supelcogel 610H resin column, 7.8 x 300 mm
Solvent: 0.1% H₃PO₄
Flow Rate: 0.5 mL/min
Detector: UV @ 210 nm
Injector: Waters WISP Model 712, 100 µL
Integrator: HP 3392
Retention Times: Oxalic acid - 9.61 min
Tartaric + Pyruvic acids - 13.21 min
Glyoxylic acid - 14.09 min
Glycolic acid - 17.91 min
Formic acid - 19.96 min
Acetic acid - 21.82 min

RESULTS

A. TNT

A five point calibration standard of TNT, ranging from 0 to 1.5 ppm gave a correlation coefficient of 0.9999, slope of 1.242×10^6 , and an intercept of 7.367×10^3 by linear regression analysis. Each sample was analyzed directly by HPLC and the results are shown in Table 2.

Table 2. TNT (PPM) Remaining in SRI Samples
MINUTES

Sample	0	3	5	10	15	20	25	60
SRI-1	1.00	0.74	0.56	0.38	0.16	0.14	ND	ND
SRI-2	0.95	0.82	0.83	0.64	0.43	0.29	0.14	0.10
SRI-3	1.11	0.70	0.53	0.37	trace	ND	ND	ND
SRI-4	0.93	0.61	ND	0.18	trace	ND	ND	ND
SRI-5	19.0	14.4	7.9	6.4	NS	11.1	6.3*	1.3

* This sample was labelled as SRI 5-40; Also this set of samples contained a sample identified as SRI 5-00 which analyzed for 9.52 ppm TNT.
ND = not detected; NS = no sample.

Additional products observed in the chromatographic profile were 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrobenzaldehyde (TBAL). These components were quantified and the results appear in Table 3. A chromatographic profile for sample SRI 5-10 appears in Figure 1.

Table 3. PPM Levels of TNB and TBAL (/) Found in SRI Samples

Sample	0	3	5	10	15	20	25	60
SRI-1	ND	0.09	0.04	0.04	0.05	0.11	ND	ND
SRI-2	ND	ND	0.05	0.08	0.06	0.06	trace	trace
SRI-3	ND	0.10	0.09	0.08	trace	ND	ND	ND
SRI-4	ND	trace	ND	0.07	ND	ND	ND	ND
SRI-5	ND	0.32 / 0.24	0.29 / 0.27	0.45 / 0.56	NS	0.85 / 0.62	0.67* / 0.69*	0.22 / 0.24

* This sample was labelled as SRI 5-40; ND = not detected; NS = no sample.

B. ALDEHYDES

Aldehydes were identified as their 2,4-dinitrophenylhydrazone derivatives by their characteristic absorption at 370 nm and their cochromatography with authentic standards. The major aldehydes identified and quantified were formaldehyde, acetaldehyde, glyoxal, and glyoxylic acid. Sample results appear in Table 3. A typical chromatographic profile of aldehyde derivatives appears in Figure 2.

C. NITRATE and NITRITE ANALYSES

The analysis of nitrite and nitrate by ion-exchange HPLC did not identify nitrite in any samples. However, nitrate was found in overwhelming amounts compared to the theoretically expected value based on the amount of TNT present (4 μM) in these samples. The identity of nitrate was confirmed by ion chromatography using a conductivity detector. The data for nitrate appear below and suggest an exogenous source of nitrogen to generate nitrate in the oxidizing system. Theoretically, 12 μM (0.74 ppm) of nitrate could be produced from TNT in Samples SRI 1 through SRI 4. On the other hand, samples in set SRI 5 showed a theoretical conversion of TNT nitrogen to nitrate at 60 min (initial TNT was 83.7 μM).

Table 3. Quantitation of Aldehydes (ppm) Found in SRI Samples.

SAMPLE	Formaldehyde	Acetaldehyde	Glyoxal	Glyoxylic Acid
SRI 1-0	ND	ND	ND	ND
1-3	0.088	0.070	0.040	0.174
1-5	0.084	0.076	0.022	0.114
1-10	0.102	0.087	0.035	0.179
1-15	0.096	0.053	0.032	0.107
1-20	0.102	0.064	0.049	0.210
1-25	0.060	0.040	0.068	0.422
1-60	0.075	0.063	0.136	0.763
SRI 2-0	0.021	ND	ND	ND
2-3	0.125	0.108	0.022	0.130
2-5	0.104	0.085	0.020	0.116
2-10	0.107	0.077	0.047	0.303
2-15	0.103	0.078	0.030	0.176
2-20	0.129	0.082	0.023	0.118
2-25	0.081	0.075	0.031	0.193
2-60	0.120	0.071	0.040	0.189
SRI 3-0	0.040	ND	ND	ND
3-3	0.082	0.071	0.011	0.069
3-5	0.062	0.058	0.015	0.075
3-10	0.090	0.072	0.013	0.072
3-15	0.084	0.030	0.017	0.090
3-20	0.070	0.040	0.015	0.070
3-25	0.077	0.030	0.025	0.070
3-60	0.10	0.080	0.045	0.270
SRI 4-0	0.019	ND	ND	ND
4-3	0.045	0.07	0.01	0.05
4-5	0.044	0.13	ND	0.04
4-10	ND	ND	ND	0.07
4-15	0.04	0.02	0.004	0.05
4-20	0.04	ND	0.09	ND
4-25	0.04	ND	0.015	trace
4-60	0.076	0.05	0.04	0.36
SRI 5-0	0.05	ND	ND	ND
5-00	0.05	ND	ND	ND
5-3	0.05	ND	ND	ND
5-5	0.04	ND	ND	ND
5-10	0.03	ND	ND	ND
5-25	0.04	ND	ND	ND
5-40	0.02	ND	ND	ND

Table 4. Nitrate (PPM) Found in Oxidized Samples

Sample I.D.	SRI 1	SRI 2	SRI 3	SRI 4	SRI 5
SRI X-0	0	0	0	0.25	0.46
SRI X-3	7.5	0.5	7.8	0.23	0.89
SRI X-5	17.5	5.0	12.4	0.17	0.94
SRI X-10	24.7	18.8	24.3	15.6	2.1
SRI X-15	31.9	30.0	39.6	23.6	NS*
SRI X-20	34.5	36.0	55.1	40.9	NS
SRI X-25	46.3	45.6	69.6	43.7	2.3
SRI X-40	NS	NS	NS	NS	2.6
SRI X-60	72.4	78.4	102	98.2	5.9

* NS = No Sample for this time point

A typical HPLC profile for nitrite and nitrate standards and sample SRI 1- 10 appears in Figure 3. A plot of nitrate formation in samples SRR 1 - SRI 4 appears in Figure 4.

CARBOXYLIC ACIDS

Sample SRI 1-60 was evaluated for carboxylic acids by lyophilization of a 100-mL sample to a dried residue followed by methylation with methanol in sulfuric acid, chloroform extraction, and GC/MS analysis. From this procedure, oxalic acid, malonic acid, and citric acid were identified as their methyl esters (Figure 5). The amount of citric acid observed appeared to be inconsistent with the amount of available TNT. Because the esters of formic, acetic, glyoxylic, and glycolic acids were not evident, we chose to evaluate other approaches.

The formation of p-bromophenacyl esters could not be performed consistently. Although pure reagents were obtained from Pierce Chemical (p-Bromophenacyl-8), the HPLC profile of the derivatives showed many coupled products from the reagent (Figure 6). The pure derivative of formic acid was synthesized so its exact retention time could be obtained. Derivatives of other acids were also prepared. The complexity of the HPLC profile is shown in Figure 6 for sample SRI 1-60. In Figure 6, Peak 3 corresponded to glycolic acid, Peak 4 to formic acid, and Peak 6 to acetic acid, however, these and other components in the profile gave no molecular ions for known carboxylic acids as their p-bromophenacyl esters by thermo spray, negative ion, or filament assisted ionization. Also, no chromatographable derivatives of dicarboxylic acids (oxalic and malonic) or citric acid could be formed. The SRI X-60 samples were analyzed and the results showed only small levels of formic acid present in the final oxidized samples.

The aqueous samples were analyzed directly using an ion-exchange resin column designed for carboxylic acid analysis (Supelco 610H resin column). A typical profile of standards is shown in Figure 7 (Top). Sensitivities for carboxylic acids, such as formic acid, were found to be low (≈ 1 ppm/ 100 μ L injection). Dicarboxylic acids, such as oxalic acid, were not resolved from the large amounts of nitrate ion observed in these samples (see Figure 7, Bottom). A major component coeluted with citric acid, however, other acids, such as oxalacetic, elute in the same vicinity. While peak area determinations of formate were at the level of detection, we were unable to generate quantitative information with any degree of accuracy. The remaining sample sets showed near baseline levels of formate, indicating that further method development is required to improve the methodology for low

level carboxylic acid analysis or that the Peroxone oxidation process is efficient and carbon dioxide is a major end product in the treatment process.

If you have any questions regarding the methodologies or the results found in this study, please feel free to write or call me.

Sincerely,

Ronald J. Spangord, Ph.D.
Director, Bio-Analytical Chemistry
(415) 859-3822 (phone)
(415) 859-2753 (Fax)

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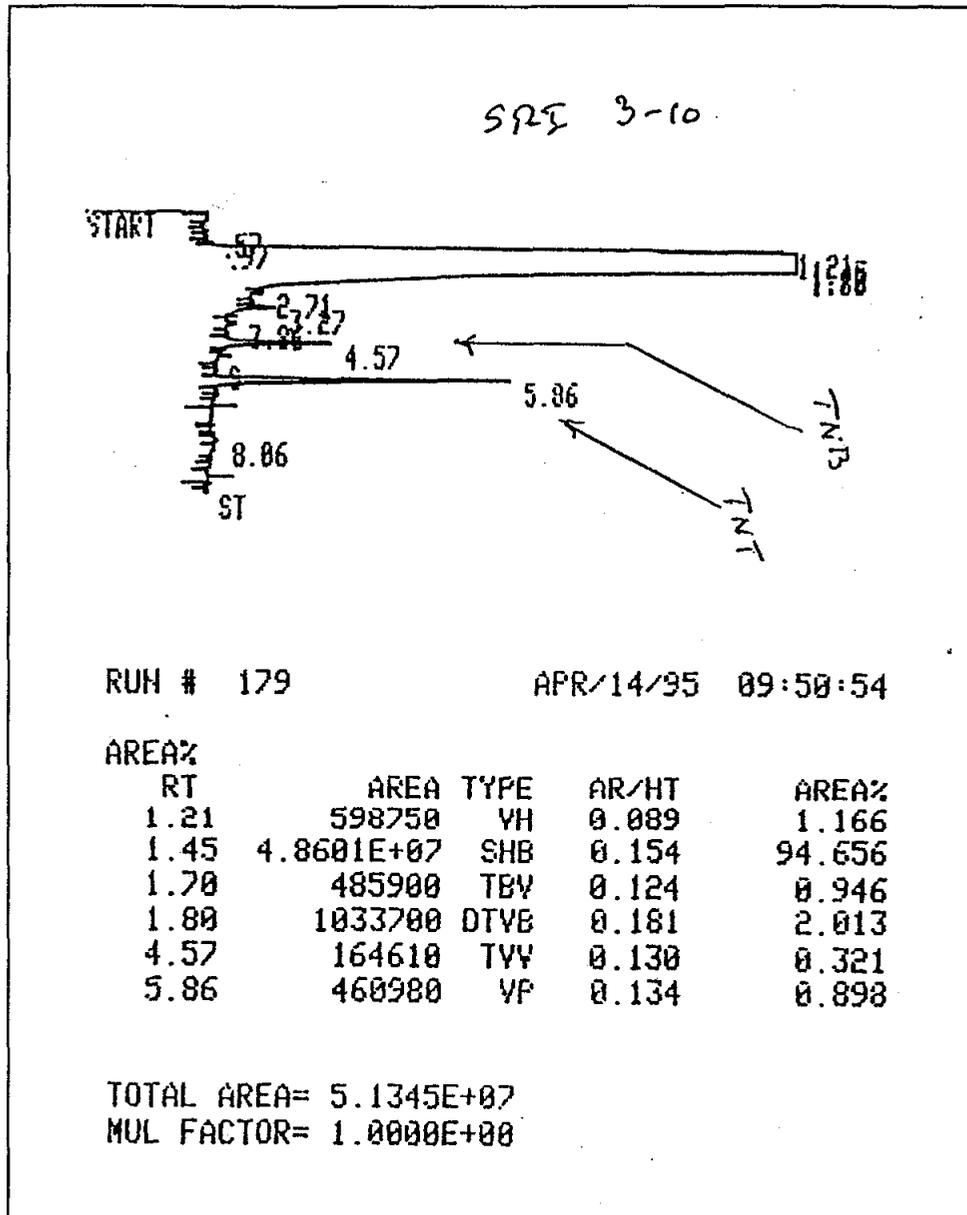


Figure 1. HPLC Profile for Sample SRI 3-10 indicating the presence of 1,3,5-trinitrobenzene

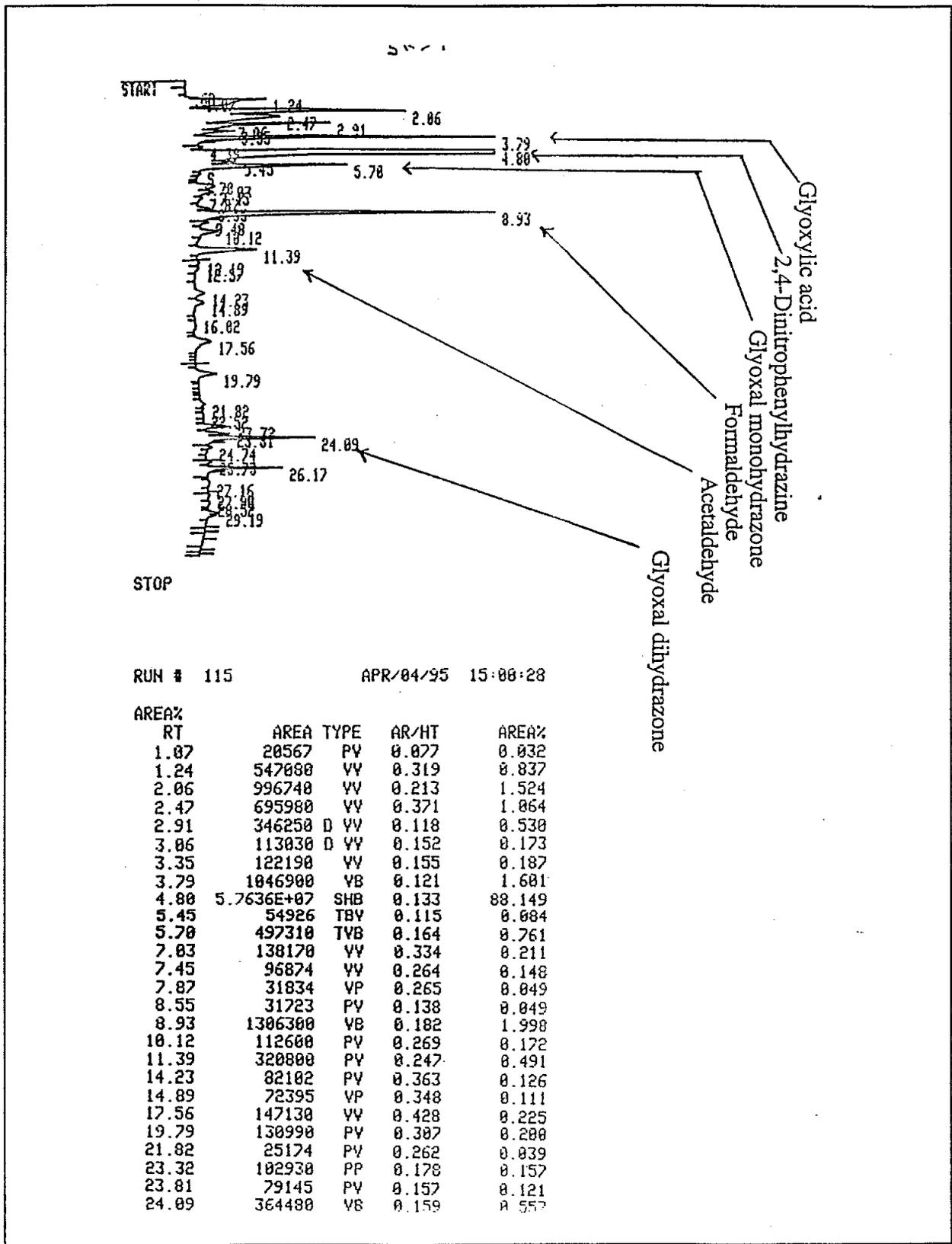


Figure 2. HPLC profile of aldehydes observed in Sample SRI 2-15 as the 2,4-dinitrophenylhydrazones

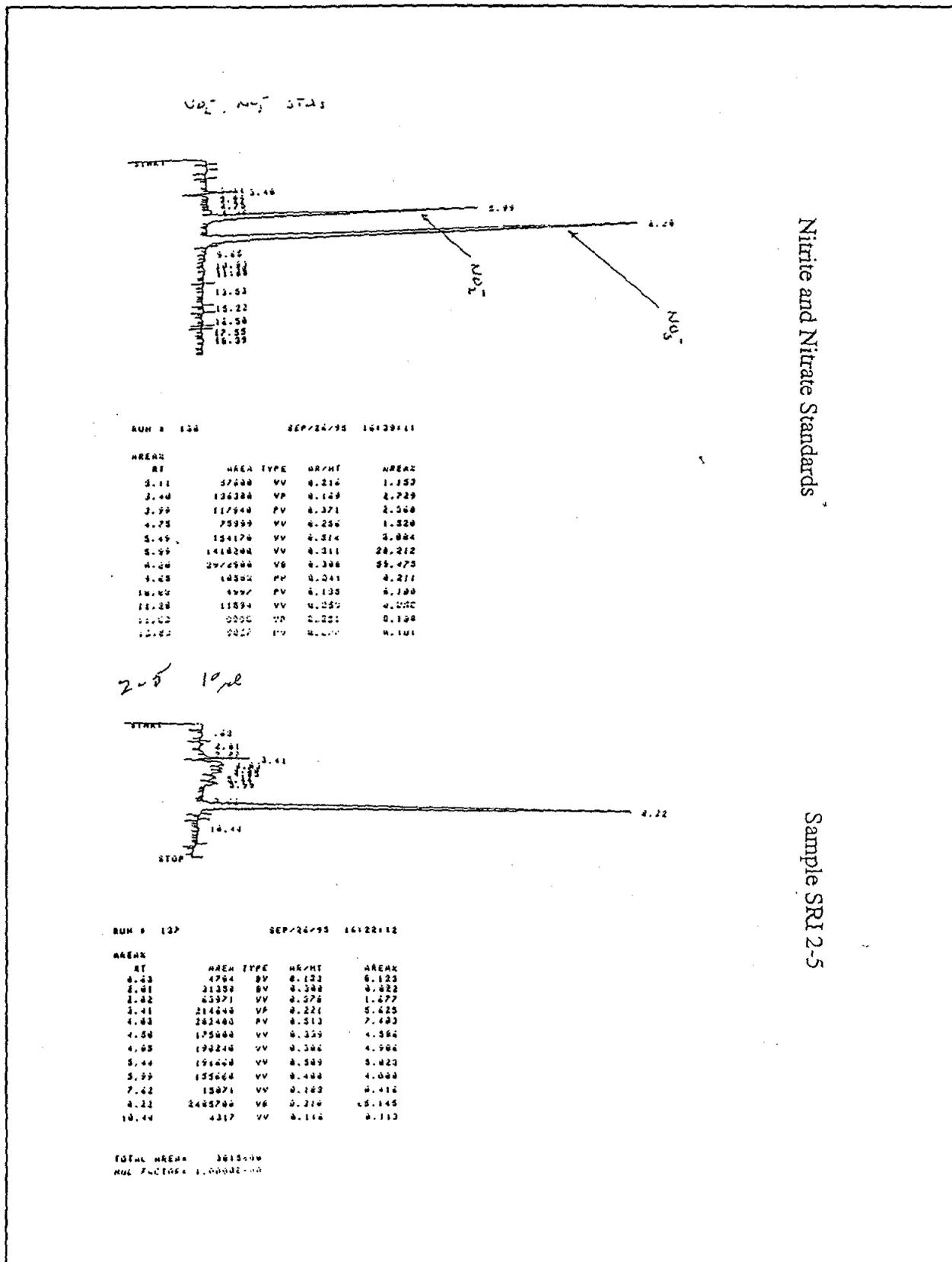


Figure 3. HPLC profile of nitrite and nitrate standards (left) and sample SRI 2-5 (right).

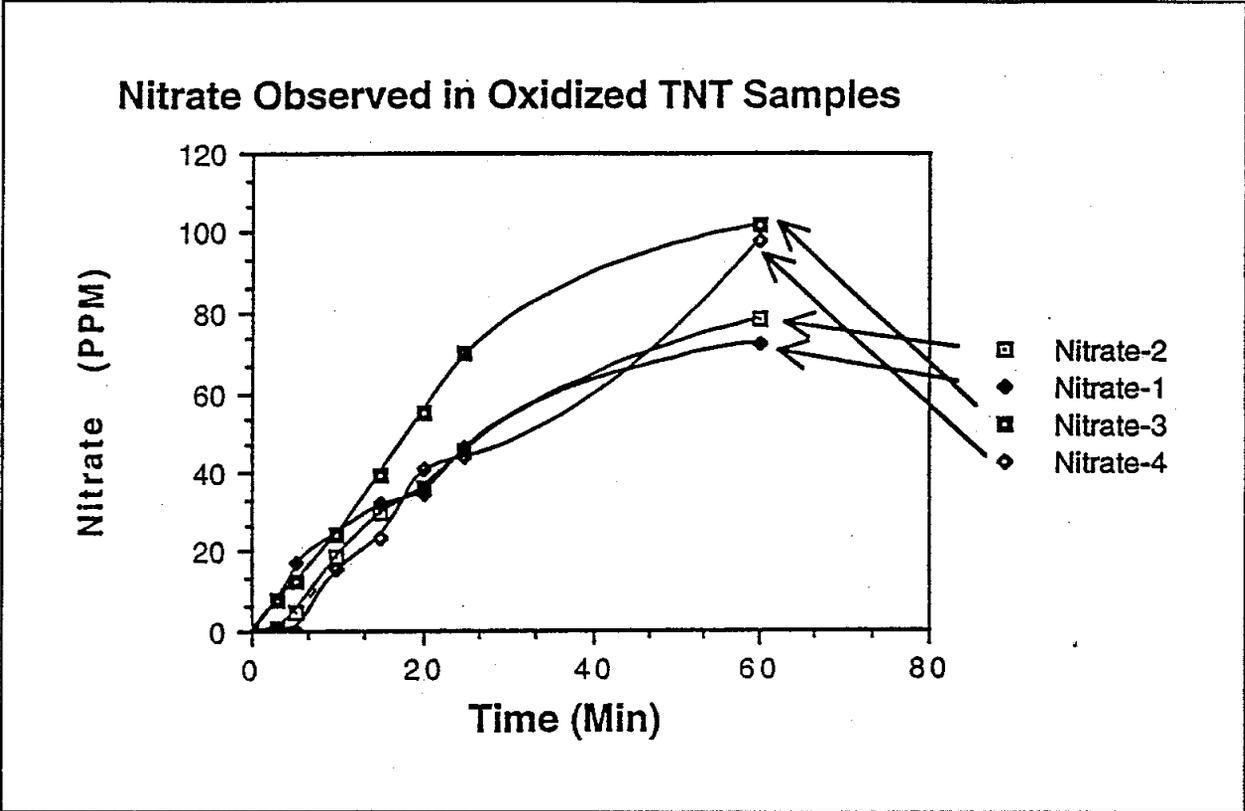


Figure 4. Formation of nitrate observed in samples SRI 1-SRI 4.

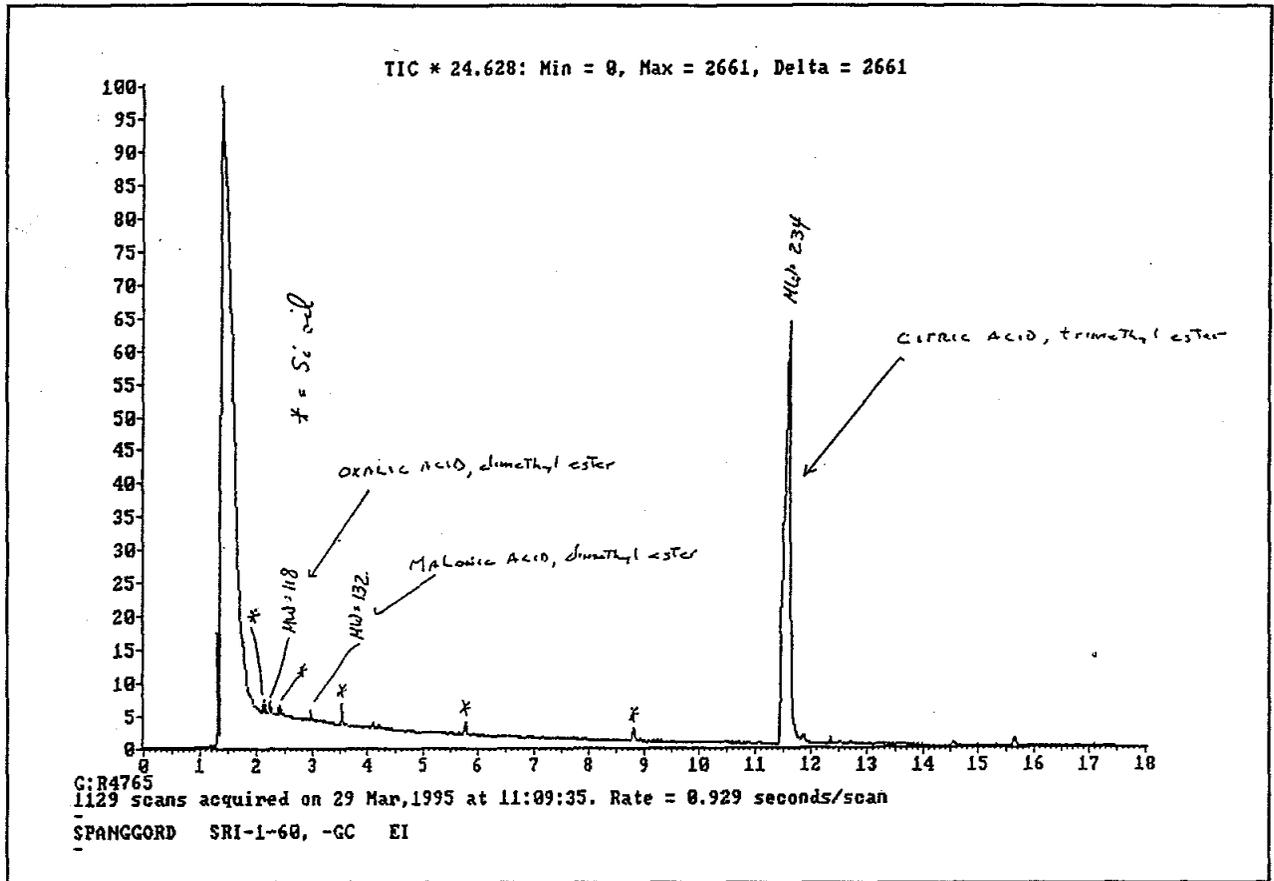


Figure 5. GC profile of methyl esters of carboxylic acids identified by GC/MS in Sample SRI 1-60

Date: Sat. Nov 11, 1995 11:45 AM
Data: 2347-001

Sample: Spangord SRI 1-60
Alltech C18 #95089174
A [ACN] / B [0.1M AA, 10% ACN], 40% A to 90% @30 min
1 ml/min
250 nm

Processing File: process file
Method: 30 min
Sampling Int: 0.1 Seconds
Data:

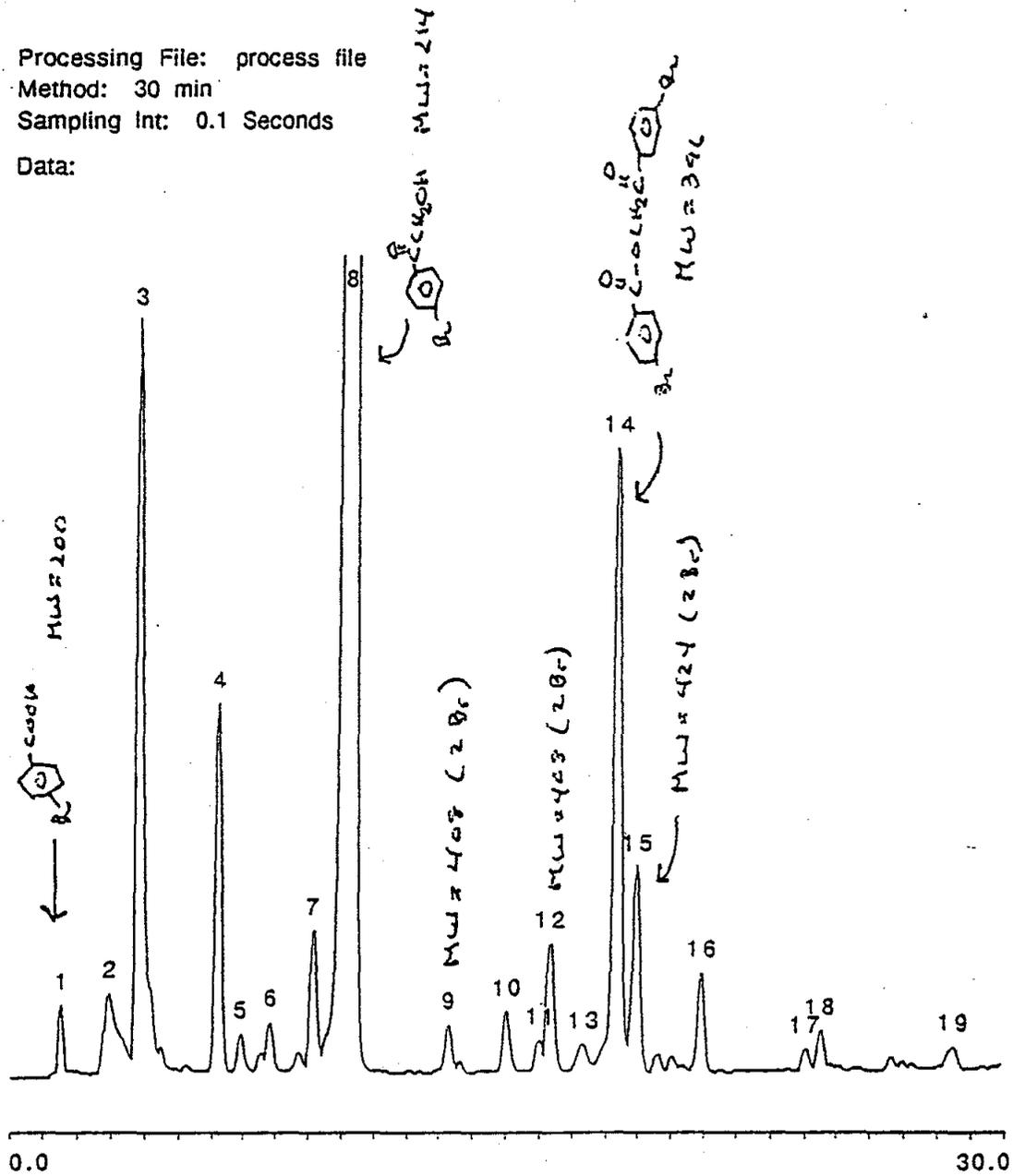


Figure 6. HPLC/MS profile of components observed in the p-bromophenacyl derivatization of carboxylic acids in Sample SRI 1-60

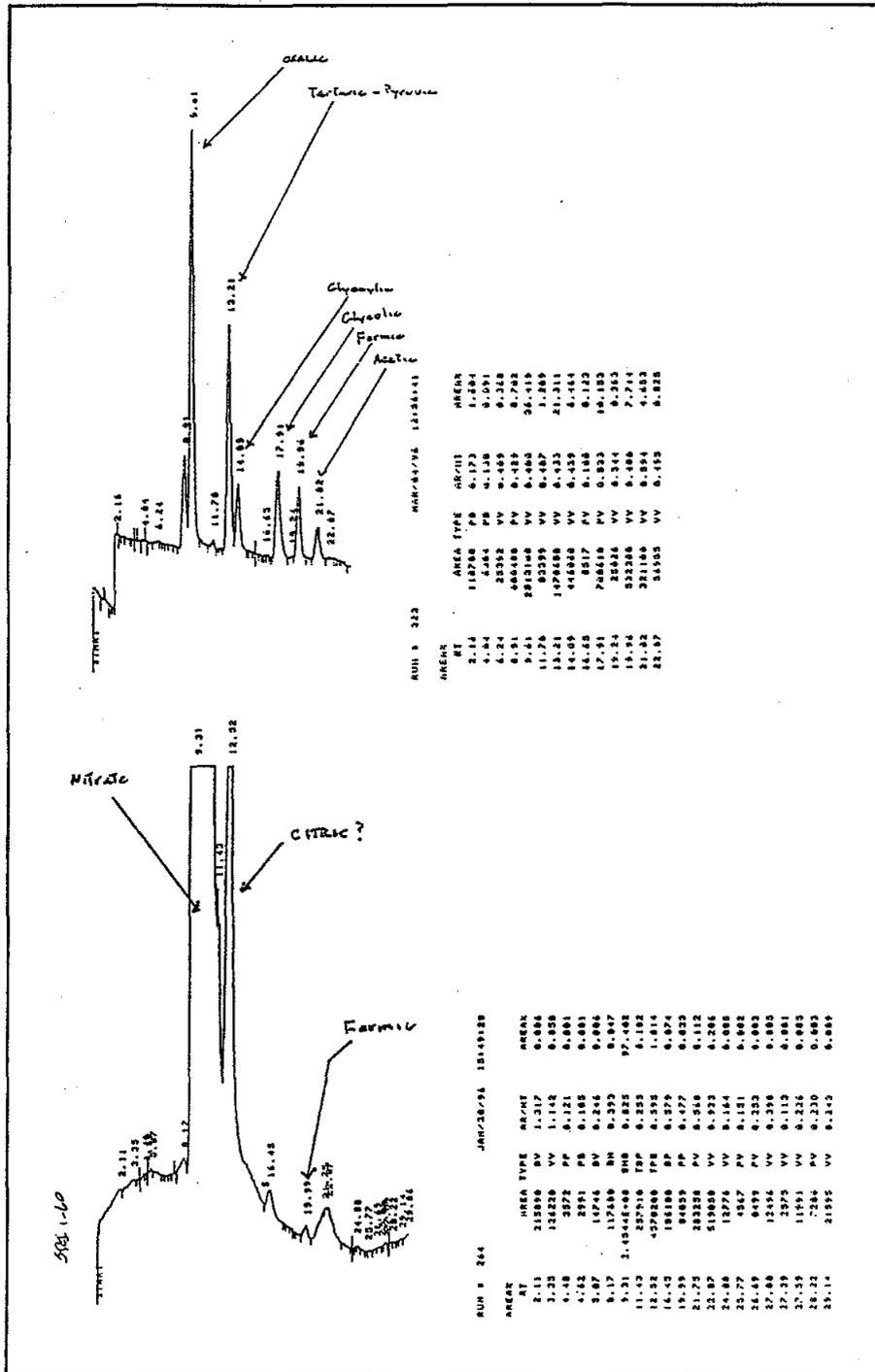


Figure 7. Ion-exchange HPLC profile of acid standards (right) and sample SRI 1-60 (left)

US Army Corps of Engineers
Waterways Experiment Station
3909 Halls Ferry Rd
Vicksburg, MS 39180

8 March 1995

Dr. Ronald Spanggard
SRI International-Bldg PS-353
333 Ravenswood Ave.
Menlo Park, CA 94025

SUBJECT: Synthetic TNT samples for SRI International to analyze
for acid and aldehyde determination.

Dear Dr. Spanggard:

As concurred in your phone conversation with Mr. Mark Zappi, the experiments for SRI International will begin by March 13, 1995 at the USAE Waterways Experiment Station (WES), Environmental Laboratory in Vicksburg, MS. A total of 40-1L samples, eight per run, should be the maximum number that SRI International should have received by March 22. The samples collection and shipping schedule (Federal Express no later than 2:30pm) follows:

Condition*	Collection Day	Shipping Day
10ppm H2O2/8ppm O3	March 13, 1995	March 14, 1995
10ppm H2O2/6ppm O3	March 15, 1995	March 16, 1995
100ppm H2O2/8ppm O3	March 15, 1995	March 16, 1995
100ppm H2O2/6ppm O3	March 20, 1995	March 21, 1995
TiO2 with best decay rate	March 20, 1995	March 21, 1995

*Time= 0, 3, 5, 10, 15, 20, 25, and 60 minutes

Although the Chemical Oxidation staff at WES has a very busy schedule we will make every effort to maintain the one here proposed.

If you have any questions please do not hesitate in contact Mr. Mark Zappi or Ms. Evelyn Toro. They can be reached at (601)634-2856 or 3579, respectively. Thank you for your cooperation and time. We look forward to hearing from you soon.

Sincerely,



Evelyn Toro
Civil Engineer

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13. ABSTRACT (Maximum 200 words) Peroxone technology is based on the combination of hydrogen peroxide (H ₂ O ₂) and ozone (O ₃) for the generation of the hydroxyl radical (OH*), which is a powerful reactive species in water, to further oxidize the organic contaminants. The main objective of this study was to determine the technical feasibility of using peroxone systems for treatment of contaminated groundwaters at the Cornhusker Army Ammunition Plant (CAAP). The U.S. Army Engineer Waterways Experiment Station (WES) selected CAAP for the evaluation of peroxone oxidation technology since this site is included on the National Priorities List and due to the relatively high concentration of explosives, namely octahydro-1,3,5,7-tetranitro-1,3,5-tetrazine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), trinitrobenzene (TNB), trinitrotoluene (TNT), 4-amino-dinitrotoluene (4A-DNT), 2-amino-dinitrotoluene (2A-DNT), and 2,4-dinitrotoluene (DNT) present. The peroxone oxidation pilot system used in this study was constructed and assembled by the WES Environmental Restoration Branch and the WES Public Works Division. The unit consisted of four glass columns (6 ft in diameter and 14 ft in height) plumbed in series, a holding tank (500 gal) for influent water supply, two 3-lb per day ozone generators, a microcomputer for data logging, oxidizer injection systems, and monitors for vapor and aqueous phase concentrations of hydrogen peroxide and ozone.			
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The feasibility of using peroxone treatment for remediation of explosives-contaminated water was evaluated using water from three different wells: Wells 22, 66, and a "New Well" that was constructed during the peroxone evaluations. Several oxidizer mass ratios (H_2O_2/O_3), modes of hydrogen peroxide injection (batch or continuous), and hydraulic residence times were studied. A concentration of 2-percent ozone by weight in the sparged air stream, hydrogen peroxide concentrations of 10 to 25 ppm (continuously injected) in the influent to each column, and hydraulic residence times of 80 and 120 min were the operating conditions that achieved the highest removal for the majority of the explosives compounds in the water.

The results demonstrated that the peroxone treatment is a viable alternative to reduce low-level explosives concentrations to U.S. Environmental Protection Agency drinking water standards. Water systems with higher concentrations of explosives such as Well 66 and New Well attained a high degree of remediation, for example, up to 96- and 98-percent TNT degradation in Well 66 and the New Well, respectively. Peroxone, a dark oxidation process, appears to be an economically competitive alternative to ultraviolet-illuminated oxidation systems.

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