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U.S. Army Toxic and Hazardous Materials Agency

INSTALLATION RESTORATION PROGRAM
ENVIRONMENTAL TECHNOLOGY
DEVELOPMENT

Task Order - 3 Use of Activated Carbon for Treatment of Explosives-Contaminated Groundwater at the Badger Army Ammunition Plant (BAAP)

Contract Number DAAA15-88-D-0010
Report No. CETHA-TE-CR-89216

August 1989

Prepared for:
COMMANDER, U.S. ARMY TOXIC AND HAZARDOUS
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Aberdeen Proving Ground (Edgewood Area),
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USE OF ACTIVATED CARBON FOR TREATMENT
OF EXPLOSIVES-CONTAMINATED GROUNDWATER AT THE
BADGER ARMY AMMUNITION PLANT (BAAP)

Final Report

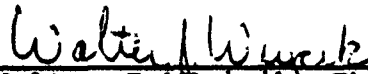
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Commander United States Army Toxic and
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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The primary objective of this task was to evaluate the use of GAC to treat groundwater contaminated with explosives to United States Army Biomedical Research and Development Laboratory (USABRDL) criteria. An additional goal was to examine the potential discharge of the explosives 2,4-DNT and 2,6-DNT from a conventional packed column air stripper used to remove volatile organic compounds from groundwater. Laboratory GAC isotherm studies were conducted to select the two best performing carbon types for further testing using the continuous flow pilot columns. Pilot scale continuous flow GAC column tests were conducted at Badger Army Ammunition Plant in Baraboo, Wisconsin, using the two carbons (Hydrodarco 4000 and Filtrasorb 300) selected during the laboratory isotherm studies. A pilot scale, conventional packed column air stripper was used to remove volatile organics from the groundwater prior to treatment by the pilot scale GAC columns. A method was developed to permit lower detection levels for 2,4-DNT and 2,6-DNT. The data from the laboratory and pilot studies were analyzed and a final report prepared to present the results and (continued)			
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conclusions. The study concluded that concurrent removal of 2,4-DNT and 2,6-DNT from groundwater using continuous flow GAC is feasible. It was not possible to certify an analytical method for the quantification of 2,4-DNT and 2,6-DNT concentrations at USABRDL criteria for these contaminants. Consequently, verification of compliance with these criteria could not be achieved.

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CONTENTS

		<u>Page</u>
Paragraph ES	EXECUTIVE SUMMARY.....	ES-1
1	INTRODUCTION.....	1-1
1.1	Background.....	1-1
1.2	Problem statement.....	1-1
1.3	Previous work.....	1-2
1.4	Project objectives.....	1-2
2	BACKGROUND.....	2-1
2.1	Literature update.....	2-1
2.2	Previous USATHAMA studies.....	2-1
2.2.1	Preliminary activated carbon screening.....	2-1
2.2.2	Isotherm tests.....	2-2
2.2.3	Preliminary column tests.....	2-3
2.2.3.1	Four-in-series column tests.....	2-3
2.2.3.2	Effects of pH on adsorption of explosives.....	2-3
2.2.4	Carbon regeneration properties.....	2-5
2.3	Other technologies.....	2-5
2.3.1	Polymetric adsorption resins.....	2-5
2.3.2	UV light with ozonation and hydrogen peroxide.....	2-6
2.3.3	Chlorination.....	2-6
2.3.4	Activated sludge.....	2-6
2.4	Regulatory issues.....	2-7
2.4.1	Surface water discharge.....	2-7
2.4.2	Groundwater discharge.....	2-9
3	ISOTHERM TESTS.....	3-1
3.1	Test program.....	3-1
3.1.1	Procedures.....	3-2
3.1.2	Carbon selection.....	3-4
3.2	Results.....	3-4
3.2.1	2,4-DNT removal.....	3-6
3.2.2	2,6-DNT removal.....	3-8
3.2.3	TOC removal.....	3-10
3.2.4	pH effects.....	3-10
3.3	Carbon selection.....	3-10
4	TEST PROGRAM AT BAAP.....	4-1
4.1	Air stripper test program.....	4-1
4.1.1	Description of planned test program.	4-1
4.1.1.1	Description of planned test methods.	4-4
4.1.1.2	Test procedures.....	4-6
4.1.1.3	Sample recovery and analytical procedures.....	4-7
4.1.2	Actual test program.....	4-8
4.1.3	Variance analysis.....	4-9

CONTENTS (continued)

		Page
Paragraph 4.2	Activated carbon.....	4-9
4.2.1	Description of planned test program.	4-9
4.2.1.1	Test conditions and experimental variables.....	4-10
4.2.1.2	Operational monitoring.....	4-10
4.2.1.3	Evaluation criteria.....	4-12
4.2.2	Actual test program.....	4-13
4.2.2.1	Continuous flow column test conditions for run one.....	4-13
4.2.2.2	Continuous flow column test conditions for run two.....	4-14
4.2.3	Variance analysis.....	4-14
4.3	Analytical method development for 2,4-DNT and 2,6-DNT.....	4-15
4.3.1	Analytical procedures for explosives analysis in field laboratory.....	4-15
4.3.2	Analytical procedure for explosives analysis by WESTON's Analytics Division.....	4-15
4.3.3	Analytical procedures for volatile organics in water.....	4-15
4.3.4	Analytical procedure for total organic carbon in water.....	4-15
5	PRESENTATION OF EXPERIMENTAL RESULTS...	5-1
5.1	Air stripper.....	5-1
5.1.1	Explosives.....	5-1
5.2	Activated carbon.....	5-1
5.2.1	Explosives.....	5-1
5.2.1.1	Field lab results.....	5-1
5.2.1.2	WESTON's Analytics Division results.	5-9
5.2.2	Total organic carbon.....	5-9
5.2.3	Volatile organics.....	5-9
5.2.4	Temperature and pH.....	5-9
6	DISCUSSION OF RESULTS.....	6-1
6.1	Air stripper test program.....	6-1
6.1.1	Explosives emission.....	6-1
6.2	Continuous flow (pilot plant) activated carbon testing.....	6-2
6.2.1	Effluent characteristics.....	6-2
6.2.2	Operating summary.....	6-5
7	DESIGN CONSIDERATIONS.....	7-1
7.1	General.....	7-1
7.2	Process variables and parameters....	7-1
7.2.1	Influent and effluent.....	7-1
7.2.2	GAC column operating characteristics	7-1
8	CONCLUSIONS AND RECOMMENDATIONS.....	8-1

CONTENTS
(continued)

	<u>Page</u>
Paragraph 9 REFERENCES.....	9-1
APPENDIX A - Certification Package for WESTON's Low-Level HPLC Method for DNT in Water	

FIGURES

			<u>Page</u>
FIGURE	3-1	2,4-DNT isotherms for five GACs.....	3-7
	3-2	2,6-DNT isotherms for five GACs.....	3-9
	3-3	TOC isotherms for five GACs.....	3-11
	3-4	Filtrisorb 400 isotherms showing effects of varying pH on 2,4-DNT removal....	3-12
	3-5	Filtrisorb 400 isotherms showing effects of varying pH on 2,6-DNT removal....	3-13
	3-6	Filtrisorb 400 isotherms showing effects of varying pH on TOC removal.....	3-14
	4-1	Schematic of air stripper system employed at BAAP.....	4-2
	4-2	EPA Modified Method 5 sampling train for collection of explosives.....	4-5
	5-1	2,4-DNT concentration, using early morning data from field laboratory results for run one at BAAP.....	5-14
	5-2	2,4-DNT concentration, using early morning data from field laboratory results for run one at BAAP.....	5-15
	5-3	2,6-DNT concentration, using early morning data from field laboratory results for run one at BAAP.....	5-16
	5-4	2,6-DNT concentration, using early morning data from field laboratory results for run one at BAAP.....	5-17
	5-5	2,4-DNT concentration, using early morning data from field laboratory results for run two at BAAP.....	5-18
	5-6	2,4-DNT concentration, using early morning data from field laboratory results for run two at BAAP.....	5-19
	5-7	2,6-DNT concentration, using early morning data from field laboratory results for run two at BAAP.....	5-20
	5-8	2,6-DNT concentration, using early morning data from field laboratory results for run two at BAAP.....	5-21

TABLES

			Page
TABLES	2-1	Point source effluent goals.....	2-4
	2-2	Known groundwater pollutants and prescribed effluent water quality BPJ limits.....	2-8
	3-1	Isotherm test matrix.....	3-3
	3-2	Empirical constants of Freundlich adsorption equation for five GACs using groundwater from Monitor Well PBN82-02C.....	3-5
	3-3	Maximum saturation capacities for five GACs.....	3-16
	4-1	Air stripper emissions test plan.....	4-3
	4-2	Planned experimental conditions for continuous flow pilot tests.....	4-11
	5-1	Summary of explosives test data and test results from air stripper stack testing at BAAP.....	5-2
	5-2	Field laboratory results for 2,4-DNT and 2,6-DNT for air stripper influent and condensate collected in the air stripper U-joint during stack testing at BAAP.	5-4
	5-3	Field laboratory results for 2,4-DNT from run one.....	5-5
	5-4	Field laboratory results for 2,6-DNT from run one.....	5-7
	5-5	Field laboratory results for 2,4-DNT from run two.....	5-10
	5-6	Field laboratory results for 2,6-DNT from run two.....	5-12
	5-7	WESTON's Analytics Division results for 2,4-DNT and 2,6-DNT from run one....	5-22
	5-8	WESTON's Analytics Division results for 2,4-DNT and 2,6-DNT from run two....	5-23
	5-9	WESTON's Analytics Division total organic carbon data from run one.....	5-24
	5-10	WESTON's Analytics Division total organic carbon data from run two.....	5-25
	5-11	WESTON's Analytics Division GAC influent volatile organics data from run one starting 15 February 1989 at BAAP...	5-
	5-12	Morning temperature of influent to GAC columnals pilot treatment study at BAAP.....	5-27
	6-1	WESTON's Analytics Division results vs. WESTON field laboratory results for run two at BAAP.....	6-4

TABLES
(continued)

			<u>Page</u>
TABLES	6-2	Activated carbon column operating and performance data for run one at BAAP	6-6
	6-3	Activated carbon column operating and performance data for Hydrodarco 4000 from runs one and two at BAAP.....	6-7

EXECUTIVE SUMMARY

The United States Army operates explosives manufacturing plants to produce various forms of explosives used in military ordnance. Manufacturing activities at such plants result in the production of organic wastewaters that contain both explosive residues and other organic chemicals. Several treatment technologies have been developed to treat these wastewaters for final discharge.

Past waste handling practices at explosives manufacturing plants commonly included the use of the unlined lagoons or pits for containing process wastewaters. As a result of these past practices, some explosives residues may leach through the soil and contaminate groundwater. Therefore, the treatment of contaminated groundwater may be required. Although potentially applicable treatment technologies exist, based upon process wastewater treatment experience, the similarities and differences between process wastewaters and contaminated groundwater should be considered in efforts to transfer technologies from one application to another.

Groundwater in the area of the Propellant Burning Grounds at Badger Army Ammunition Plant (BAAP) in Baraboo, Wisconsin, has been found to be contaminated with explosives compounds, volatile organic compounds (VOCs), and related degradation products [1]. A barrier well network designed to intercept the advancing contaminant plume with associated treatment using air stripping and/or granular activated carbon (GAC) had been proposed. This pilot study was conducted to evaluate GAC for dinitrotoluene (DNT) removal to the United States Army Bio-medical Research and Development Laboratory (USABRDL) criteria.

The primary objective of this pilot study was to evaluate the use of GAC to treat groundwater contaminated with explosives to USABRDL criteria. The explosives contaminants studied were 2,4-DNT and 2,6-DNT. The study included preliminary batch (isotherm) testing followed by column testing using a continuous flow pilot plant.

As an additional goal, this study examined the potential discharge of the explosives 2,4-DNT and 2,6-DNT from a conventional packed column air stripper used to remove volatile organic compounds from groundwater. This phase of the study was conducted using a commercially available air stripper installed in conjunction with the GAC pilot plant.

A literature review was performed to determine the feasibility of using GAC for treatment of explosives-contaminated

waters. The literature review also included other technologies for the removal of explosives from wastewaters, including:

- Polymeric adsorption resins.
- UV light with ozonation and hydrogen peroxide.
- Chlorination.
- Activated sludge biological treatment.

It was recommended that the pilot study proceed with the investigation of the use of activated carbon for the treatment of explosives-contaminated groundwater.

Laboratory GAC isotherm studies were conducted to evaluate the capability of carbon adsorption to remove 2,4-DNT and 2,6-DNT to the levels of USABRDL criteria and to select the two best performing carbon types for further testing using the continuous flow pilot columns. Calgon Filtrasorb 300 and Hydrodarco 4000 were the best performing GACs in isotherm tests for removing both 2,4-DNT and 2,6-DNT from groundwater from monitor well PBN 82-02C at BAAP.

Pilot scale, continuous flow GAC column tests were conducted at BAAP using the two carbons selected during the laboratory isotherm studies. The test program's focus was to determine the potential feasibility of using activated carbon adsorption for treatment of explosives-contaminated groundwater based on pilot-scale testing. An air stripper was used to remove solvents from groundwater prior to its entering the GAC pilot plant. The primary function of the air stripper in this project was to minimize any effects of these solvents on the evaluation of activated carbon adsorption of explosives. The air stripper was designed to provide approximately 99 percent removal of identified volatile components from the groundwater. After passing through the air stripper, the groundwater was passed through the continuous flow GAC pilot plant unit. The primary function of the GAC unit was to evaluate its effectiveness for removing explosives from groundwater.

This study of activated carbon for treatment of explosives-contaminated groundwater was conducted over one 6-week period. Two test runs of 16 days each were conducted from 15 February 1989 until 29 March 1989. The variables examined were 2,4-DNT, 2,6-DNT, and TOC water concentrations and 2,4-DNT and 2,6-DNT gaseous emissions from the air stripper. Other variables including pH, influent water temperature, air and water flow rates, and atmospheric conditions, were also measured. Samples were analyzed for dinitrotoluenes by liquid/liquid extraction and electron capture gas chromatography. Roy F. Weston, Inc. (WESTON) obtained USATHAMA certification for these compounds. Detection limits were determined by WESTON's low-level HPLC method for DNT in water. The certification package for this method is presented in Appendix A.

At the influent concentrations of groundwater from monitor well PBN82-02C, influent surface loading rates of 3.0 to 7.0 gpm/ft² and an influent hydraulic loading rate of 1.5 to 3.5 gpm/ft³, GAC columns employing either Filtrasorb 300 or Hydrodarco 4000 can provide run lengths of at least 16 days while providing 2,4-DNT and 2,6-DNT removals of greater than 90 percent. Under conditions employed in this study, explosives concentrations could be reduced below detection limits (in this study, approximately 0.46 ug/L for 2,4-DNT and 0.017 ug/L for 2,6-DNT) for approximately 98 hours at the highest loading rate for 2,4-DNT and approximately 6 hours at an intermediate loading rate for 2,6-DNT.

The following conclusions were drawn from this study:

- The concurrent removal of 2,4-DNT and 2,6-DNT from groundwater using continuous flow granular activated carbon columns is feasible.
- It was not possible to certify an analytical method for the quantification of 2,4-DNT and 2,6-DNT concentrations at USABRDL criteria for these contaminants.
- Based upon the isotherm tests performed in this study, the best performing carbons of the five studied were Calgon Filtrasorb 300 and Hydrodarco 4000.
- Based upon testing performed in this study, there is little potential for airborne emissions of 2,4-DNT or 2,6-DNT in the exhaust of an air stripper used to remove volatile compounds.

1. INTRODUCTION

1.1 Background. The United States Army operates explosives manufacturing plants to produce various forms of explosives used in military ordnance. Manufacturing activities at such plants result in the production of organic wastewaters that contain both explosive residues and other organic chemicals. Several treatment technologies have been developed to treat these wastewaters for final discharge.

Past waste handling practices at explosives manufacturing plants commonly included the use of the unlined lagoons or pits for containing process wastewaters. As a result of these past practices, some explosive residues may leach through the soil and contaminate groundwater. Therefore, the treatment of contaminated groundwater may be required. Although potentially applicable treatment technologies exist, based upon process wastewater treatment experience, the similarities and differences between process wastewaters and contaminated groundwater should be considered in efforts to transfer technologies from one application to another.

The investigation of remedial needs and solutions at Army-controlled sites is under the overall management of the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). USATHAMA retained Roy F. Weston, Inc. (WESTON) to provide technical support in the development of appropriate remedial approaches. Under this contract, USATHAMA has decided to investigate treatment technologies for the treatment of explosives-contaminated groundwater.

Process wastewaters at explosives manufacturing plants are often treated by activated carbon adsorption, and published literature is available on its use in this application. Investigation of carbon adsorption for treatment of contaminated groundwater might be based upon process wastewater treatment experience. However, differences between groundwater and process wastewaters should be evaluated.

1.2 Problem statement. Groundwater in the area of the Propellant Burning Grounds at Badger Army Ammunition Plant (BAAP) in Baraboo, Wisconsin, has been found to be contaminated with explosives compounds, volatile organic compounds (VOCs), and related degradation products [1]. A barrier well network designed to intercept the advancing contaminant plume with associated treatment using air stripping and/or granular activated carbon (GAC) had been proposed. This pilot study was conducted to evaluate GAC for dinitrotoluene (DNT) removal to the United States Army Biomedical Research and Development Laboratory (USABRDL) criteria.

1.3 Previous work. Much of the currently available literature involves the use of granular activated carbon (GAC) for the treatment of explosives-contaminated wastewater or pink water rather than treatment of groundwater with similar contaminants [2,3,4,5]. Pink water is the explosives-contaminated wash water produced from the loading, assembly, and packing of ammunition. While the treatment of wastewater and groundwater is expected to be similar, there are several important differences that may affect the application of this technology to groundwater.

- Explosives concentrations in pink water are likely to be substantially higher, and the concentration levels are expected to be more variable than in groundwater.
- The pH of pink water is typically acidic and relatively constant, while the pH of groundwater may be neutral or basic and more variable.
- Effluent criteria for treated groundwater may be more stringent than for pink water, particularly if recharge to groundwater is required.
- Interferences and competition among other components of the groundwater may affect removal of the explosive components by GAC.

1.4 Project objectives. The primary objective of this pilot study was to evaluate the use of GAC to treat groundwater contaminated with explosives to USABRDL criteria. The explosive contaminants studied were 2,4-DNT and 2,6-DNT. The study included preliminary batch (isotherm) testing followed by column testing using a continuous flow pilot plant.

As an additional goal, this study examined the potential discharge of the explosives 2,4-DNT and 2,6-DNT from a conventional packed column air stripper used to remove volatile organic compounds from groundwater. This phase of the study was conducted using a commercially available air stripper installed in conjunction with the GAC pilot plant.

2. BACKGROUND

2.1 Literature update. As discussed in Section 1, much of the currently available literature is on the treatment of explosives-contaminated wastewater or pink water, rather than treatment of groundwater with similar contaminants. References are available on the use of activated carbon to remove explosives from the pink water [2]. The use of this technology applied to groundwater is limited.

2.2 Previous USATHAMA studies. The USATHAMA report prepared by Hinshaw, et al.[4], presents a multiphase study providing quantitative data on the capability of activated carbon to remove the nitrocompounds TNT, 2,4-DNT, RDX, and HMX from pink water. The study included the following phases:

- Preliminary activated carbon screening.
- Isotherm tests of activated carbon.
- Preliminary column tests of selected activated carbons.
- Four in-series column tests.
- Economic analysis of activated carbon.

These phases are described in the following subsections.

2.2.1 Preliminary activated carbon screening. Using manufacturer's data and literature references, activated carbon screening was conducted to evaluate and select various carbons for further testing. The carbon selection process was based upon the following criteria [4]:

- High surface area. This is the amount of surface area per unit weight of carbon. The surface area of activated carbon is usually determined from the nitrogen adsorption isotherm by the Brunauer, Emmett, and Teller Method (BET Method). Surface area is usually expressed in square meters per gram of carbon.
- High pore volume. This is the sum of the macro and micro pores in a carbon, or, in other words, the total pore volume. This is expressed as volume per unit weight.
- High iodine number. The iodine number is the milligrams of iodine adsorbed by 1 gram of carbon at an equilibrium filtrate concentration of 0.02N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02N by an assumed isotherm slope. The iodine number can be correlated with the ability to adsorb low molecular weight substances.

- Low average (mean) particle diameter. This is a weighted average diameter of a granular carbon. A screen analysis is run and the average particle diameter calculated by multiplying the weight of each fraction by its average diameter, adding the products, and dividing by the total weight of the sample. The average diameter of each fraction is taken as the size midway between the sieve opening through which the fraction has passed and the sieve opening on which the fraction was retained.
- Low pressure drop (headloss). This is the drop of pressure across an adsorption column due to the resistance of the carbon particles to the flow of liquids or gases through the system.
- High "popular" use. This is the frequency of use of an activated carbon at AAP facilities.
- Low cost. This is the cost based on manufacturer's published prices for truckload lots of activated carbon.
- Manufacturer's recommendation. Activated carbon is recommended to have the best pink water adsorption performance.

Five carbons were selected for further evaluation based upon these criteria. These carbons include:

- Calgon Filtrasorb 200.
- Calgon Filtrasorb 300.
- Calgon Filtrasorb 400.
- Westvaco Nuchar WV-G.
- Witco Witcarb 950.

2.2.2 Isotherm tests. An isotherm test is a constant temperature experiment in which wastewater is treated with a dosage of activated carbon and agitated until equilibrium is reached. The activated carbon is filtered out and the filtrate is analyzed to determine the equilibrium concentration of the pollutants of interest.

Isotherm tests on the five carbons listed above were conducted to select the best performing carbon for further testing using continuous flow columns. These results indicated that the consistently best performing activated carbon was Witco Witcarb 950. (Note that Witco Chemical Corporation stopped production of all activated carbon in late 1985 [4]). The isotherm tests indicated that equilibrium conditions could be reached at the desired effluent limits (indicated below) given a high enough carbon dosage (i.e., >1,000 mg/L of carbon).

2.2.3 Preliminary column tests. Four explosives compounds of interest were studied in column testing. The point source effluent goals used as performance criteria are shown in Table 2-1.

In addition to initial performance with respect to effluent criteria, significant factors to be considered in the investigation of continuous flow carbon adsorption include the total sorptive capacity of the carbon and the breakthrough characteristics of the components of interest. In the case of multicomponent wastes, competitive adsorption is a factor to be considered. In general, the effective life of the column is determined by the first compound to break through in the effluent.

Preliminary column tests were performed in the laboratory using synthetic pink water to develop design parameters for a pilot-scale multiple column test. To prepare the synthetic pink water, the four nitroaromatics of interest (TNT, RDX, HMX, and 2,4-DNT) were initially dissolved in acetone then diluted so that the resulting acetone level was only 0.20 to 0.44 percent on a volume basis. From these tests, activated carbon was shown to become saturated with RDX and HMX more rapidly than with respect to TNT and DNT. In addition, it was determined that fewer than five columns in series were necessary for optimum performance.

2.2.3.1 Four-in-series column tests. Based on the findings discussed above, pilot-scale column tests were performed with four columns in series using the Witco Witcarb 950 activated carbon for the treatment of actual AAP pink water. The effluent criteria were generally met for RDX, HMX, and 2,4-DNT, but not for TNT. The TNT performance limitation was determined to be a physicochemical phenomenon with little change in TNT concentration beyond the first column in series. This phenomenon did not appear during the isotherm tests and points to the importance of performing actual column tests with the wastewaters to be treated.

2.2.3.2 Effects of pH on adsorption of explosives. The effect of pH on the ability of activated carbon to remove nitroaromatic compounds from a munition-manufacturing waste has been evaluated [3]. Experiments reveal that activated carbon should have a greater reserve capacity for TNT and other nitroaromatics if wastes applied to it are acidic. A comparison of the slopes of the isotherms showed that the adsorption efficiency was greater at pH 2.0 than 7.6. During column tests at a neutral pH, breakthrough of TNT was almost immediate and the carbon was exhausted in less than one-half the time required to exhaust the column used to treat acidic wastes.

TABLE 2-1. POINT SOURCE EFFLUENT GOALS

Nitrobody Compound	Criteria (µg/L)
TNT	40
RDX	30
HMX	30
2,4-DNT	0.7

2.2.4 Carbon regeneration properties. A primary factor in determining the cost effectiveness of activated carbon treatment, assuming effluent criteria can be met with acceptably long carbon bed life, is the extent to which the carbon can be regenerated for reuse. Regeneration of carbon that has been used for adsorption of organics is usually accomplished by a thermal regeneration process. If carbon cannot be effectively regenerated, it must be disposed, possibly as a hazardous waste. Cost effectiveness of carbon adsorption is reduced both by the cost of such disposal and by the continuing replacement cost of virgin carbon.

The process of carbon regeneration for explosives-contaminated carbons has been met with mixed reviews. A report prepared for the U.S. Army Armament Research and Development Command indicates the effectiveness and economic feasibility of using a rotary calciner furnace to thermally regenerate spent carbon containing explosives [6]. Other references show limited success with thermal regeneration due to the explosive nature of adsorption components [7]. In general, the carbon is broken down by the explosive components during regeneration, resulting in carbon losses due to fires and reduced adsorption capacity. It should be noted, however, that activated carbon treatment systems remain in operation for the treatment of pink water without the regeneration capacity. This is due, in all likelihood, to the proven ability of activated carbon to remove the explosive component from wastewater streams.

2.3 Other technologies. Other technologies are reported in the literature for the removal of explosives from wastewater. These include:

- Polymeric adsorption resins.
- UV light with ozonation and hydrogen peroxide.
- Chlorination.
- Activated sludge biological treatment.

These four technologies are briefly described below.

2.3.1 Polymeric adsorption resins. The use of polymeric adsorption resins was shown to be effective in the removal of TNT from a munition wastewater stream; however, nonaromatic nitroaromatics, such as RDX, could not be effectively removed [8]. The polymeric adsorption resins have the desirable benefit of being regenerated in a solvent process. This is in contrast (as indicated in the previous subsection) with the regeneration of the activated carbon, which is unsuccessful. While the use of such a resin for the treatment of explosives-contaminated groundwater may prove effective in the removal of TNT, the resin system would have to be combined with a carbon adsorption system to remove other nitroaromatics.

2.3.2 UV light with ozonation and hydrogen peroxide. As referenced by Semmens, et al.[9], data are available on the destruction of TNT and RDX by ultraviolet light-catalyzed oxidation using ozone and hydrogen peroxide. These processes are reported to be as competitive as activated carbon, with the added advantage of oxidizing the explosives to CO_2 and H_2O , while with carbon, the contaminant is removed from the wastewater but remains on the carbon, which must be regenerated or disposed.

Preliminary tests were conducted to evaluate removal of TNT and RDX by coagulants, ozone, and hydrogen peroxide. The results are as follows:

- When coagulants were added, the volume of sludge increased but no apparent benefit was derived in terms of explosives removal.
- Excessive dosages of ozone and hydrogen peroxide were tested without UV light. TNT was slightly degraded; RDX was unchanged.
- The use of iron-catalyzed hydrogen peroxide (Fentons reagent) also proved unsuccessful.

The UV light, in conjunction with oxidants, was not evaluated by the authors due to limited access to UV light equipment and the reported attenuation of the light by other components in the wastestream. The application of this technology to the treatment of groundwater could be more feasible because it is less likely to contain high concentrations of light-inhibiting components.

2.3.3 Chlorination. Additional tests were conducted by Semmens, et al., on the effectiveness of chlorination in the oxidation of the explosive [9]. Test results show calcium hypochlorite $\text{Ca}(\text{OCL})_2$ preferentially eliminated TNT, and the adjustment of pH to 10.0 by NaOH preferentially removed RDX. While the results indicate the feasibility of removing TNT and RDX from a wastewater by chlorination, the test conditions required elevated pH and temperature and may not be reasonable for application to contaminated groundwater.

2.3.4 Activated sludge. A study [10] prepared for a continuous flow-activated sludge system indicates the wastewater from an AAP facility was treatable. The mode of treatment differed from conventional activated sludge processes in that attached, filamentous microorganisms, rather than suspended, flocculent biomass, were the active biota. The fixed activated sludge process was shown to be an effective method of treatment for a munitions-manufacturing waste containing ethanol, diethyl ether, and dinitrotoluene. However, the emphasis of the study was on BOD removal, as opposed to the removal of the explosives components from the wastewater.

All of these processes may have potential application for treating some explosive wastewaters. Each, also, has certain disadvantages and may require additional preliminary investigation prior to pilot-scale testing for treating groundwater. It was recommended that the pilot study proceed with the investigation of the use of activated carbon for the treatment of explosives-contaminated groundwater.

2.4 Regulatory issues. The Wisconsin Department of Natural Resources (WDNR) has recently formulated interim remedial action limits for groundwater and surface water effluent discharge at the request of BAAP. BAAP plans to use these limits in determining the most cost-effective means of effluent disposal during the treatment/remediation of contaminated groundwater. The following discussion of these effluent requirements is excerpted from a memo by Kathy Cartwright of the Wisconsin DNR [11].

Surface water (Lake Wisconsin) and groundwater (reinfiltration through seepage ponds) effluent disposal were considered since both options are available to BAAP. Determining effluent limits in both cases involved calculating allowable water quality concentrations (according to Sections NR 105, 106, and 207) and comparing to technology-based removal standards. The most restrictive of these standards would then apply. In some cases, where allowable discharge limits have not been promulgated, as is the case with groundwater remedial action, limits were developed using the Best Professional Judgment (BPJ) (according to Section NR 220.2) concept. BPJ limits are based on the Best Available Technology for control of wastewater characteristics. Initial BPJ assumptions included using carbon adsorption (without air stripping) and 99 percent removal efficiency of the groundwater constituents of concern. These considerations are assumed to satisfy BAT requirements. Table 2-2 lists the known groundwater pollutants and the prescribed effluent water quality BPJ limits.

Compliance for certain compounds should be demonstrated by having no detectable limits since instrumentation detection limits are greater than the BPJ limits. For the balance of the listed compounds, BPJ limits would have to be demonstrated. It has not yet been decided whether the BPJ limits are considered daily maximum or monthly average concentrations. These proposed limits, however, as a recommendation from the WDNR, should be used as daily maximums for either groundwater or surface water effluent disposal.

2.4.1 Surface water discharge. In addition to meeting these effluent discharge limits, surface water discharge will require application for a Wisconsin Pollutant Discharge Elimination System (WPDES) permit. The levels of concern for the effluent pollutants as promulgated by such a permit should not be difficult to achieve using the carbon adsorption technology.

TABLE 2-2. KNOWN GROUNDWATER POLLUTANTS AND PRESCRIBED
EFFLUENT WATER QUALITY BPJ LIMITS^a

<u>Compound</u>	<u>Untreated Wastewater</u>	<u>Water Quality Number^b</u>	<u>BPJ Limit</u>
Benzene	N.D. ^c	513 µg/L	N/A ^d
1,1,1-trichloroethane	12 µg/L	121 µg/L	0.12 µg/L
Carbon tetrachloride	22 µg/L	114 µg/L	0.22 µg/L
Chloroform	10 µg/L	319 µg/L	0.1 µg/L
1,2-Dichloroethane	47 µg/L	1,357 µg/L	0.47 µg/L
Methylene Chloride (dichloromethane)	73 µg/L	13.2 µg/L	0.73 µg/L
2,4-Dinitrotoluene	1,515 µg/L	953 µg/L	15 µg/L
2,6-Dinitrotoluene	661 µg/L	N/A ^d	7 µg/L
Trichloroethane	50 µg/L	1,320 µg/L	0.5 µg/L

^aThese limits are from a memo by Kathy Cartwright of Wisconsin DNR to Mark Tuslen and Sue Bangert of Wisconsin DNR [11].

^bCalculated using equation from Section NR106.06, for discharge to Lake Wisconsin, water quality criteria from NR 105, and the antidegradation provisions in NR 207 for waters classified for fish and aquatic life.

^cNot detected.

^dNot available.

It is still advisable that bioassay sampling be conducted prior to permit application and will more than likely be required as part of the final discharge permit. Assuming this remedial activity is a temporary effluent discharge application, additional environmental assessments will not be required.

2.4.2 Groundwater discharge. There are certain limitations imposed upon the scenario for groundwater discharge. Recapturing of the groundwater discharge will be by means of reinfiltration through the seepage ponds. Detectable concentrations (1 ppb maximum detection limit) of 2,4-DNT and 2,6-DNT will not be discharged to the ponds. The drinking water standards of 50 ppt for both these compounds must be strived for when operating the groundwater treatment system. In addition to normal operational sampling schedules and meeting the 1 ppb discharge detection limit for these two compounds, semi-annual testing will be instituted using a lower level of detection. This additional testing will reinforce the operational efficiency of the treatment system. Other sampling/testing requirements may involve bimonthly or monthly monitoring of the groundwater monitoring wells between the infiltration ponds and the boundary wells.

3. ISOTHERM TESTS

3.1 Test program. The isotherm test program's focus was to determine the potential feasibility of activated carbon adsorption for treatment of explosives-contaminated groundwater. This determination was made by adsorption isotherm tests using pulverized samples of GAC.

An isotherm test consists of a series of batch adsorption experiments in which multiple aliquots of wastewater are treated with varying dosages of GAC. The test containers are agitated until equilibrium is established between the liquid phase and the solid phase. The GAC is then filtered out of the solution and the filtrate analyzed to determine the equilibrium concentration (C_e) of the pollutants (or adsorbate) of interest. The data thus obtained are interpreted by comparing the amount of adsorbate adsorbed per unit weight of activated carbon (q_e) to the equilibrium concentration of adsorbate remaining in solution (C_e).

The primary objectives of isotherm testing for the Explosives-Contaminated Groundwater Treatment Pilot study for BAAP were:

- To evaluate the capability of carbon adsorption to remove 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) to levels approaching U.S. Army Biomedical Research and Development Laboratory (USABRDL) criteria. The USABRDL proposed water quality criteria for 2,4-DNT and 2,6-DNT are 0.2 ug/L and 0.007 ug/L, respectively. The detection limits that were employed in the sample analysis for isotherm tests were 0.6 ug/L for 2,4-DNT and 0.55 ug/L for 2,6-DNT. At that time a method to detect 2,4-DNT and 2,6-DNT near the USABRDL criteria had not been developed. Because of these low limits, it was necessary to use relatively high dosages of GAC in the isotherm tests.
- To select the two best performing carbon types, out of the five GACs used in the isotherm tests, for further testing using continuous flow columns. Isotherm tests were conducted with five different GACs, using identical test conditions. The GAC producing the highest q_e values at the C_e values approaching influent concentrations of 2,4-DNT and 2,6-DNT was considered the best performing GAC.

Thus, isotherm tests were conducted in a manner that permitted evaluation of the following two variables for each reference parameter:

- Type of carbon.
- Carbon dosage.

The reference parameters for all carbon isotherm testing were total organic carbon (TOC), 2,4-DNT, and 2,6-DNT.

3.1.1 Procedures. Table 3-1 summarizes the test matrix that was followed in conducting the isotherm tests. A test time of 20 hours and ambient room temperature ($20^{\circ}\text{C} \pm 2^{\circ}\text{C}$) were used. The same groundwater solution was used in all the tests (groundwater from monitor well PBN82-02C at BAAP).

The groundwater samples were aerated for a period of 1 hour and 15 minutes to strip off volatiles present in the groundwater. The pHs of the groundwater samples before aeration were in the range of 7.0 to 7.5. After aeration, the pH of the groundwater samples increased to 8.3 to 8.7. Sulfuric acid (H_2SO_4) was added to the aerated groundwater samples to lower the pH to required levels (7.0/4.0) prior to contacting the groundwater with carbon.

Carbons to be tested were pulverized prior to use in the isotherm tests. This procedure assured that equilibrium conditions would be obtained at a faster rate. Pulverizing carbon has no significant effect on adsorption capacity, but it does increase the rate of adsorption so that laboratory time is not extensive [2].

Glass, 2,000-mL Erlenmeyer flasks, stoppered with rubber stoppers, were used in the isotherm tests. Before each test, the flasks, filtering funnels, sample bottles, and other glassware were washed in laboratory cleaning solution (Alconox) and rinsed with deionized water.

Seven 1,200-mL aliquots of groundwater were used for each isotherm test. Following aeration and pH adjustment of the groundwater samples, preweighed amounts of pulverized granular carbon were added to the aliquots excluding the control sample. The nominal dosages ranged from 10 to 5,000 mg/L solution. The nominal weights of carbon used in each flask ranged from 0.012 to 6 grams.

Temperature and pH readings of the solution were taken at the beginning of the agitation period. The sample containers (Erlenmeyer flasks) were covered to minimize liquid and vapor losses during agitation. A shaker assembly was employed for agitation of the samples for a period of 20 hours.

Following agitation, each sample was vacuum filtered through Whatman No. 5 filter paper into a clean filter flask. The filtered solution was then poured into a labeled sample bottle. The pH was measured in all the filtrate samples and in the control sample.

TABLE 3-1. ISOTHERM TEST MATRIX

20-hr Isotherm Test	Samples	Number of Variables
Isotherm tests to select best-performing GAC	35 ^a	5 GACs 1 temperature 1 solution 7 GAC dosages ^b 1 pH ^c
Isotherm tests to determine effect of pH	5 ^a	1 GAC 1 temperature 1 solution 1 pH ^d 5 GAC dosages ^e

^aEach sample was analyzed for TOC, 2,4-DNT, and 2,6-DNT.

^bSix varying GAC dosages (10, 200, 500, 1,000, 2,500, and 5,000 mg/L) plus one control (no GAC).

^cpH studied was 7.0.

^dpH studied was 4.0.

^eFive varying GAC dosages (10, 200, 500, 2,500, and 5,000 mg/L).

Each filtrate sample was analyzed for the selected parameters, TOC, 2,4-DNT, and 2,6-DNT, according to procedures given in Appendix A of "Use of Activated Carbon for Treatment of Explosives-Contaminated Wastewaters - Test Plan," December 1988 [12]. Each filtrate analysis represents a single point on an isotherm for a given parameter. The control sample (untreated groundwater) was analyzed concurrently for TOC, 2,4-DNT, and 2,6-DNT, and the control sample data were compared with the filtrate (treated sample) analyses to identify the carbon adsorption efficiency.

3.1.2 Carbon selection. Using manufacturers' data and literature references, activated carbon screening was conducted to evaluate and select various carbons for isotherm testing. The following criteria were considered:

- High surface area.
- High pore volume
- High iodine number.
- Low average (mean) particle diameter.
- Low pressure drop (head loss).
- Frequency of use at existing facilities.
- Low cost.
- Manufacturers' recommendations.

The following five carbons were selected for evaluation by isotherm testing based upon these criteria:

- Calgon Filtrasorb 200.
- Calgon Filtrasorb 300.
- Calgon Filtrasorb 400.
- Hydrodarco 3000.
- Hydrodarco 4000.

3.2 Results. The Freundlich adsorption equation $q_e = KC^{1/n}$, where K and $1/n$ are empirical constants, was used in presenting the carbon isotherm test results. Isotherms were developed for 2,4-DNT, 2,6-DNT, and TOC by plotting the adsorption data on logarithmic coordinates as carbon loading (q_e) versus the equilibrium concentration (C_e) of compound remaining in the groundwater sample. The empirical constants of the Freundlich equation for the five test carbon isotherms are presented in Table 3-2. These plots are shown in Figures 3-1 through 3-3.

The carbon loading (q_e) was calculated from the following equation:

$$q_e = X/M = \frac{C_o - C_e}{M}$$

TABLE 3-2. EMPIRICAL CONSTANTS OF FREUNDLICH
ADSORPTION EQUATION FOR FIVE GACs
USING GROUNDWATER FROM MONITOR WELL PBN82-02C^a

Activated Carbon Type	2,4-DNT Isotherms		2,6-DNT Isotherms	
	K ^b	1/n ^c (slope)	K	1/n (slope)
Filtrisorb 200	0.085	0.077	0.03	0.022
Filtrisorb 300	0.075	0.067	0.09	0.086
Filtrisorb 400	(0.9) ^d	(2.72)	0.09	0.086
Hydrodarco 3000	0.02	0.014	0.03	0.029
Hydrodarco 4000	0.2	0.263	0.035	0.024

a $f_e = X/M = KC^{1/n}$

b Intercept of the isotherm plot at $C = 1$.

c Slope of the line within the concentration range of 0.01 - 1.0 mg/L.

d By extrapolation from the maximum equilibrium concentration of 0.06 mg/L (obtained at the lowest carbon dosage of 10 ug/L) to a concentration of 1.0 mg/L.

where:

q_e = Carbon loading, mg compound/mg carbon.

$x = C_0 - C_e$, the amount of compound adsorbed from 1.0 liter solution, mg/L.

C_0 = Initial concentration of compound, mg/L.

C_e = Concentration of compound remaining in solution, mg/L.

M = Carbon dosage, mg/L.

For a given C_e , the greater the q_e value, the better that GAC is in adsorbing a particular compound out of solution [3]. Thus, for the isotherms presented in Figures 3-1 through 3-3, the best performing GAC is identified by the line closest to the top of the isotherm graph.

Another criterion that was used in selecting a carbon type for further evaluation in continuous flow columns was the GAC's capability of achieving the desired effluent levels for each of the nitroaromatics of concern (2,4-DNT and 2,6-DNT).

The data that resulted in an equilibrium concentration less than the detection level are shown in the figures with an arrow pointing to the upper left-hand quadrant of the graph.

3.2.1 2,4-DNT removal. 2,4-DNT isotherms for all five GACs are presented in Figure 3-1. At lower carbon dosages (higher q_e), Hydrodarco 4000 was found to be the best performing GAC as indicated by greater values of q_e in comparison with the other carbon types. Due to an elevated detection limit caused by sample interference, the exact value for the data point corresponding to a carbon dosage of 10 mg/L for Filtrasorb 400 could not be determined. Even though Filtrasorb 400 gave equivalent q_e to that of Hydrodarco 4000, it was not considered so because of this unknown value. Filtrasorb 200 and Filtrasorb 300 were found to yield adsorption capacities at levels lower than that for Hydrodarco 4000. Hydrodarco 3000 gave the lowest adsorption capacity.

At the highest carbon dosage (lowest q_e), Filtrasorb 300 resulted in an equilibrium concentration (C_e) that was less than the detection level of 0.6 ug/L for 2,4-DNT, although the exact value is unknown.

Hydrodarco 4000 yielded the next lower equilibrium concentration (C_e) for 2,4-DNT, of 0.69 ug/L at the highest carbon dosage of 5,000 mg/L.

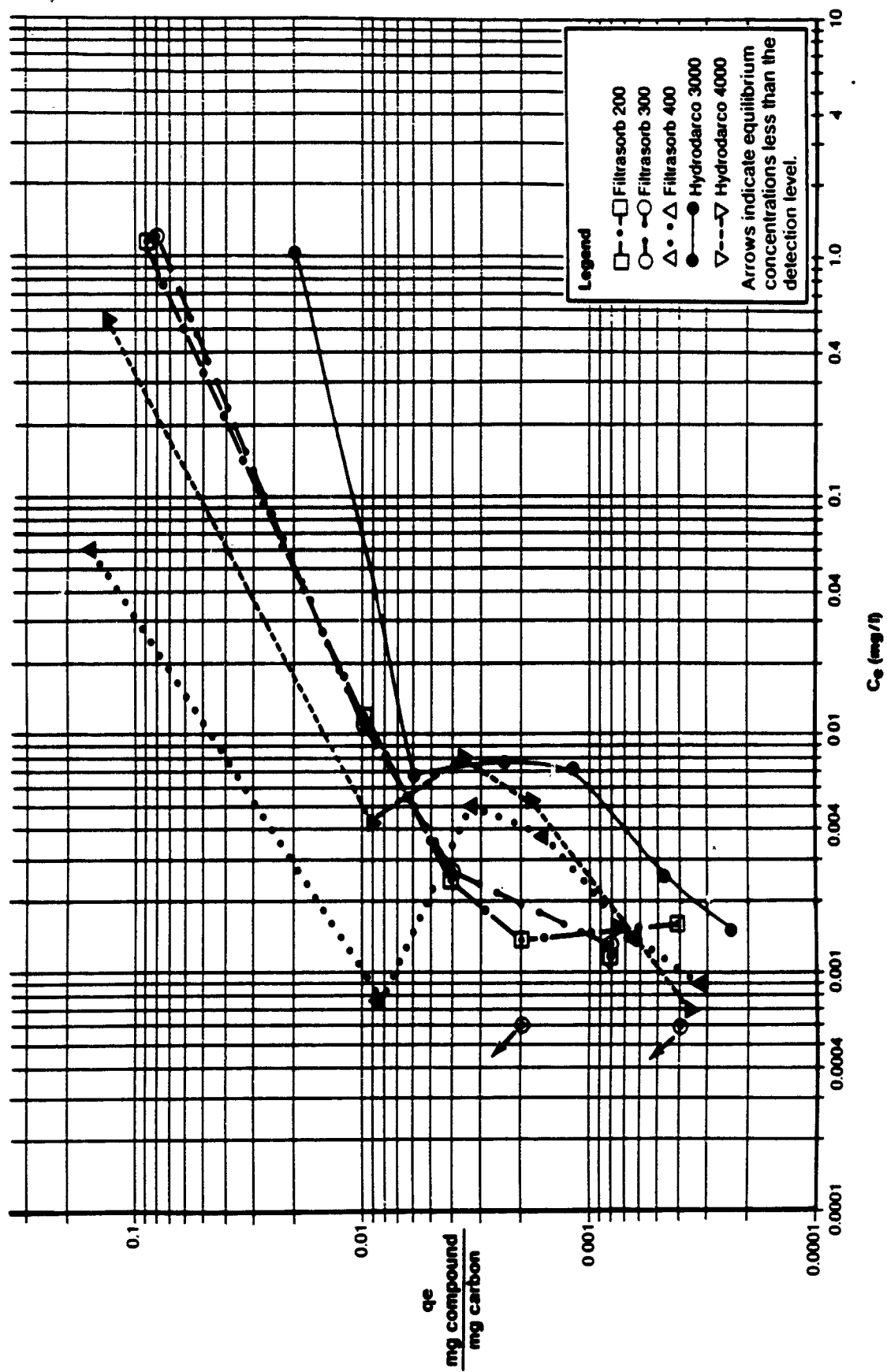


Figure 3-1. 2,4-DNT isotherms for five GACs using groundwater from monitor well PBN82-O2C at BAAP.

An interesting feature of the 2,4-DNT isotherms (Figure 3-1) is that for two carbons (Filtrisorb 400 and Hydrodarco 4000), at intermediate levels of q_e , the equilibrium concentration of 2,4-DNT increased as the carbon dosage increased (or as q_e decreased). This indicates that desorption of 2,4-DNT may be taking place at carbon dosage levels in the range of 200 to 500 mg/L. The slope of the isotherms for Filtrisorb 400 and Hydrodarco 4000, from which the above observation was derived, might have resulted from errors associated with the experiments (such as error in weighing out carbon, etc.) and/or errors in sample analysis. Since 2,4-DNT and 2,6-DNT were measured in the same solution and 2,6-DNT isotherms for all the five carbons, as presented in Figure 3-2, did not indicate the presence of this phenomenon, the possibility of experimental error was ruled out. It was confirmed by WESTON's Analytics Division after checking the analytical procedures and associated calculations that no analytical errors were involved in reporting the data. Competitive adsorption, due to the presence of other compounds in groundwater, may be a factor in causing this phenomenon.

For Filtrisorb 200 and Hydrodarco 3000, the phenomenon (i.e., an increase in equilibrium concentration with an increase in the carbon dosage) was not found to be significant, as seen on Figure 3-1. For Filtrisorb 300, the equilibrium concentration decreased as the carbon dosage was increased within the entire range of 10 to 5,000 mg/L.

These isotherm results indicate that among the five carbon types studied, Filtrisorb 300 and Hydrodarco 4000 were the best performing GACs in adsorbing 2,4-DNT out of solution.

3.2.2 2,6-DNT removal. Figure 3-2 presents 2,6-DNT isotherms for all five GACs used in this experimental program. It is seen from the 2,6-DNT isotherms that for all five GACs the equilibrium concentration (C_e) increased with an increase in the adsorption capacity (q_e) (i.e., with a decrease in the carbon dosage) over the entire carbon dosage range of 10 to 5,000 mg/L employed in the experimental program.

Filtrisorb 300 gave the highest value for adsorption capacity (q_e) followed by Hydrodarco 4000. Due to an elevated detection limit caused by sample interference, the exact value for the data point corresponding to a carbon dosage of 10 mg/L for Filtrisorb 400 could not be determined. Even though Filtrisorb 400 gave equivalent q_e to that of Filtrisorb 300, it was not considered so because of this unknown value. Both Filtrisorb 300 and Hydrodarco 4000, at the highest carbon dosage (5,000 mg/L), gave an equilibrium concentration (C_e) lower than the detection level of 0.55 ug/L for 2,6-DNT, although the exact value was not known.

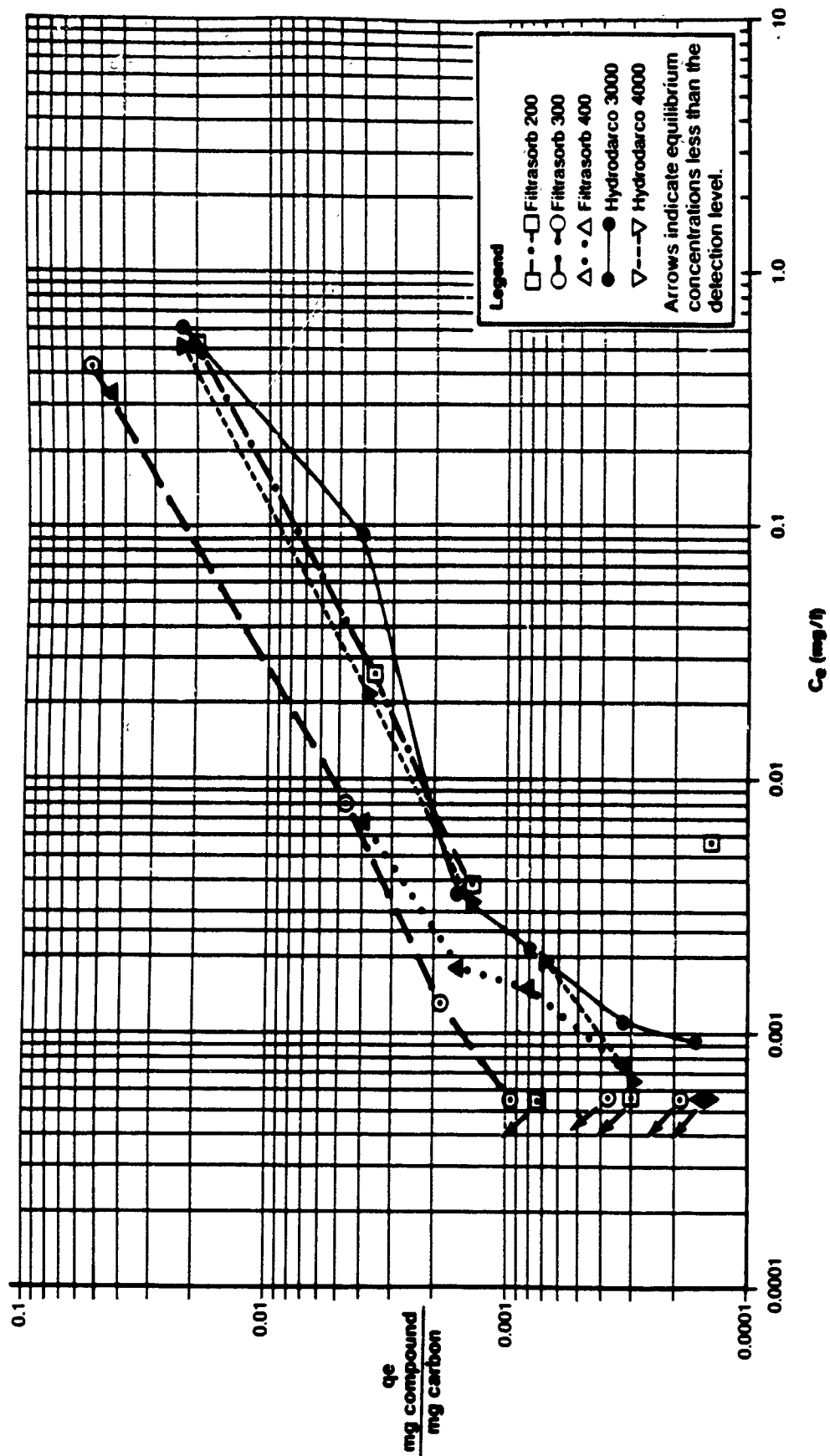


Figure 3-2. 2,6-DNT isotherms for five GACs using groundwater from monitor well PBN82-02C at BAAP.

It was therefore concluded that Filtrasorb 300 and Hydrodarco 4000 were the best performing GACs for adsorbing 2,6-DNT out the groundwater from well PBN82-02C at BAAP.

3.2.3 TOC removal. Figure 3-3 presents TOC isotherms for all five GACs used in this experimental program. It is seen from Figure 3-3 that within the range of carbon dosages used in the isotherm tests, an equilibrium concentration (C_e) around 1 mg/L for TOC was achieved for all five GACs. The average TOC concentration in the untreated groundwater sample was 3 mg/L. The presence of nonadsorbable compounds in the groundwater sample is indicated by the vertical line portions of the TOC isotherms for all five carbons. Because of the sensitivity of the TOC analysis at the low concentrations (1 to 3 mg/L) encountered in this experimental program, it is not possible to conclude with confidence that nonadsorbable compounds were present in the groundwater sample. The results indicate that, for groundwater from monitor well PBN82-02C located at BAAP, TOC reduction below 1 mg/L by activated carbon adsorption treatment system may not be possible.

3.2.4 pH effects. From 2,4-DNT and 2,6-DNT isotherms for Filtrasorb 400, presented in Figures 3-4 and 3-5, it is seen that at higher carbon dosage levels shifts in q_e due to pH variation (from 7.0 to 4.0) were quite small. However this conclusion regarding the effect of pH on Filtrasorb 400 performance in adsorbing 2,4-DNT (Figure 3-4) may not be valid because of a questionable data point, due to sample interference, corresponding to a carbon dosage of 10 mg/L.

However, the results do indicate that for both 2,4-DNT and 2,6-DNT at low levels of carbon dosage better performance (higher q_e) was achieved as pH increased from 4.0 to 7.0.

From TOC isotherms (Figure 3-6) it is seen that relatively higher adsorption capacities for TOC were achieved at pH $\approx$ 4.0 as compared to those at neutral pH (7.0). However, because of the sensitivity of the TOC analysis at low concentrations, it is not possible to conclude with confidence the pH effects on Filtrasorb 400 performance in adsorbing TOC.

3.3 Carbon selection. On the basis of adsorption capacities for 2,4-DNT and 2,6-DNT, Filtrasorb 300 and Hydrodarco 4000 were found to be the best performing GACs for removing both contaminants from groundwater from monitor well PBN82-02C at BAAP. The maximum saturation capacities (theoretical maximum loading) for Filtrasorb 300 and Hydrodarco 4000 were estimated by extrapolating the isotherms to $(q_e)C_0$. The carbon loading thus obtained by definition corresponds to a condition when all the carbon is in equilibrium with the influent concentration (C_0). In a carbon column treatment system, this equates to operating a GAC system until the concentration of a particular

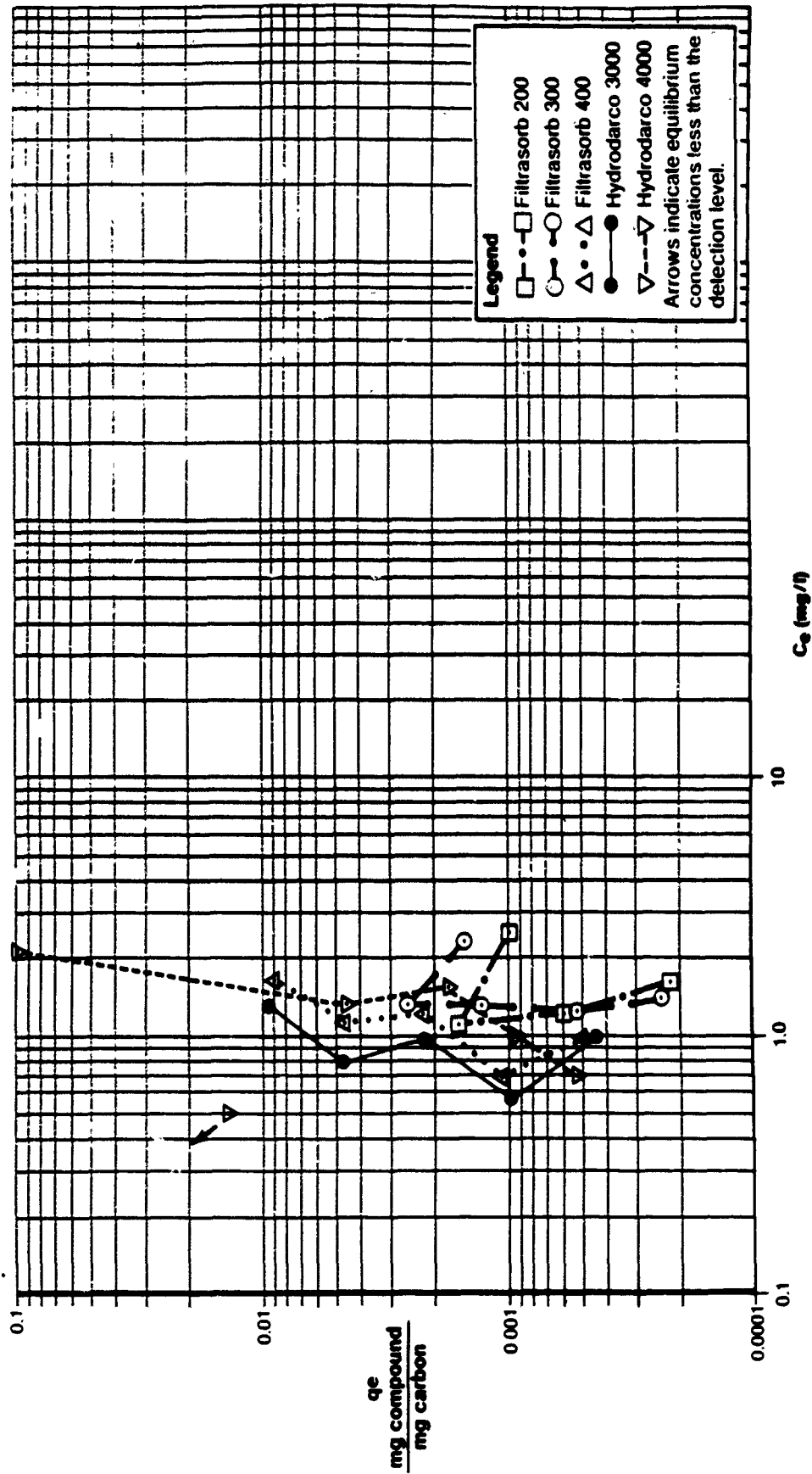


Figure 3-3. TOC isotherms for five GACs using groundwater from monitor well PBN82-O2C at BAAP.

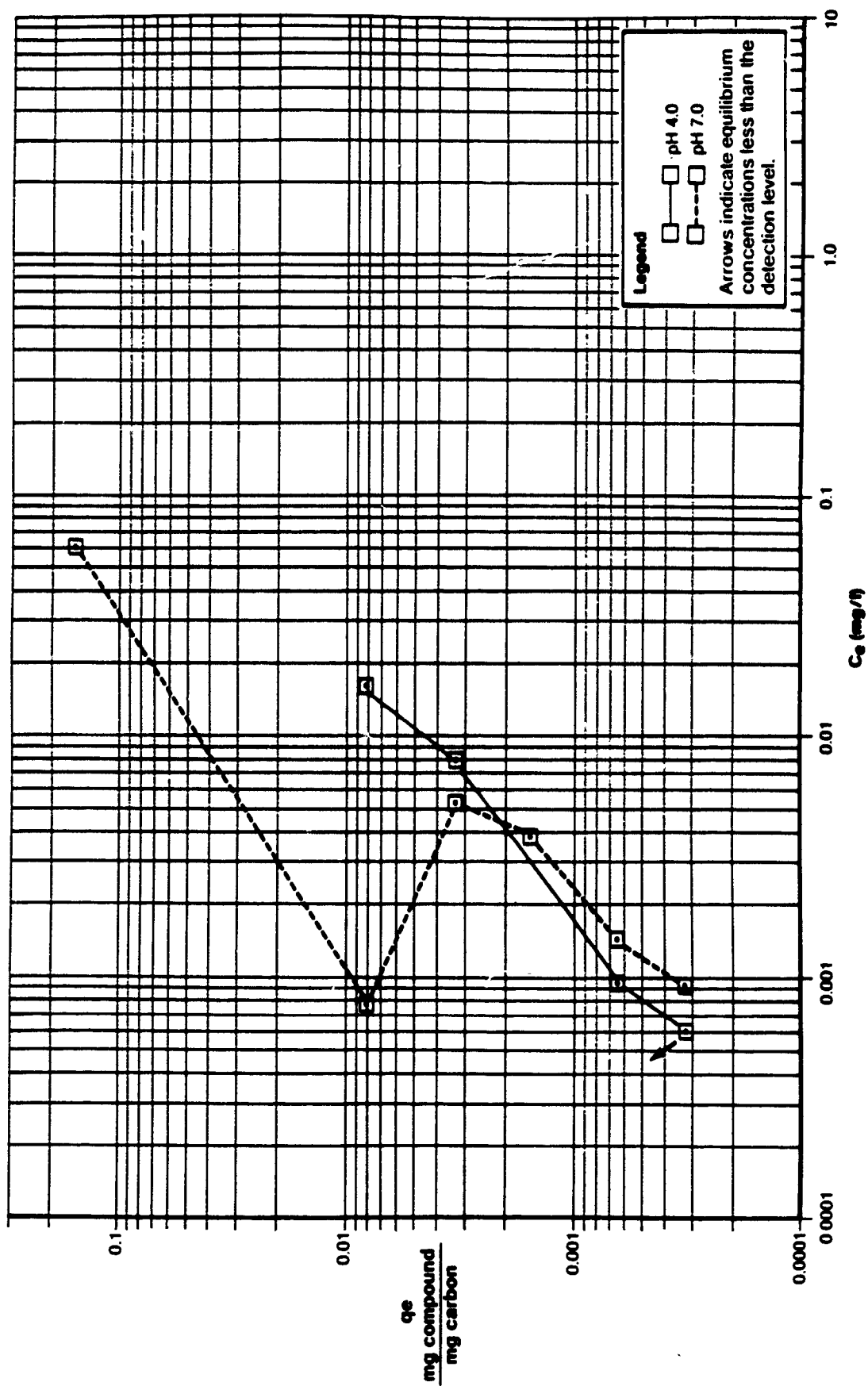


Figure 3-4. Filtrasorb 400 isotherms showing effects of varying pH on 2,4 DNT removal using groundwater from monitor well PBNs2-O2C at BAAP.

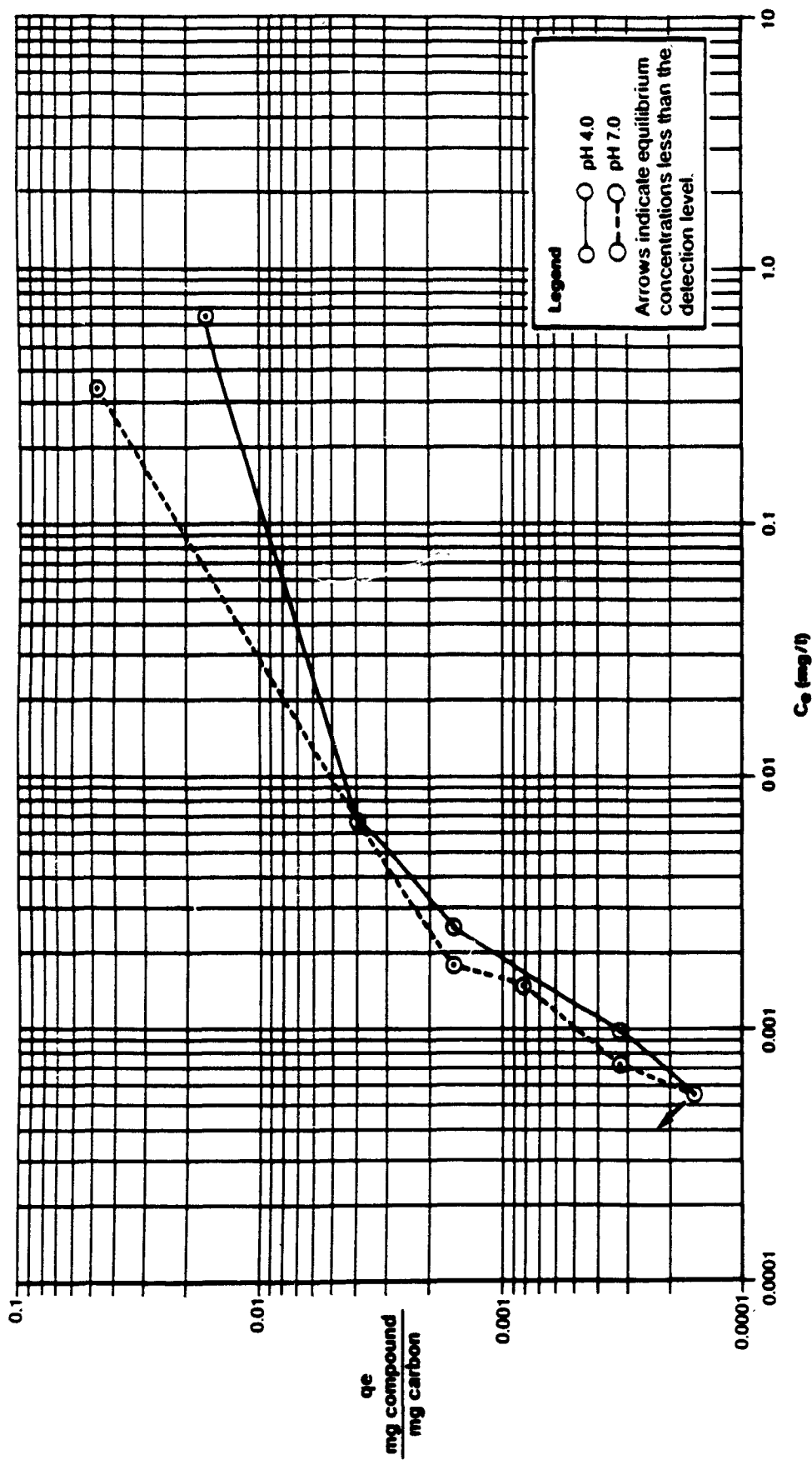


Figure 3-5. Filtrosorb 400 isotherms showing effects of varying pH on 2,6 DNT removal using groundwater from monitor well PBN82-02C at BAAP.

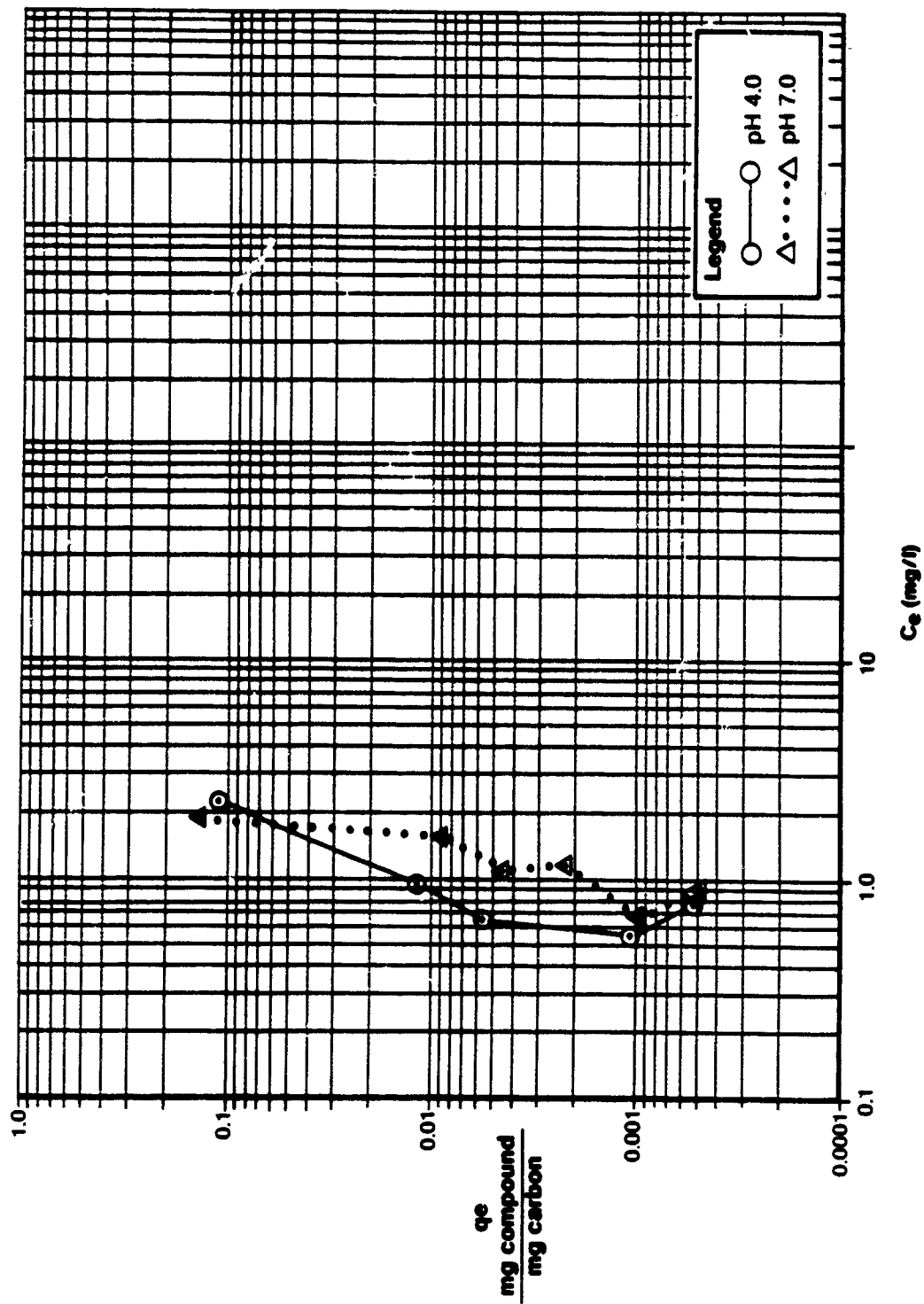


Figure 3-6. Filtrasorb 400 isotherms showing effects of varying pH on TOC removal using groundwater from monitor well PBN82-O2C at BAAP.

compound at the column effluent equals the influent concentration. In actual operation, this is usually not achieved because the column service is terminated when the effluent concentration reaches a predetermined effluent limit. The q_e values representing maximum saturation capacities (where $C_e = C_o$) at different influent concentrations of 2,4-DNT and 2,6-DNT for the five GACs are presented in Table 3-3.

In addition to yielding the greatest adsorption capacities, Filtrasorb 300 and Hydrodarco 4000 appear to give the lowest effluent levels for 2,4-DNT and 2,6-DNT. Because these two carbons, at the highest dosage, resulted in equilibrium concentrations (C_e) that were less than the detection limit, it was postulated that Filtrasorb 300 and Hydrodarco 4000 may have the potential for achieving the desired effluent levels for 2,4-DNT and 2,6-DNT.

Based on literature reports [4], relatively greater adsorption capacities at acidic pH conditions, for TNT and other nitroaromatics, were expected. However, the results of the isotherm tests for Filtrasorb 400 conducted with explosives-contaminated groundwater from monitoring well PBN82-02C located at BAAP indicate that relatively higher adsorption capacities were obtained at neutral pH (7.0) as compared to those at acidic pH (4.0). The conclusion reached here regarding the effects of pH on adsorption capacity of GAC for 2,4-DNT and 2,6-DNT is specific to Calgon Filtrasorb 400 GAC and to groundwater from monitoring well PBN82-02C located at BAAP. Because the data obtained in this experimental program are limited to a specific carbon type and to a site-specific groundwater, it is not possible to conclude with confidence the pH effects on the performance of other carbon types in removing explosives other than 2,4-DNT and 2,6-DNT from groundwater.

As a result of this isotherm testing program, Filtrasorb 300 and Hydrodarco 4000 were selected for further testing, using continuous flow GAC columns at BAAP.

TABLE 3-3. MAXIMUM SATURATION CAPACITIES (q_e) FOR FIVE GACs

Carbon Type	Nitrobody	Influent Concentration C_0 (mg/L) ^a	Saturation Capacity (q_e) (mg/mg)
Filtrisorb 300	2,4-DNT	2	0.1
		10	0.21
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 4000	2,4-DNT	2	0.28
		10	0.62
	2,6-DNT	1	0.03
		4	0.07
Filtrisorb 200	2,4-DNT	2	0.10
		10	0.22
	2,6-DNT	1	0.03
		4	0.06
Filtrisorb 400	2,4-DNT	2	-- ^b
		10	-- ^b
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 3000	2,4-DNT	2	0.02
		10	0.03
	2,6-DNT	1	0.03
		4	0.12

^aInfluent concentrations correspond to those reported in the Test Plan (10 mg/L for 2,4-DNT and 4 mg/L for 2,6-DNT) and to those found in the groundwater sample used for isotherm tests reported here (2 mg/L for 2,4-DNT and 1 mg/L for 2,6-DNT).

^bDue to an elevated detection limit caused by sample interference, the exact value for the data point corresponding to this carbon dosage could not be determined.

4. TEST PROGRAM AT BAAP

The test program's focus was to determine the potential feasibility of using activated carbon adsorption for treatment of explosives-contaminated groundwater based on pilot-scale testing. An air stripper was used to remove solvents from the groundwater prior to its entering the GAC pilot plant. The primary function of the air stripper in this project was to minimize any effects of these solvents on the evaluation of activated carbon adsorption of explosives. The air stripper was designed to provide approximately 99 percent removal of identified volatile components from the groundwater. After passing through the air stripper, the groundwater was passed through the continuous flow GAC pilot plant unit. The primary function of the GAC unit was to evaluate its effectiveness for removing explosives from groundwater. The planned test program and actual test programs for these units are discussed in the following subsections.

4.1 Air stripper test program. A diagram of the air stripper, showing exhaust gas sampling locations, is presented in Figure 4-1. The exhaust gas ductwork was configured so as to permit the air stripper to be installed, operated, and tested entirely indoors. The exhaust was routed out of the building through an existing exhaust roof vent in the building. As shown in Figure 4-1, the ductwork on the final vertical leg prior to sampling was expanded from 4 inches in diameter to 8 inches in diameter. This expanded section was used as the sampling location during the air stripper exhaust gas testing program (see Table 4-1). The expansion was necessary to accommodate the selected air sampling methodology. Sampling points were located approximately 6 feet above (downstream from) the expansion point in order to eliminate any effects of flow disturbances caused by the expansion. The location of the sampling ports was chosen to facilitate sampling activities.

4.1.1 Description of planned test program. The objective of this test program was to examine the potential for discharge of explosive components (2,4-DNT and 2,6-DNT) from an air stripper used to treat groundwater containing both explosives and volatile organic components. Monitor well PBN82-02C at BAAP was the source of groundwater for this study.

Samples from the exhaust stack were to be analyzed for explosives components (2,4-DNT and 2,6-DNT). The adequacy with which the air stripper removed volatiles was to be verified by comparing GAC pilot-plant influent levels to those in the untreated groundwater.

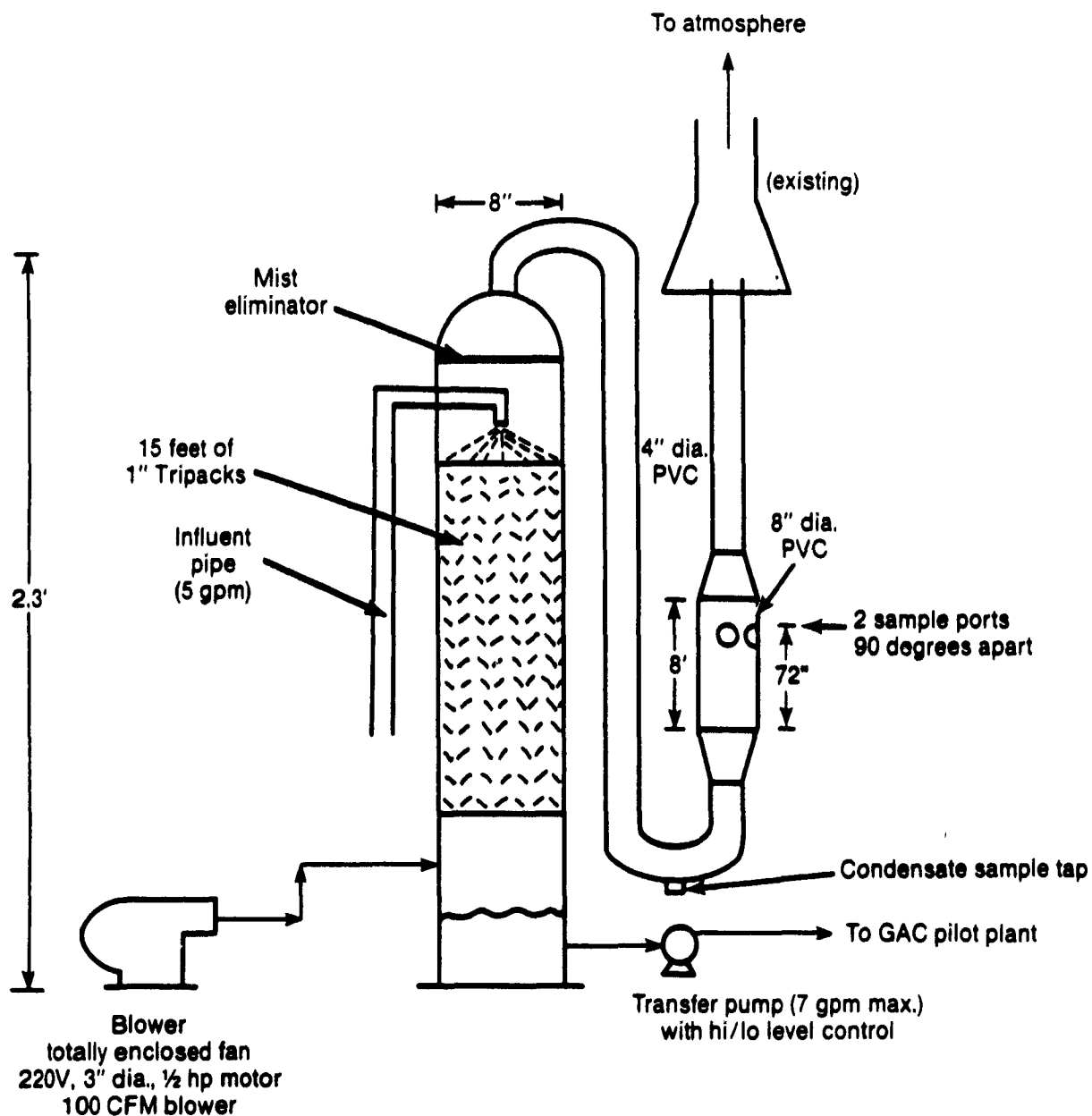


Figure 4-1. Schematic of air stripper system employed at BAAP.

TABLE 4-1. AIR STRIPPER EMISSIONS TEST PLAN

Test Parameter	Sampling Method	Analytical Method	Detection Limit
2,4-DNT, 2,6-DNT	EPA Modified Method 5	High Performance Liquid Chromato- graphy (HPLC)	1 $\mu\text{g}/\text{m}^3$
Volumetric Flow Rate	EPA Methods 1,2	NA	NA
Moisture Content	EPA Modified Method 5	NA	0.1 percent

4.1.1.1 Description of planned test methods.

4.1.1.1.1 Modified Method 5 sampling train. Explosives were to be collected from the air stripper exhaust duct using an EPA Modified Method 5 (MM5) sampling train. The air stripper exhaust was sampled at the location illustrated in Figure 4-1, in a straight section of 8-inch diameter PVC duct. The two sample ports were located 90 degrees apart, approximately 6 feet above (downstream from) the beginning of the 8-inch duct section. A schematic of the sample train is shown in Figure 4-2. The EPA Modified Method 5 sampling train consists of the following components:

- A 316 stainless steel nozzle with an inside diameter sized to sample isokinetically.
- A heated, borosilicate-lined probe, equipped with a thermocouple to measure flue gas temperature and an S-type pitot tube to measure flue gas velocity pressure.
- A heated oven containing a borosilicate filter holder with a 90-millimeter Reeve Angel 934 AH glass fiber filter. A thermocouple was inserted in the filter box chamber.
- An impinger train consisting of a Graham (spiral) type ice water cooled condenser; two ice water jacketed sorbent modules, each containing approximately 40 g of 30/60 mesh XAD-2 (pre-extracted); temperature sensors (thermocouples); a 1-L condensate trap; two standard Greenberg-Smith impingers, each containing 100 mL distilled water (HPLC grade); and a final impinger containing 300 g of dry, preweighed silica gel plus a thermocouple to detect sample gas exit temperature.
- A vacuum line (umbilical cord) to connect the outlet of the impinger train to a control module.
- A control module containing a 3 cubic foot per minute (cfm) carbon vane vacuum pump (sample gas mover), a calibrated dry gas meter (sample gas volume measurement device), a calibrated orifice (sample gas flow rate monitor), and inclined manometers (orifice and gas stream pressure indicators).
- A switchable calibrated digital pyrometer to monitor flue and sample gas temperatures.

Note that the train was further modified by the inclusion of an additional XAD-2 resin trap (a total of two) to assure complete collection of target explosives. Sampling was con-

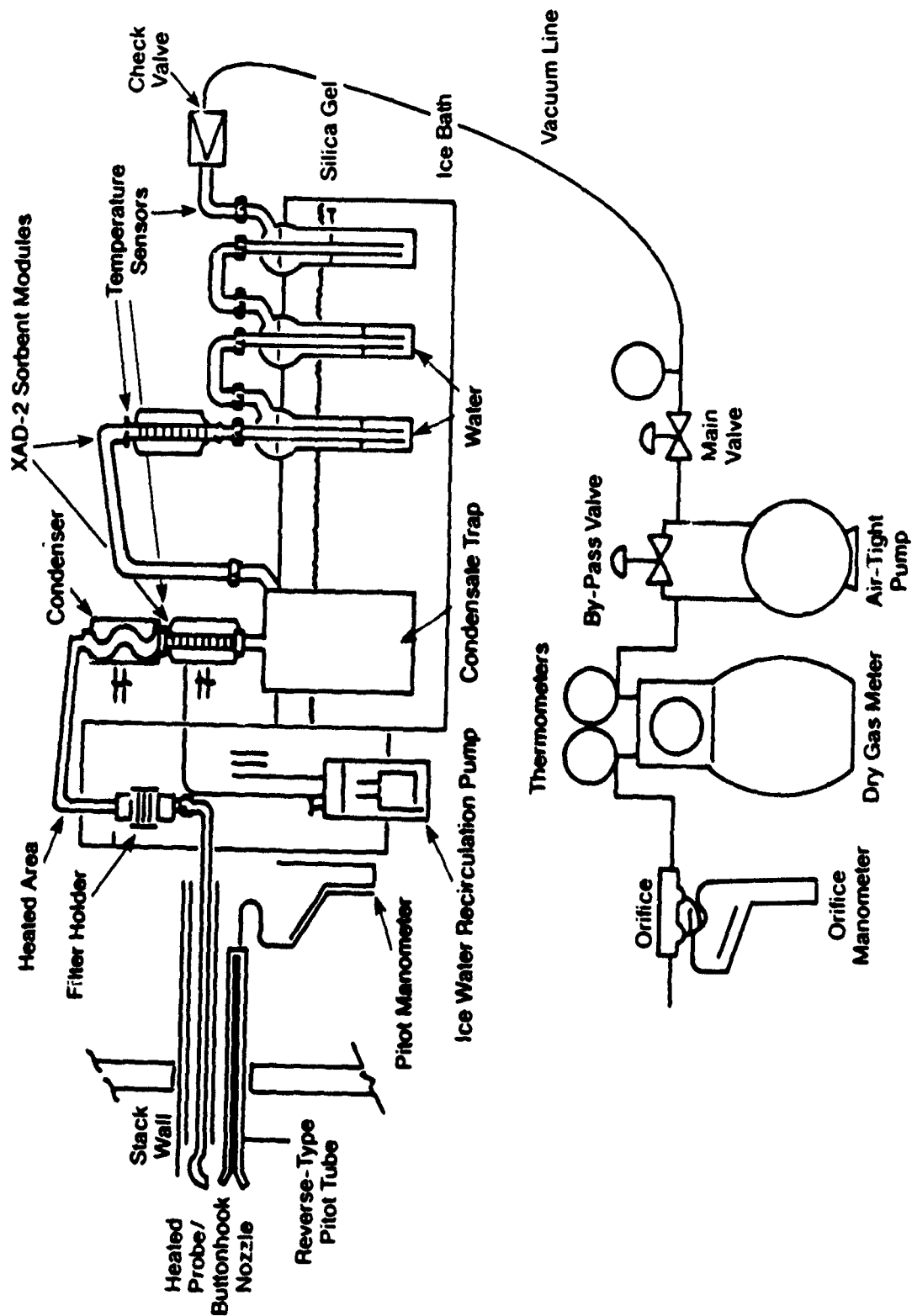


Figure 4-2. EPA Modified Method 5 sampling train for collection of explosives.

ducted along the horizontal axis of the 8-inch inner diameter duct. The number of sample points and the sampling duration were determined onsite, with a 4-hour sample time anticipated at four traverse points. Sampling was to be isokinetic (90 to 110 percent).

Volumetric flow rate was determined by EPA Methods 1 and 2 as part of the MM5 train. Moisture content was determined using the EPA MM5 sample train used for collection of explosives (one sample per train; three trains total).

4.1.1.2 Test procedures.

4.1.1.2.1 Preliminary tests. Preliminary test data, including temperature and exhaust gas flow rate (gas velocity measurements) at the sampling location, were obtained prior to collection of any air samples. Stack or duct geometry measurements were recorded and traverse point distances calculated. A preliminary velocity traverse was performed at the test location to determine velocity profiles using a calibrated S-type pitot tube and a Dwyer inclined manometer. This sampling location was after the packed column, in the 8-inch-diameter PVC duct section (Figure 4-1).

Exhaust stack gas temperatures were measured with a calibrated direct readout pyrometer equipped with a chromel-alumel thermocouple. Water vapor content was to be measured by a wet bulb-dry bulb thermometer or by an EPA Method 4 moisture train.

The size of the nozzle for the EPA MM5 probe was to be determined onsite during preliminary testing after measuring the gas velocity at the sampling location. Selection and use of the proper nozzle size is important to ensure that isokinetic sampling occurs.

Calibration of sampling nozzles, pitot tubes, metering systems, thermocouples/pyrometers, and temperature gauges were to be performed as specified in Section 5 of EPA Method 5 test procedures.

4.1.1.2.2 Formal tests. Triplicate test repetitions were performed for each emission parameter.

4.1.1.2.3 Modified Method 5 test for semivolatile organics (explosives). A series of three test repetitions was to be performed at the stack under normal process operating conditions. Process operating conditions were monitored for each test.

During MM5 sampling, gas stream velocities were measured by inserting a calibrated S-type pitot tube into the gas stream

adjacent to the sampling nozzle. The velocity pressure differential was observed immediately after positioning the nozzle at each point, and the sampling rate was adjusted to maintain isokineticity. The air stripper was operated at ambient temperature (minimum 50°F in the test area). Temperature measurements in the stack and of the MM5 sampling train were recorded periodically (every 5 minutes) during the testing in accordance with EPA procedures. These measurements were used to calculate or correct for standard gas conditions and ensure that MM5 sampling procedures were met. Stack gas temperature was monitored at each point with a pyrometer and thermocouple. Temperature readings of the filter box exit, sorbent module exit, final impinger, and dry test meter gas streams were recorded. Test data were to be recorded at each traverse point during all test periods.

Gas stream composition was determined using an Orsat apparatus. A minimum of three grab samples was taken and analyzed for carbon dioxide and oxygen content during the first test to verify ambient concentrations.

Leak checks were performed according to EPA Method 5 instructions prior to and after each run or component change.

4.1.1.3 Sample recovery and analytical procedures.

4.1.1.3.1 Sample recovery procedures for explosives (MM5 train). At the conclusion of each test, the sampling train was dismantled, the openings sealed, and the components transported to the field laboratory.

A consistent procedure was to be employed for sample recovery:

1. The aluminum foil covered, sealed XAD-2 resin tubes were labeled (sample type 1).
2. The glass fiber filter was removed from its holder with tweezers and placed in its original container (glass petri dish) along with any loose particulates and filter fragments (sample type 2).
3. The particulate adhering to the internal surfaces of the nozzle, probe, and front half of the filter was rinsed with solvent into a borosilicate container while brushing a minimum of three times until no visible particulate remained. Particulate adhering to the brush was rinsed into the same container. The container was sealed with a teflon-lined closure (sample type 3).

4. The volume of liquid collected in the condensate trap was measured to the nearest mL, the value recorded, and the contents poured into a glass sample bottle along with a rinse of the back half of the filter holder, connectors, condenser coil, and condenser trap. The sample container was capped with a teflon-lined closure and the liquid level marked (sample type 4). The train components in the aforementioned step were washed with solvent and the rinses placed in a borosilicate container with a teflon-lined closure. The liquid level was marked (sample type 5).
5. The volume of the liquid in impingers one and two was measured to the nearest mL, the values recorded, and the contents placed in glass sample bottles. Solvent rinses of each impinger and connector were added to the respective impinger contents sample container. The sample bottles were sealed with a teflon-lined closure and the liquid levels marked.
6. The silica gel in the third and final impinger was weighed (and the weight gain value recorded).
7. A single blank train identical to that used for sampling was assembled and transported with the sampling train to the test location and maintained there during the test period. Recovery of the blank sampling train was conducted in the same manner as, and at the same time as, that for the stack test train.
8. Each sample container was labeled to clearly identify its contents. The height of the fluid level was marked on the container of each sample to provide a reference point for a leakage check after transport. All samples were placed in a locked shipping crate, then transported to the WESTON laboratory for analysis.

4.1.1.3.2 Analytical procedures for explosives. Following receipt of the samples at WESTON's laboratories, components of each individual source sample were combined and extracted. The blank train was to be treated in a similar manner.

Samples were to be analyzed using high performance liquid chromatography (HPLC). WESTON's Analytics Division is currently USATHAMA-certified for analysis of explosives in soil and water.

4.1.2 Actual test program. This test program was carried out as planned to examine the potential for discharge of explosive compounds such as 2,4-DNT and 2,6-DNT from an air stripper used to treat groundwater containing both explosives and volatile organic compounds.

Samples from the air stripper stack were analyzed for explosive components (2,4-DNT and 2,6-DNT). These results are presented in Section 5. The efficiency of the air stripper to remove volatile organic compounds was determined by comparing the concentrations in GAC pilot-plant effluent to those in the groundwater feed.

4.1.3 Variance analysis. The primary goals of the test program were:

- Analyze the air stripper stack gas for explosives.
- Determine the adequacy with which the air stripper removes volatile organics from groundwater.

All procedures for sampling and analysis were followed during the test program and the goals set forth in Subsection 4.1 were met. As such, there are no significant variations between the planned test program and the actual test program which was carried out.

4.2 Activated carbon. The primary goal of this project was to evaluate granular-activated carbon to treat groundwater contaminated with explosives. This goal was pursued through a combination of batch (isotherm) testing and continuous flow pilot plant testing.

Batch (isotherm) testing was discussed in Section 3 of this report. The continuous flow pilot plant testing is discussed below. The intended test program is presented in Subsection 4.2.1. Field conditions necessitated several changes to the intended program. The actual test program as implemented is presented in Subsection 4.2.2. Variances between the planned and actual testing are discussed in Subsection 4.2.3.

4.2.1 Description of planned test program. The continuous flow column testing was to be conducted using the two types of carbons selected from the batch (isotherm) testing. The primary objectives of performing GAC groundwater treatment pilot plant tests at BAAP were:

- To determine if GAC technology can treat 2,4-DNT and 2,6-DNT to USABRDL criteria (0.2 ug/L 2,4-DNT and 0.007 ug/L 2,6-DNT).
- To select the best carbon out of the two GACs based on their relative rates of adsorption.

The test conditions, experimental variables, operational monitoring, and evaluation criteria for the test program are presented in the following subsections.

4.2.1.1 Test conditions and experimental variables. A total of four test runs was originally planned. Three of these runs were to be conducted using air stripper effluent as the feed to the GAC system. The fourth run was to use contaminated groundwater with the air stripper being bypassed. This run would evaluate the effects of volatiles on the adsorption of explosives.

The planned test conditions for all four column tests are summarized in Table 4-2. For each test, a total flow rate of 1.0 gpm was to be employed. The total flow was to be split between the two test trains (A and B) at different proportions depending on the required hydraulic loading rates. The two columns in Train A and Train B were to contain carbon types A and B, respectively.

All the tests were to be conducted at ambient temperatures in the pilot-test area located in Building 6874-1. The test area was to be maintained at a minimum temperature of 50°F. Monitor well PBN82-02C was the groundwater source for this study.

The hydraulic surface loading rates that were to be employed during the pilot tests were 3, 5, and 7 gpm/ft². These values are within the range of hydraulic surface loading rates that are normally used in full-scale operation of GAC systems. DNT isotherms reported in an earlier study by USATHAMA indicated a carbon capacity of 0.02 lb DNT/lb carbon [4]. Based upon this carbon capacity, a bed volume of 0.4 ft³ (bed depth 4 ft), carbon density of 29 lb/ft³, anticipated influent concentration (2,4-DNT + 2,6-DNT) of 13.8 mg/L (based upon previous USATHAMA data [1]), and influent flow rate of 0.5 gpm, each test was expected to require approximately 66 hours before the carbon bed in the first column became exhausted. For planning purposes, a run length of 66 hours was used. The estimated run lengths at flow rates of 0.3 and 0.7 gpm were 110 and 47 hours, respectively.

Adsorption and breakthrough characteristics were to be studied in the first column of each parallel pair. The function of the second column was to maintain effluent (discharge) quality within acceptable limits while allowing contaminant leakage up to influent levels (total exhaustion of capacity) of the first column. Therefore, during the planned pilot testing the two columns within each train were not to be switched around as the first column (lead) reached exhaustion. The exhausted carbon in the first column was to be replaced with fresh carbon and put back for service as the lead column. This mode of operation was to ensure that fresh carbon was used for all the test runs.

4.2.1.2 Operational monitoring. Effluent samples from the first column of each train were to be taken at regular time intervals as per the sampling program described in the test

TABLE 4-2. PLANNED EXPERIMENTAL CONDITIONS FOR CONTINUOUS FLOW PILOT TESTS

Test	Train	Carbon Type	Flow Rate (gpm)	Hydraulic Loading (gpm/ft ²)	Bed Depth (ft)	Contact Time (min)	Influent
1	A	A	0.5	5	4	6	Air stripper effluent
	B	B	0.5	5	4	6	
2	A	A	0.7	7	4	4.3	Air stripper effluent
	B	B	0.3	3	4	10	
3	A	A	0.3	3	4	10	Air stripper effluent
	B	B	0.7	7	4	4.3	
4	A	A	0.5	5	4	6	Contaminated groundwater (air stripper bypassed)
	B	B	0.5	5	4	6	

plan [12]. Feed samples were to be collected at different times during each test run but less frequently than effluent samples. Additional feed samples were to be taken when additional groundwater was added to the feed tank.

Samples were to be taken at the outlet of the second column, as necessary, to ensure that the effluent from the pilot plant does not exceed the effluent discharge guidelines. The carbon in the second column was to be replaced with fresh carbon. This was to be done at the same time as the first column.

Flow measurements as indicated by the flow meters at the inlet to each column were to be recorded at regular time intervals during each test run. Influent and effluent (first column as well as second column) were to be monitored for pH and temperature at regular time intervals and logged in data sheets. Inlet pressure and outlet pressure at each column were to be monitored by means of pressure gauges mounted on the column. This information was intended to give an indication of pressure drop across each column and was necessary in determining when the columns must be cleaned by backwashing.

4.2.1.3 Evaluation criteria. The performance of the two carbons that were used in the continuous flow pilot testing was to be compared on the basis of adsorption rate and adsorption capacity under the same flow conditions. For this purpose, the analytical data gathered during pilot test runs were to be used in plotting the breakthrough curves. The concentration of the adsorbable substance (2,4-DNT or 2,6-DNT) in the column effluent was to be plotted as the ordinate against the volume of water treated as the abscissa.

These breakthrough curves were to be plotted for each contaminant of concern (2,4-DNT and 2,6-DNT) and for each hydraulic loading rate (3, 5, and 7 gpm/ft²). As mentioned previously, the slope of the breakthrough curves would determine the adsorption rate and the service life of a particular carbon. The carbon with the steepest breakthrough curve would have the longest service life.

The carbon exhaustion rates in terms of pounds of carbon per 1,000 gallons of wastewater were to be calculated from the breakthrough curves based upon the cumulative volume at which the contaminant concentration exceeds its effluent objective concentration and based on the additive weight of carbon contacted. The carbon exhaustion rates for each constituent were to be plotted as a function of contact time (hydraulic loading rate). This curve was to be used to evaluate the economic balance between contact time for a single fixed bed, which translates into capital cost, and carbon exhaustion rate, which translates into direct operating expense [13]. This type of evaluation was to be carried out for both carbons.

For test run four (in which the air stripper was to be bypassed), the contaminated groundwater containing volatile organics and explosives was to be directly fed to the pilot plant. Because of the presence of different organic species (explosives and volatile organics) with different adsorbabilities in the groundwater, competitive adsorption may take place on the GAC bed. The quantitative analysis of breakthrough curves, in this case, may not be possible. However, the breakthrough curves for each contaminant would give an indication as to the adsorbability of that particular component in the presence of other components. The impact of the presence of volatile organics on GAC adsorption system performance in removing 2,4-DNT and 2,6-DNT to USABRDL criteria was to be qualitatively evaluated.

4.2.2 Actual test program. During the field test program conducted at BAAP, two continuous flow column tests were performed, each using two carbon column trains. These test runs will be described in the following subsections. Variance between this program and that planned are discussed in Subsection 4.2.3.

4.2.2.1 Continuous flow column test conditions for run one. In run one the groundwater flow rates for columns A1 and B1 were 0.5 gallon per minute (gpm) each. Columns A1 and A2 contained Calgon Filtrasorb 300 carbon while columns B1 and B2 contained Hydrodarco 4000 carbon. For the duration of this test the influent groundwater stream was split to maintain 0.5 gpm through each of the primary columns A1 and B1.

Run one started with the influent water being fed to the air stripper at approximately 1 gpm. The air stripper effluent groundwater was sent to the GAC column feed tank. The system was operated under these conditions for 12 hours to establish a 2-foot working volume in the feed tank before beginning to feed groundwater through the GAC columns. The feed to the GAC columns was started when a 26-inch water level was achieved in the GAC feed tank. The system was operated under these conditions for approximately 35 hours. During this time the GAC feed tank water level began dropping at a rate of approximately 0.5 inch per hour. The air stripper feed rate could not be maintained above 1 gpm. The air stripper manufacturer was contacted to see if they could rectify this problem. The problem was thought to be the large pressure drop created by the nozzle in the air stripper. A new nozzle with a smaller pressure drop was recommended, but this could not be implemented without shutting down the system (which would affect the test run). Therefore, a decision was made between WESTON and USATHAMA to bypass the air stripper in order to increase the GAC feed tank level as needed for the remainder of run one. This bypassing of the air stripper was performed as needed throughout the duration of run one in order to maintain an adequate supply of water in the GAC feed tanks.

The need to periodically bypass the air stripper would result in the presence of volatile components in the feed to the GAC unit. The actual concentrations of volatiles in the GAC feed would depend upon the relative proportions of air-stripped and raw groundwater in the GAC feed tank at any particular time.

Prior to bypassing the air stripper for the first time VOA (volatile organic analysis) samples were taken from the GAC columns influent. In an attempt to compare the influent results before bypassing the air stripper to after the air stripper had been bypassed, VOA samples were taken from the GAC columns influent. The results of this analysis were inconclusive (see Subsection 5.2.3).

Test run one continued for 16 days with primary column 2,4-DNT and 2,6-DNT effluent concentrations reaching approximately one-tenth the influent concentrations. At this point, the decision was made between WESTON and USATHAMA to terminate run one and proceed with subsequent tests.

4.2.2.2 Continuous flow column test conditions for run two. In run two the groundwater flow rates through columns A1 and B1 were 0.3 gpm and 0.7 gpm, respectively. Both sets of columns contained Hydrodarco 4000 carbon, which appeared to be the better performing carbon based on run one results. For the duration of this test the influent groundwater stream was split to maintain 0.3 gpm and 0.7 gpm through columns A1 and B1, respectively.

Prior to beginning run two the air stripper nozzle was replaced as recommended by the manufacturer. During this time, the nozzle was found to be clogged with PVC shavings from the piping. The nozzle was reinstalled and for run two the air stripper feed rate was controlled at 4 gpm to maintain the 2-foot water level in the GAC feed tank. The system was operated under these conditions for 16 days. During this time, the influent groundwater concentrations decreased, thereby increasing run length required for effluent concentrations to meet influent concentrations. A decision was made between WESTON and USATHAMA to end the test at this point.

4.2.3 Variance analysis. A total of four test runs was planned, three with the influent passing through the air stripper and one with the influent bypassing the air stripper. All four sets of test runs were to utilize two types of carbons selected from the batch (isotherm) testing.

Two test runs were executed but stopped before breakthrough of the primary columns was achieved. During the first run, both carbons were used at flowrates of 0.5 gpm as planned. The one deviation from the planned test run was the intermittent bypassing of the air stripper.

The second test run was performed using only one carbon type (Hydrodarco 4000) with primary column flowrates of 0.3 gpm and 0.7 gpm for columns A1 and B1, respectively.

Test runs three and four were not completed because the influent groundwater explosives concentrations were considerably lower than anticipated, resulting in order of magnitude increases in predicted run lengths needed to reach breakthrough. As such, it was deemed not practical and/or economical to continue the tests in order to achieve complete breakthrough of explosives in columns A1 and B1 effluents.

4.3 Analytical method development for 2,4-DNT and 2,6-DNT.
The analytical methods developed for both the field laboratory and WESTON's Analytics Division, as well as procedures and equipment, are presented in the following subsections.

4.3.1 Analytical procedures for explosives analysis in field laboratory. Samples were analyzed for dinitrotoluenes by liquid/liquid extraction and electron capture gas chromatography. Detection limits were determined by instrument sensitivity.

4.3.2 Analytical procedure for explosives analysis by WESTON's Analytics Division. Samples were analyzed for dinitrotoluenes by liquid/liquid extraction and electron capture gas chromatography. WESTON obtained USATHAMA certification for these compounds. Detection limits were determined by WESTON's low-level HPLC method for DNT in water. The certification package for this method is presented in Appendix A.

4.3.3 Analytical procedures for volatile organics in water by WESTON's Analytics Division. Samples were analyzed by U.S. EPA Method 8010 for carbon tetrachloride, chloroform, trichloroethylene, and 1,1,1-trichloroethane. Detection levels of 1 ppb were obtained with Method 8010.

4.3.4 Analytical procedure for total organic carbon in water by WESTON's Analytics Division. Samples were analyzed by U.S. EPA Method 415.1.

5. PRESENTATION OF EXPERIMENTAL RESULTS

This study of activated carbon for treatment of explosives-contaminated groundwater was conducted over a 6-week period. Two test runs of 16 days each were conducted from 15 February 1989 until 29 March 1989. The variables examined were 2,4-DNT, 2,6-DNT, and TOC water concentrations and 2,4-DNT and 2,6-DNT gaseous emissions from the air stripper. Other variables including pH, influent water temperature, air and water flow rates, and atmospheric conditions were also measured. Results of these test runs are presented in this section.

5.1 Air stripper.

5.1.1 Explosives. For test runs one and two, the air stripper was used to remove volatile organics from the influent feed water. Stack testing was conducted during test run two. Three 4-hour sampling runs were employed over a 2-day period in order to achieve composite results. The stack testing data compiled consist of the following items:

- Test data (general).
- Sampling conditions.
- Gas stream composition.
- Gas stream velocity and volumetric flow data.
- Explosives emissions.
- Source operations data.

These data have been tabulated by sampling run and are presented in Table 5-1.

Samples were collected during the air stripper stack testing of the influent flow and the condensate that collected in the U-joint of the exhaust gas ductwork. These samples were analyzed for 2,4-DNT and 2,6-DNT. The field laboratory results for these samples are presented in Table 5-2.

5.2 Activated carbon.

5.2.1 Explosives. For test runs one and two, effluent groundwater samples taken from primary columns A1 and B1 were analyzed for 2,4-DNT and 2,6-DNT. The groundwater samples were analyzed in a field laboratory and by WESTON's Analytics Division in Lionville, Pennsylvania. These results are presented in the following subsections.

5.2.1.1 Field lab results. Samples were collected every 2 hours from the primary columns' (A1 and B1) effluent. These samples were analyzed for 2,4-DNT and 2,6-DNT. Influent to the GAC system was also collected and analyzed for 2,4-DNT and 2,6-DNT. The field laboratory results for 2,4-DNT and 2,6-DNT from test run one are presented in Tables 5-3 and 5-4, respectively. Data are presented for the system influent and the

TABLE 5-1. SUMMARY OF EXPLOSIVES TEST DATA AND
TEST RESULTS FROM AIR STRIPPER STACK
TESTING AT BAAP

TEST DATA:

	AIR STRIPPER STACK		
Test location			
Test run number	1	2	3
Test date	3/13/89	3/13/89	3/14/89
Test time period	0902-1310	1352-1758	0807-1342

SAMPLING DATA:

Sampling duration, min.	240.0	240.0	240.0
Nozzle diameter, in.	0.576	0.576	0.576
Cross sectional nozzle area, sq. ft.	0.001810	0.001810	0.001810
Barometric pressure, in. Hg	29.76	29.76	29.30
Avg. orifice press. diff., in H ₂ O	1.63	1.71	1.65
Avg. dry gas meter temp., deg F	74	79	72
Avg. abs. dry gas meter temp., deg. R	534	539	532
Total liquid collected by train, ml	51.0	66.0	53.0
Std. vol. of H ₂ O vapor coll., cu. ft.	2.4	3.1	2.5
Dry gas meter calibration factor	1.002	1.002	1.002
Sample vol. at meter cond., dcf	159.830	164.684	161.053
Sample vol. at std. cond., dcf (1)	157.954	160.505	158.994
Percent of isokinetic sampling	101.0	101.1	100.9

GAS STREAM COMPOSITION DATA:

CO ₂ , % by volume, dry basis	0.0	0.0	0.0
O ₂ , % by volume, dry basis	21.0	21.0	21.0
CO, % by volume, dry basis	0.0	0.0	0.0
N ₂ , % by volume, dry basis	79.1	79.1	79.1
Molecular wt. of dry gas, lb/lb mole	29.0	29.0	29.0
H ₂ O vapor in gas stream, prop. by vol.	0.015	0.019	0.015
Mole fraction of dry gas	0.985	0.981	0.985
Molecular wt. of wet gas, lb/lb mole	28.8	28.8	28.8

GAS STREAM VELOCITY AND VOLUMETRIC FLOW DATA:

Static pressure, in., H ₂ O	0.21	0.21	0.21
Static pressure, in. Hg	0.015	0.015	0.015
Absolute pressure, in. Hg	29.78	29.78	29.61
Avg. temperature, deg. F	65	72	65
Avg. absolute temperature, deg. R	525	532	525
Pitot tube coefficient	0.84	0.84	0.84
Total number of traverse points	8	8	8
Avg. gas stream velocity, ft./sec.	6.1	6.3	6.2
Stack/duct cross sectional area, sq. ft.	0.35	0.35	0.35
Avg. gas stream volumetric flow, wscf/min.	127	132	129
Avg. gas stream volumetric flow, dcf/min.	126	128	127

EXPLOSIVES EMISSIONS:

				Series Average
2,4 Dinitrotoluene				
Concentration, lbs/dscf	7.26E-11	9.61E-11	1.26E-10	9.83E-11
Concentration, ug/m ³	1.16	1.54	2.02	1.57
Concentration, ppm/v	1.23E-04	1.63E-04	2.14E-04	1.67E-04
Mass rate, lbs/hr	5.47E-07	7.36E-07	9.59E-07	7.48E-07

TABLE 5-1. SUMMARY OF EXPLOSIVES TEST DATA AND
TEST RESULTS FROM AIR STRIPPER STACK
TESTING AT BAAP
(continued)

2,6 Dinitrotoluene				
Concentration, lbs/dscf	1.97E-10	2.90E-10	2.11E-10	2.32E-10
Concentration, ug/m3	3.15	4.64	3.38	3.72
Concentration, ppm/v	3.34E-04	4.92E-04	3.58E-04	3.95E-04
Mass rate, lbs/hr	1.48E-06	2.22E-06	1.60E-06	1.77E-06

SOURCE OPERATIONS DATA:

Air Stripper Feed Rate, gpm	4	4	4
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(1) Standard conditions = 68 deg. F. (20 deg. C.) and
29.92 inches Hg (760 mm Hg)

TABLE 5-2. FIELD LABORATORY RESULTS FOR 2,4-DNT and 2,6-DNT
FOR AIR STRIPPER INFLUENT AND CONDENSATE COLLECTED
IN THE AIR STRIPPER U-JOINT
DURING STACK TESTING AT BAAP

Sample I.D.	<u>Concentration in $\mu\text{g/L}$</u>	
	2,4-DNT	2,6-DNT
Run One		
Air Stripper Influent	0.15	0.17
U-Joint Condensate	0.16	0.15
Run Two		
Air Stripper Influent	0.14	0.20
U-Joint Condensate	0.17	0.17
Run Three		
Air Stripper Influent	0.19	0.18
U-Joint Condensate	0.27	0.19

TABLE 5-3. FIELD LABORATORY RESULTS FOR 2,4-DNT FROM RUN ONE
STARTING ON 15 FEBRUARY 1989 AT BAAP

Date	Time	GAC Column Influent Concentration (µg/L)	<u>Calgon Filtrasorb 300</u> Column A1 Effluent Concentration (µg/L)	<u>Hydrodarco 4000</u> Column B1 Effluent Concentration (µg/L)
15 February 1989	5:00 AM	500	ND	ND
	16:00 PM	---	ND	ND
16 February 1989	5:00 AM	300	ND	ND
	7:00 AM	---	ND	ND
	9:00 AM	---	ND	ND
	12:00 AM	---	ND	ND
	14:00 PM	---	ND	ND
	18:00 PM	---	ND	ND
	22:00 PM	---	ND	ND
	24:00 PM	---	ND	ND
	4:00 AM	30	ND	ND
17 February 1989	6:00 AM	---	0.2	0.2
	9:00 AM	100	NA	NA
	11:20 AM	---	ND	ND
	16:00 PM	---	ND	ND
	24:00 PM	---	ND	ND
	4:00 AM	100	NA	NA
	8:00 AM	---	ND	ND
18 February 1989	14:00 PM	---	ND	ND
	18:00 PM	---	ND	ND
	24:00 PM	---	0.2	0.2
	4:00 AM	240	NA	NA
	10:00 AM	---	0.3	0.2
19 February 1989	12:00 AM	280	0.3	0.1
	18:00 PM	---	0.1	0.3
	24:00 PM	---	0.3	0.1
	4:00 AM	360	0.3	0.7
	8:00 AM	---	0.4	0.5
20 February 1989	10:00 AM	---	0.4	0.4
	13:30 PM	---	0.3	0.3
	18:00 PM	---	0.5	0.3
	2:00 AM	---	0.3	0.3
	6:00 AM	300	NA	NA
21 February 1989	8:00 AM	---	0.9	0.5
	12:00 AM	---	0.8	0.4
	18:00 PM	---	1.7	0.4
	2:00 AM	---	2.0	0.4
	6:00 AM	400	NA	NA
22 February 1989	8:00 AM	---	2.0	0.4
	12:30 PM	---	3.0	1.7
	18:00 PM	---	3.0	1.2

TABLE 5-3. FIELD LABORATORY RESULTS FOR 2,4-DNT FROM RUN ONE
STARTING ON 15 FEBRUARY 1989 AT BAAP
(continued)

Date	Time	GAC Column	Calgon Filtrasorb 300	Hydrodarco 4000
		Influent Concentration ($\mu\text{g/L}$)	Column A1 Effluent Concentration ($\mu\text{g/L}$)	Column B1 Effluent Concentration ($\mu\text{g/L}$)
23 February 1989	2:00 AM	---	6.0	1.2
	6:00 AM	500	NA	NA
	8:00 AM	---	6.0	1.1
	12:00 AM	---	6.0	1.3
	18:00 PM	---	6.0	1.2
	24:00 PM	---	7.0	4.5
24 February 1989	6:00 AM	600	8.0	3.6
	10:00 AM	---	8.0	3.5
	16:00 PM	---	10.0	3.4
25 February 1989	2:00 AM	---	8.0	5.6
	6:00 AM	600	NA	NA
	8:00 AM	---	9.0	4.0
	18:00 PM	---	9.0	4.0
	24:00 PM	---	10.0	6.0
26 February 1989	6:00 AM	600	10.0	5.0
	8:00 AM	---	10.0	5.0
	18:00 PM	---	20.0	5.0
	24:00 PM	---	20.0	6.0
27 February 1989	6:00 AM	600	20.0	5.0
	12:00 AM	---	20.0	6.0
	18:00 PM	---	20.0	6.5
	24:00 PM	---	20.0	6.0
28 February 1989	6:00 AM	600	20.0	6.0
	12:00 AM	---	20.0	6.0
	16:00 PM	---	20.0	6.0
	20:00 PM	---	20.0	10.0
	24:00 PM	---	25.0	10.0
1 March 1989	6:00 AM	600	20.0	10.0
	10:00 AM	---	25.0	10.0
	16:00 PM	---	30.0	10.0
	24:00 PM	---	30.0	10.0
2 March 1989	6:00 AM	600	30.0	10.0
	12:00 AM	---	30.0	10.0
	16:00 PM	---	40.0	20.0
	24:00 PM	---	40.0	15.0
3 March 1989	6:00 AM	520	NA	NA
	8:00 AM	---	40.0	14.0

Notes: ND = Below detection limit.

NA = Not analyzed.

--- = No sample collected.

Detection limit is 0.1 $\mu\text{g/L}$.

Flow rate was 0.5 gpm through both columns.

TABLE 5-4. FIELD LABORATORY RESULTS FOR 2,6-DNT FROM RUN ONE
STARTING ON 15 FEBRUARY 1989 AT BAAP

Date	Time	GAC Column Influent Concentration (µg/L)	Calgon Filtrasorb 300 Column A1 Effluent Concentration (µg/L)	Hydrodarco 4000 Column B1 Effluent Concentration (µg/L)
15 February 1989	5:00 AM	300	0.1	ND
	16:00 PM	---	0.1	ND
16 February 1989	5:00 AM	300	ND	ND
	7:00 AM	---	ND	ND
	9:00 AM	---	0.1	0.1
	12:00 AM	---	0.1	0.1
	14:00 PM	---	0.1	0.1
	18:00 PM	NA	0.1	
	22:00 PM	---	0.1	0.3
	24:00 PM	---	0.1	0.3
17 February 1989	4:00 AM	100	0.1	0.2
	6:00 AM	---	0.3	0.5
	9:00 AM	400	NA	NA
	11:20 AM	---	0.2	0.3
	16:00 PM	---	0.2	0.2
	24:00 PM	---	0.2	0.2
18 February 1989	4:00 AM	400	NA	NA
	8:00 AM	---	0.2	0.3
	14:00 PM	---	0.3	0.3
	18:00 PM	---	0.2	0.2
	24:00 PM	---	0.4	0.6
19 February 1989	4:00 AM	300	NA	NA
	10:00 AM	---	0.5	0.4
	12:00 AM	300	0.6	0.4
	18:00 PM	---	0.3	0.6
	24:00 PM	---	0.5	0.3
20 February 1989	4:00 AM	300	0.6	2.0
	8:00 AM	---	0.7	1.0
	10:00 AM	---	0.7	1.0
	13:30 PM	---	0.6	1.0
	18:00 PM	---	0.8	1.0
21 February 1989	2:00 AM	---	0.6	1.0
	6:00 AM	300	NA	NA
	8:00 AM	---	1.0	1.0
	12:00 AM	---	1.0	1.0
	18:00 PM	---	1.6	1.0
22 February 1989	2:00 AM	---	2.0	1.0
	6:00 AM	300	NA	NA
	8:00 AM	---	2.0	1.0
	12:30 PM	---	2.7	2.5
	18:00 PM	---	2.4	2.4

TABLE 5-4. FIELD LABORATORY RESULTS FOR 2,6-DNT FROM RUN ONE
STARTING ON 15 FEBRUARY 1989 AT BAAP
(continued)

Date	Time	GAC Column Influent Concentration (µg/L)	Calgon Filtrasorb 300 Column A1 Effluent Concentration (µg/L)	Hydrodarco 4000 Column B1 Effluent Concentration (µg/L)
23 February 1989	2:00 AM	---	4.7	2.0
	6:00 AM	300	NA	NA
	8:00 AM	---	4.7	2.0
	12:00 AM	---	4.8	2.2
	18:00 PM	---	4.7	2.0
	24:00 PM	---	4.7	6.7
24 February 1989	6:00 AM	300	5.0	5.0
	10:00 AM	---	5.0	5.0
	16:00 PM	---	6.0	5.0
25 February 1989	2:00 AM	---	5.4	6.0
	6:00 AM	300	NA	NA
	8:00 AM	---	6.0	5.0
	16:00 PM	---	6.0	3.0
	24:00 PM	---	7.4	6.0
26 February 1989	6:00 AM	300	7.4	6.2
	8:00 AM	---	7.0	6.0
	18:00 PM	---	10.0	5.0
	24:00 PM	---	10.0	6.7
27 February	6:00 AM	300	10.0	6.0
	12:00 AM	---	12.0	6.0
	18:00 PM	---	13.0	7.0
	24:00 PM	---	14.0	6.6
28 February	6:00 AM	300	13.0	6.0
	12:00 AM	---	14.0	7.0
	16:00 PM	---	13.0	7.0
	20:00 PM	---	14.0	13.0
	24:00 PM	---	16.0	13.0
1 March 1989	6:00 AM	240	16.0	12.0
	10:00 AM	---	16.0	11.0
	16:00 PM	---	16.0	13.0
	24:00 PM	---	18.0	11.0
2 March 1989	6:00 AM	240	19.0	12.0
	12:00 AM	---	18.0	12.0
	16:00 PM	---	22.0	19.0
	24:00 PM	---	23.0	15.0
3 March 1989	6:00 AM	250	NA	NA
	8:00 AM	---	24.0	15.0

Notes: ND = Below detection limit.
NA = Not analyzed.
--- = No sample collected.
Detection limit is 0.1 µg/L.
Flow rate was 0.5 gpm through each column.

effluent from each primary column, A1 (Calgon Filtrasorb 300) and B1 (Hydrotarco 4000). Each carbon column train received an influent flow of 0.5 gallon/minute. The influent flow rate was checked every two hours and adjusted as necessary. Influent temperature and pH data are presented in Subsection 5.2.4 along with effluent pH data.

The field laboratory results for 2,4-DNT and 2,6-DNT from test run two are presented in Tables 5-5 and 5-6, respectively. Data are presented for the system influent and the effluent from each primary column, A1 and B1; both contained Hydrotarco 4000. Column train A received an influent flow of 0.3 gallon/minute and Column train B received an influent flow of 0.7 gallon/minute. The influent flow rate was checked every 2 hours and adjusted as necessary. Influent temperature and pH data along with effluent pH data are presented in Subsection 5.2.4.

Four graphical presentations are provided for each test run, two for 2,4-DNT and two for 2,6-DNT. The first plot for each contaminant shows the primary columns' effluent concentrations as a function of elapsed time, while the second plot shows the primary columns' effluent as well as the column's influent concentration as a function of elapsed time. These graphic illustrations have been presented in Figures 5-1 through 5-8.

5.2.1.2 WESTON's Analytics Division results. Samples were taken of the primary columns effluent and shipped to WESTON's Analytics Division for 2,4-DNT and 2,6-DNT analysis. Samples representing approximately 10 percent of the field laboratory samples taken and analyzed were collected. The results of the laboratory analysis from test run one are presented in Table 5-7. The results of the laboratory analysis from test run two are presented in Table 5-8.

5.2.2 Total organic carbon. Total organic carbon analyses were performed on samples collected every eight hours from the primary columns effluent during both test runs. The total organic carbon analyses were performed by WESTON's Analytics Division. The results of this analysis for test runs one and two are presented in Tables 5-9 and 5-10, respectively.

5.2.3 Volatile organics. Volatile organic compound analyses were to be run during test run four. During this test run the air stripper was to be bypassed. Volatile organic compound analyses were performed on the influent to determine their level. Volatile organics data from test run one are presented in Table 5-11.

5.2.4 Temperature and pH. Temperature and pH were measured in the field on the influent to the GAC system. Effluent pH was also measured on primary GAC columns (A1 and

TABLE 5-5. FIELD LABORATORY RESULTS FOR 2,4-DNT FROM RUN TWO
STARTING ON 8 MARCH 1989 AT BAAP

Date	Time	GAC Column Influent Concentration (µg/L)	Hydrodarco 4000	Hydrodarco 4000
			0.3 gpm Column A1 Effluent Concentration (µg/L)	0.7 gpm Column B1 Effluent Concentration (µg/L)
8 March 1989	14:00 PM	150	0.7	0.2
	22:00 PM	---	0.5	0.2
9 March 1989	6:00 AM	---	0.5	ND
	14:00 PM	100	NA	NA
	16:00 PM	---	0.4	ND
	24:00 PM	---	0.3	ND
10 March 1989	6:00 AM	---	0.4	ND
	18:00 PM	100	NA	NA
	24:00 PM	---	0.2	ND
11 March 1989	8:00 AM	---	0.2	ND
	14:00 PM	130	NA	NA
	16:00 PM	---	0.3	ND
	24:00 PM	---	0.2	ND
12 March 1989	8:00 AM	---	0.2	ND
	14:00 PM	200	NA	NA
	16:00 PM	---	0.3	ND
	24:00 PM	---	0.1	ND
13 March 1989	8:00 AM	---	0.1	ND
	10:00 AM	---	0.2	0.2
	12:00 AM	---	0.3	0.3
	14:00 PM	200	NA	NA
	16:00 PM	---	0.4	0.4
	24:00 PM	---	0.2	0.2
14 March 1989	6:00 AM	---	0.3	0.2
	8:00 AM	---	0.3	0.3
	14:00 PM	200	NA	NA
	16:00 PM	---	0.4	0.4
	24:00 PM	---	0.1	0.2
15 March 1989	8:00 AM	---	0.3	0.3
	12:00 AM	---	0.2	0.3
	14:00 PM	220	NA	NA
	16:00 PM	---	0.3	0.4
	24:00 PM	---	0.1	0.2
16 March 1989	6:00 AM	---	0.2	0.3
	14:00 PM	210	0.3	0.4
	24:00 PM	---	0.1	0.2
17 March 1989	6:00 AM	---	0.3	0.6
	14:00 PM	100	NA	NA
	22:00 PM	---	0.1	0.4

TABLE 5-5. FIELD LABORATORY RESULTS FOR 2,4-DNT FROM RUN TWO
STARTING ON 8 MARCH 1989 AT BAAP
(continued)

Date	Time	GAC Column Influent Concentration (µg/L)	Hydrodarco 4000 0.3 gpm	Hydrodarco 4000 0.7 gpm
			Column A1 Effluent Concentration (µg/L)	Column B1 Effluent Concentration (µg/L)
18 March 1989	8:00 AM	---	0.2	0.7
	14:00 PM	100	NA	NA
	22:00 PM	---	0.2	0.5
19 March 1989	8:00 AM	---	0.2	0.7
	14:00 PM	100	0.3	1.0
	22:00 PM	---	0.1	0.6
20 March 1989	6:00 AM	---	0.3	1.0
	14:00 PM	100	0.2	1.0
	22:00 PM	---	0.2	1.3
21 March 1989	6:00 AM	---	0.4	2.8
	14:00 PM	200	0.2	1.5
	22:00 PM	---	0.2	2.3
22 March 1989	6:00 AM	---	0.4	5.6
	14:00 PM	300	0.2	2.5
	22:00 PM	---	0.2	5.0
23 March 1989	6:00 AM	---	0.4	7.8
	14:00 PM	300	0.3	6.0
	22:00 PM	---	0.5	10.0
24 March 1989	6:00 AM	---	0.5	10.0

Notes: ND = Below detection limit.
NA = Not analyzed.
--- = Not collected.
Detection limit is 0.1 µg/L.

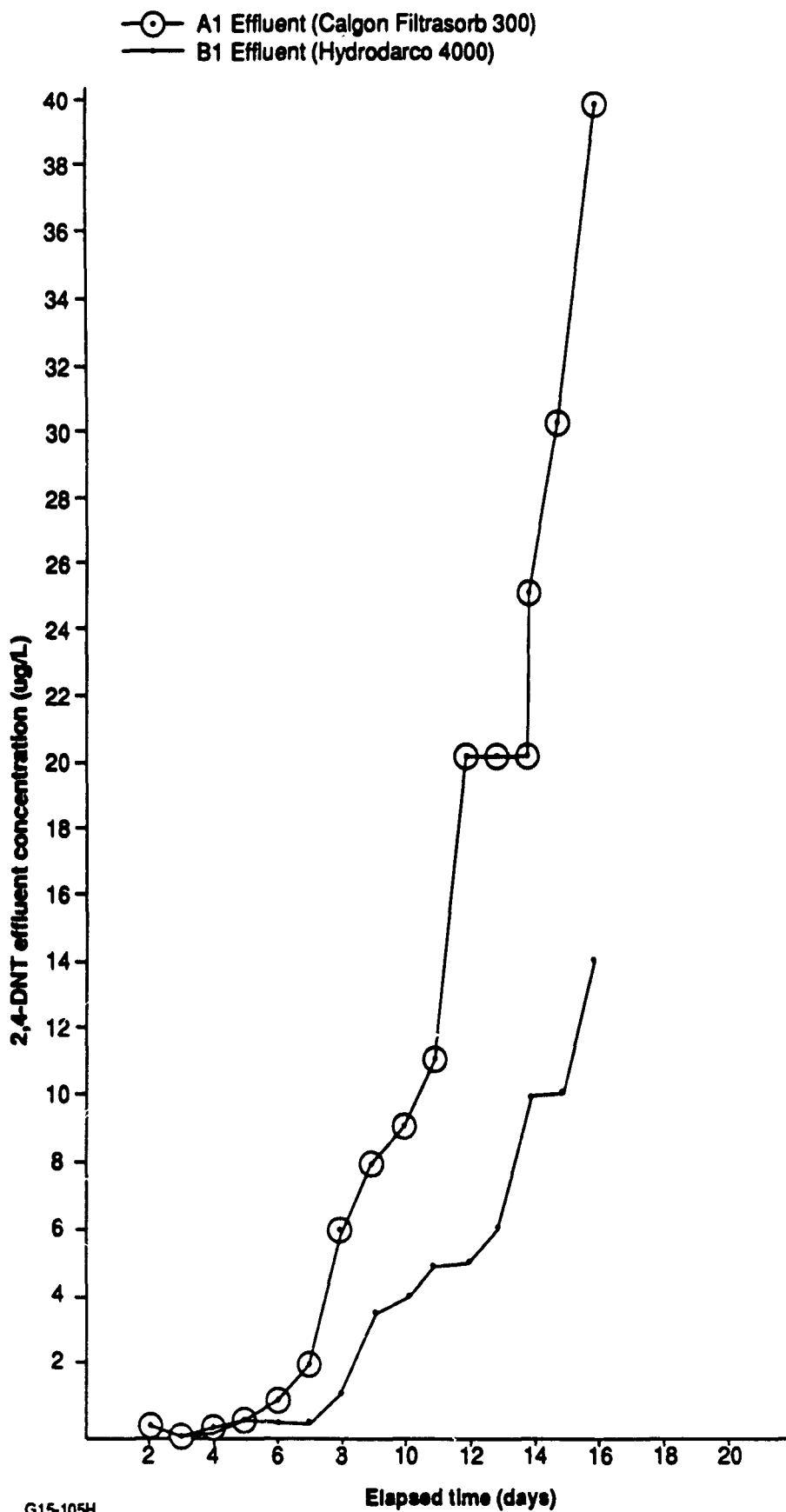
TABLE 5-6. FIELD LABORATORY RESULTS FOR 2,6-DNT FROM RUN TWO
STARTING ON 8 MARCH 1989 AT BAAP

Date	Time	GAC Column Influent Concentration (µg/L)	Hydrodarco 4000 0.3 gpm	Hydrodarco 4000 0.7 gpm
			Column A1 Effluent Concentration (µg/L)	Column B1 Effluent Concentration (µg/L)
8 March 1989	14:00 PM	230	0.6	0.2
	22:00 PM	---	0.4	0.3
9 March 1989	6:00 AM	---	0.4	0.1
	14:00 PM	220	NA	NA
	16:00 PM	---	0.4	0.1
	24:00 PM	---	0.3	0.1
10 March 1989	6:00 AM	---	0.3	0.1
	18:00 PM	200	NA	NA
	24:00 PM	---	0.3	0.1
11 March 1989	8:00 AM	---	0.3	0.1
	14:00 PM	200	NA	NA
	16:00 PM	---	0.3	0.1
	24:00 PM	---	0.3	0.1
	8:00 AM	---	0.2	0.1
12 March 1989	14:00 PM	200	NA	NA
	16:00 PM	---	0.3	0.1
	24:00 PM	---	0.2	0.1
	8:00 AM	---	0.2	0.1
13 March 1989	10:00 AM	---	0.8	1.0
	12:00 AM	---	0.7	1.0
	14:00 PM	200	NA	NA
	16:00 PM	---	0.7	1.0
	24:00 PM	---	0.7	0.8
	6:00 AM	---	0.6	0.8
14 March 1989	8:00 AM	---	0.6	0.9
	14:00 PM	200	NA	NA
	16:00 PM	---	0.7	1.0
	24:00 PM	---	0.6	1.2
	8:00 AM	---	0.6	1.2
15 March 1989	12:00 AM	---	0.5	1.1
	14:00 PM	200	NA	NA
	16:00 PM	---	0.5	1.1
	24:00 PM	---	0.4	1.1
	6:00 AM	---	0.4	1.2
16 March 1989	14:00 PM	200	0.5	1.3
	24:00 PM	---	0.5	1.3
	6:00 AM	---	0.7	2.0
17 March 1989	14:00 PM	200	NA	NA
	22:00 PM	---	0.6	2.2

TABLE 5-6. FIELD LABORATORY RESULTS FOR 2,6-DNT FROM RUN TWO
STARTING ON 8 MARCH 1989 AT BAAP
(continued)

Date	Time	GAC Column Influent Concentration ($\mu\text{g/L}$)	Hydrodarco 4000 0.3 gpm	Hydrodarco 4000 0.7 gpm
			Column A1 Effluent Concentration ($\mu\text{g/L}$)	Column B1 Effluent Concentration ($\mu\text{g/L}$)
18 March 1989	8:00 AM	---	0.6	2.6
	14:00 PM	200	NA	NA
	22:00 PM	---	0.8	3.0
19 March 1989	8:00 AM	---	0.7	3.4
	14:00 PM	200	0.7	3.3
20 March 1989	6:00 AM	---	0.7	4.4
	14:00 PM	200	1.0	5.7
	22:00 PM	---	0.9	7.0
21 March 1989	6:00 AM	---	0.9	8.0
	14:00 PM	200	0.9	8.2
	22:00 PM	---	0.9	9.4
22 March 1989	6:00 AM	---	0.9	11.0
	14:00 PM	200	0.9	12.0
	22:00 PM	---	1.0	13.0
23 March 1989	6:00 AM	---	1.0	15.0
	14:00 PM	200	1.0	15.0
	22:00 PM	---	1.2	16.0
24 March 1989	6:00 AM	---	1.2	16.0

Notes: ND = Below detection limit.
NA = Not analyzed.
--- = Not sampled.
Detection limit is 0.1 $\mu\text{g/L}$.



G15-105H

Figure 5-1 2,4-DNT concentration, using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

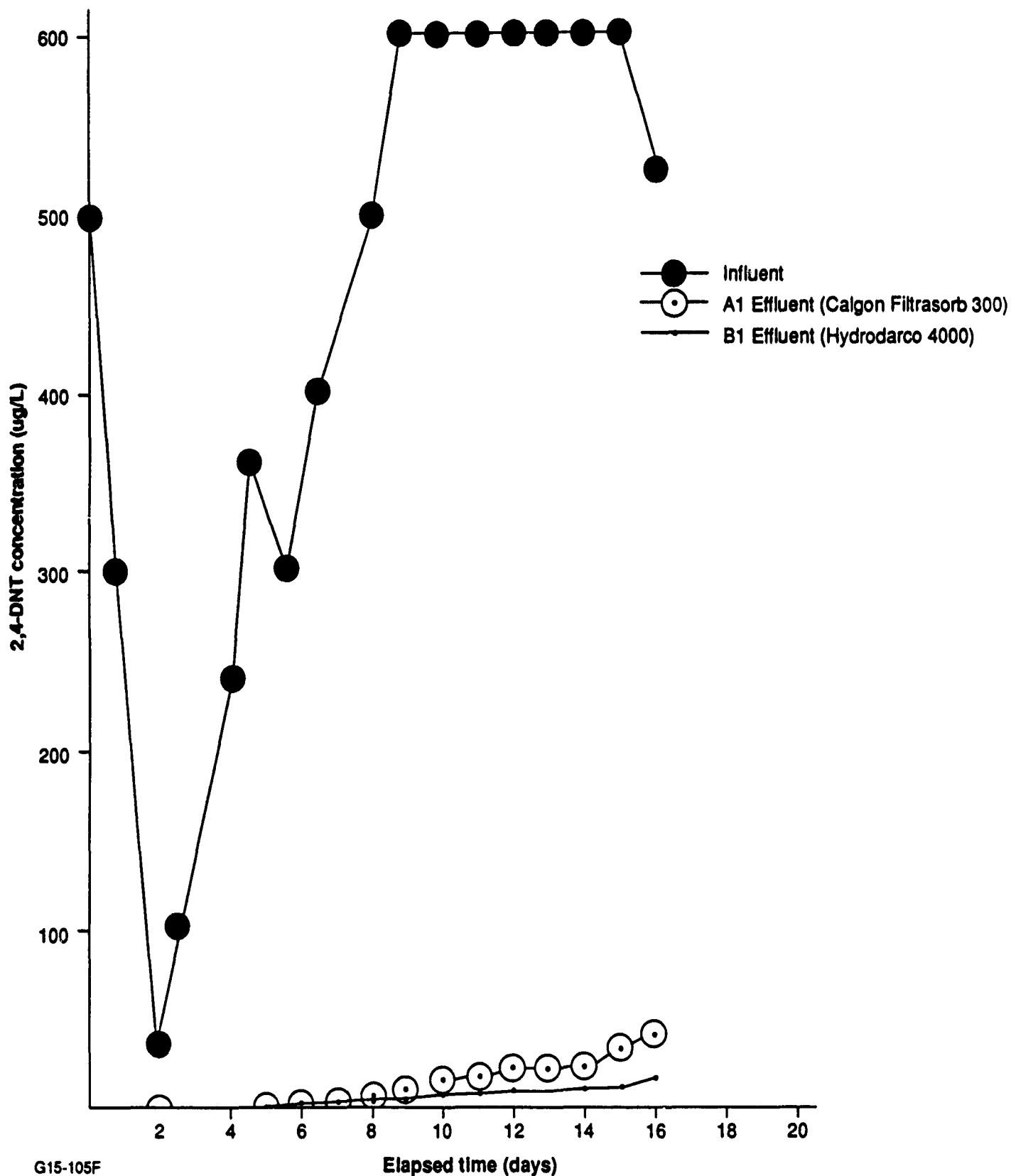
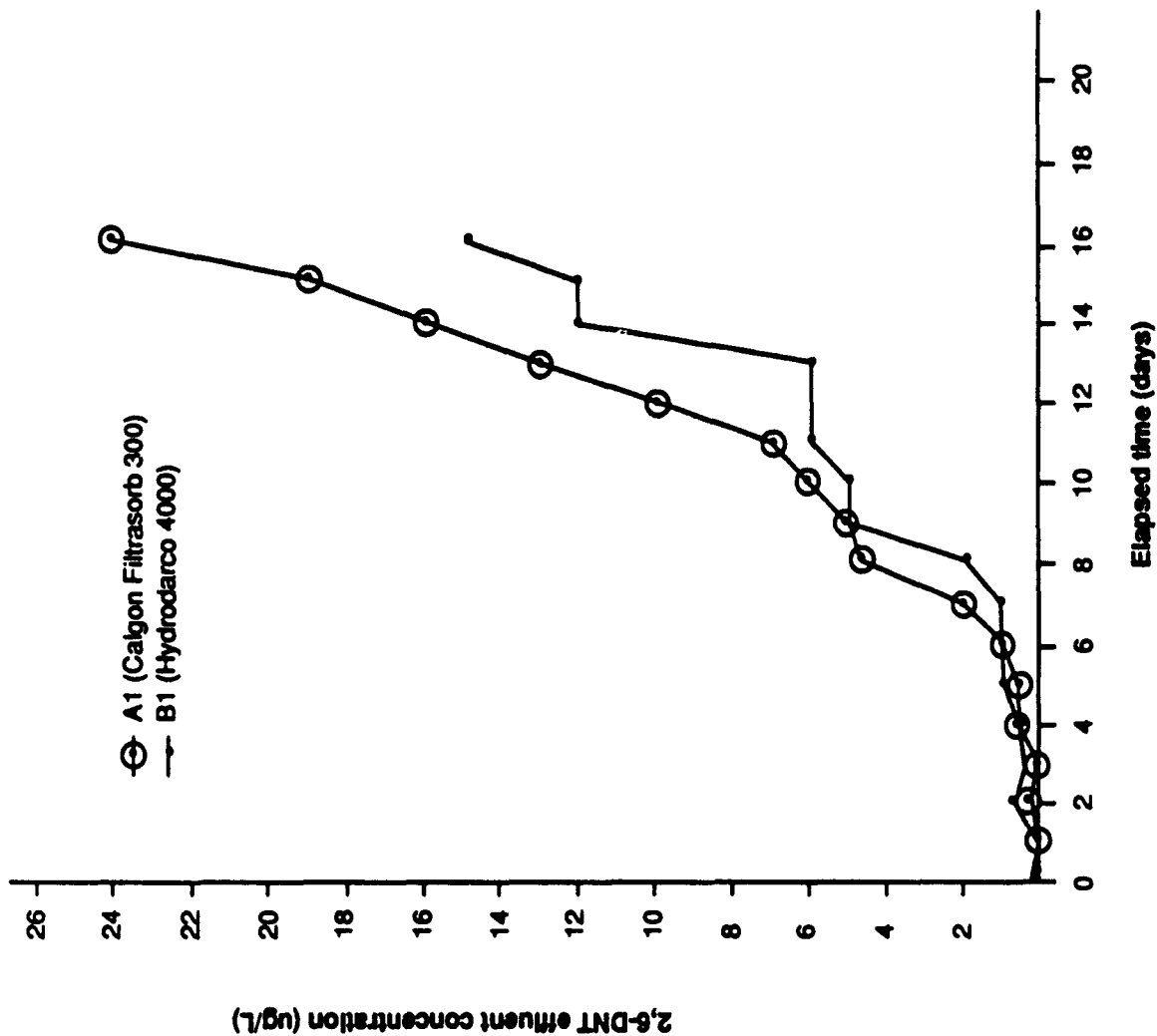


Figure 5-2 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.



G-15-1058

Figure 5-3 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

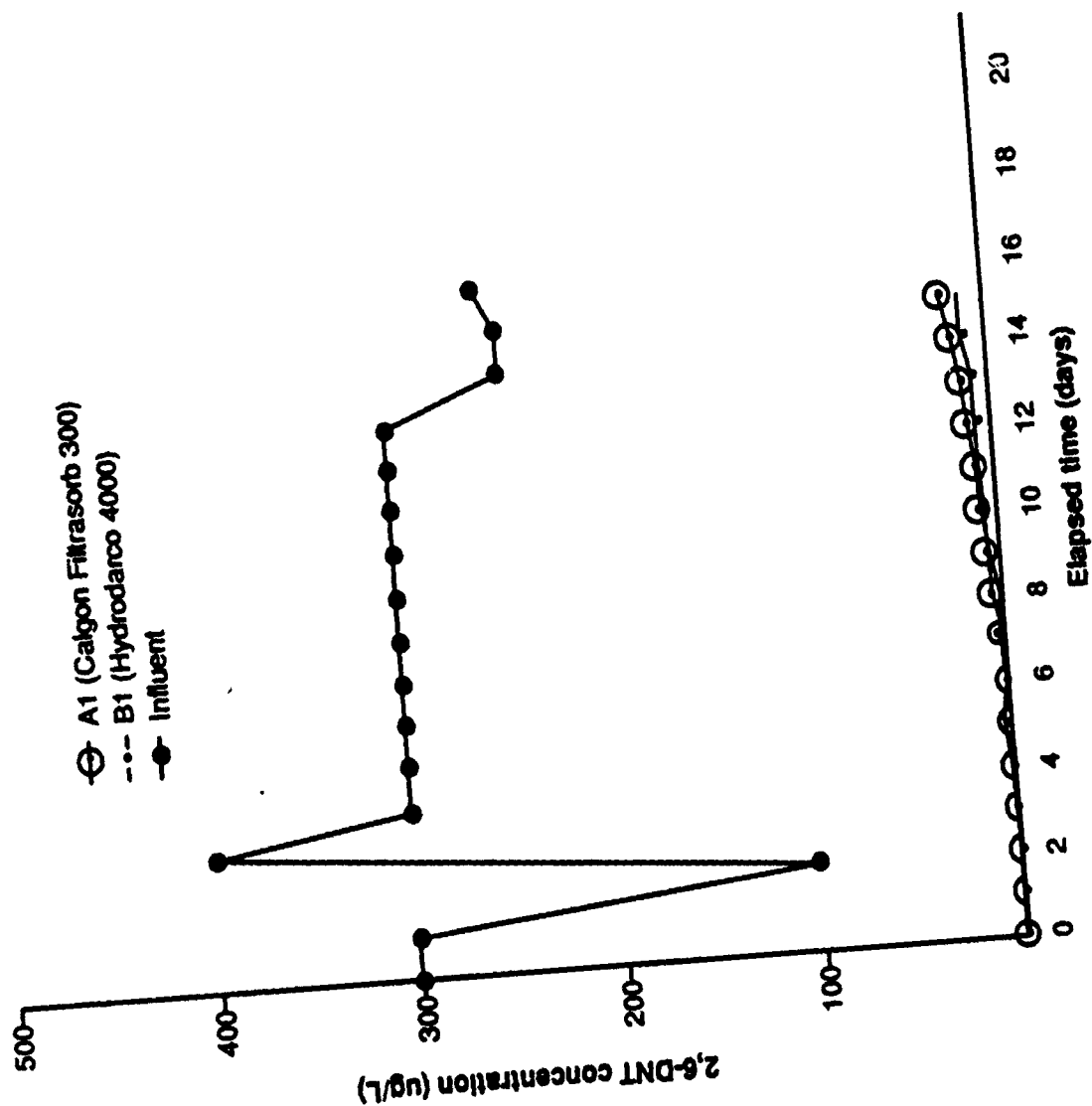
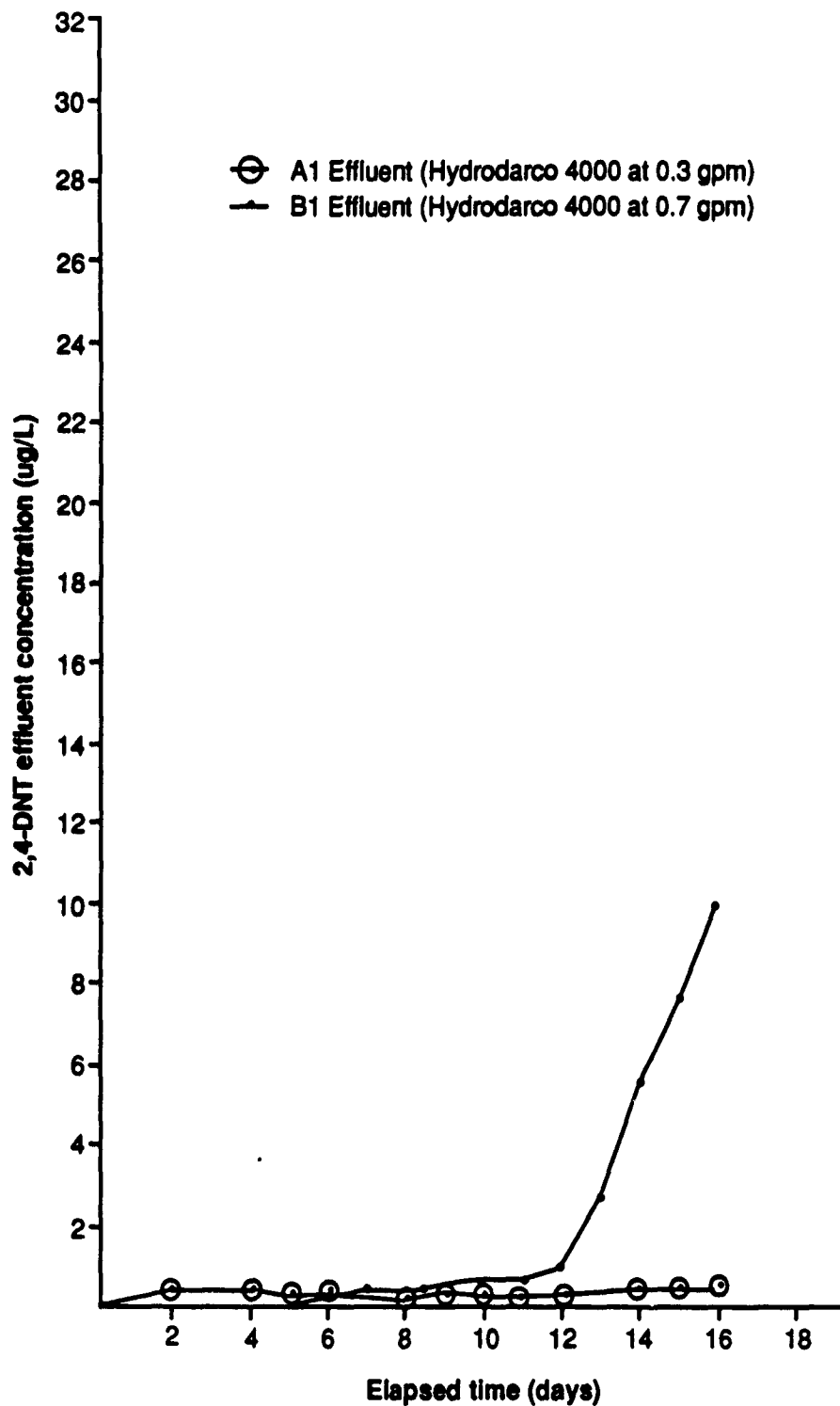


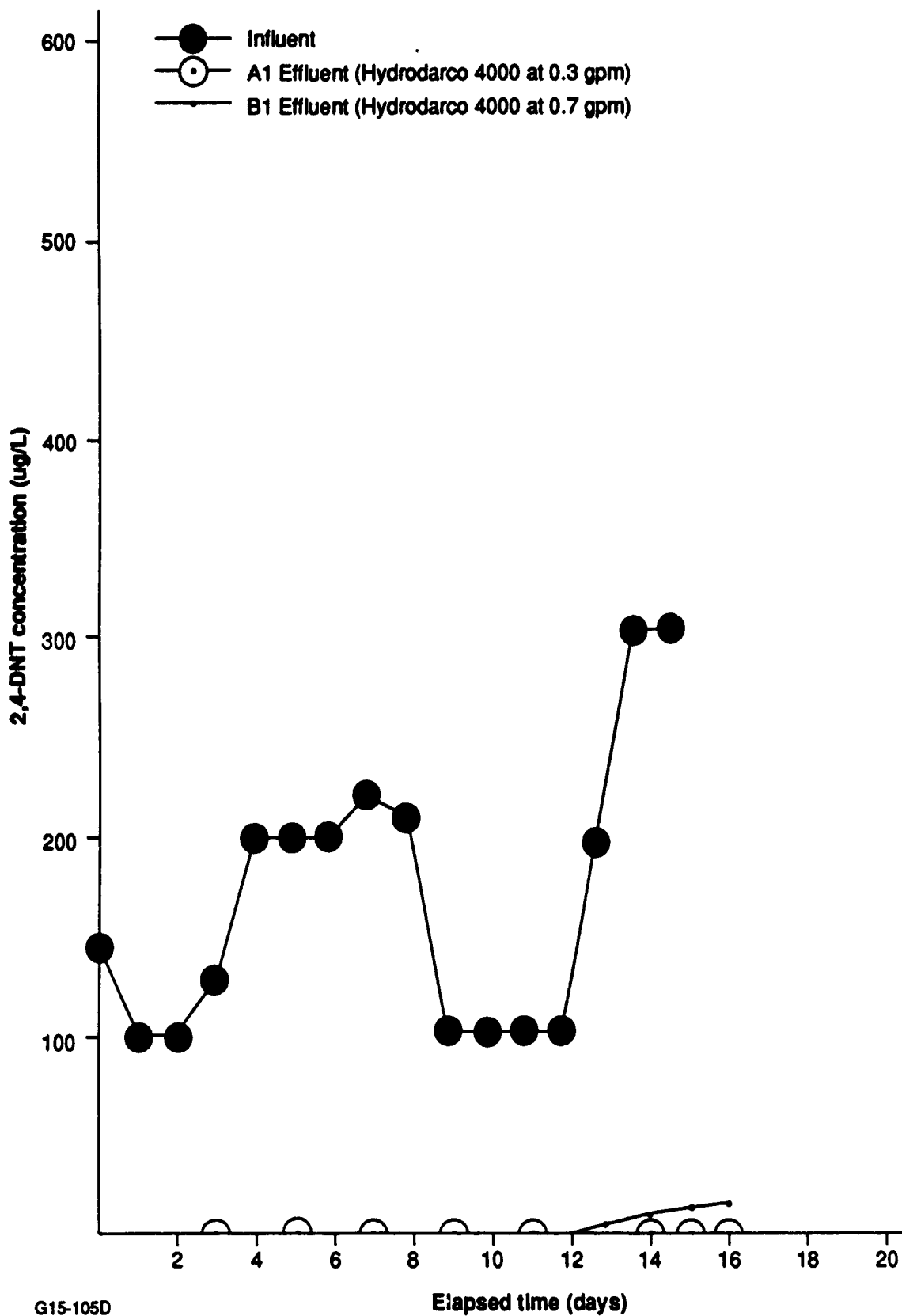
Figure 5-4 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

G-15-105A



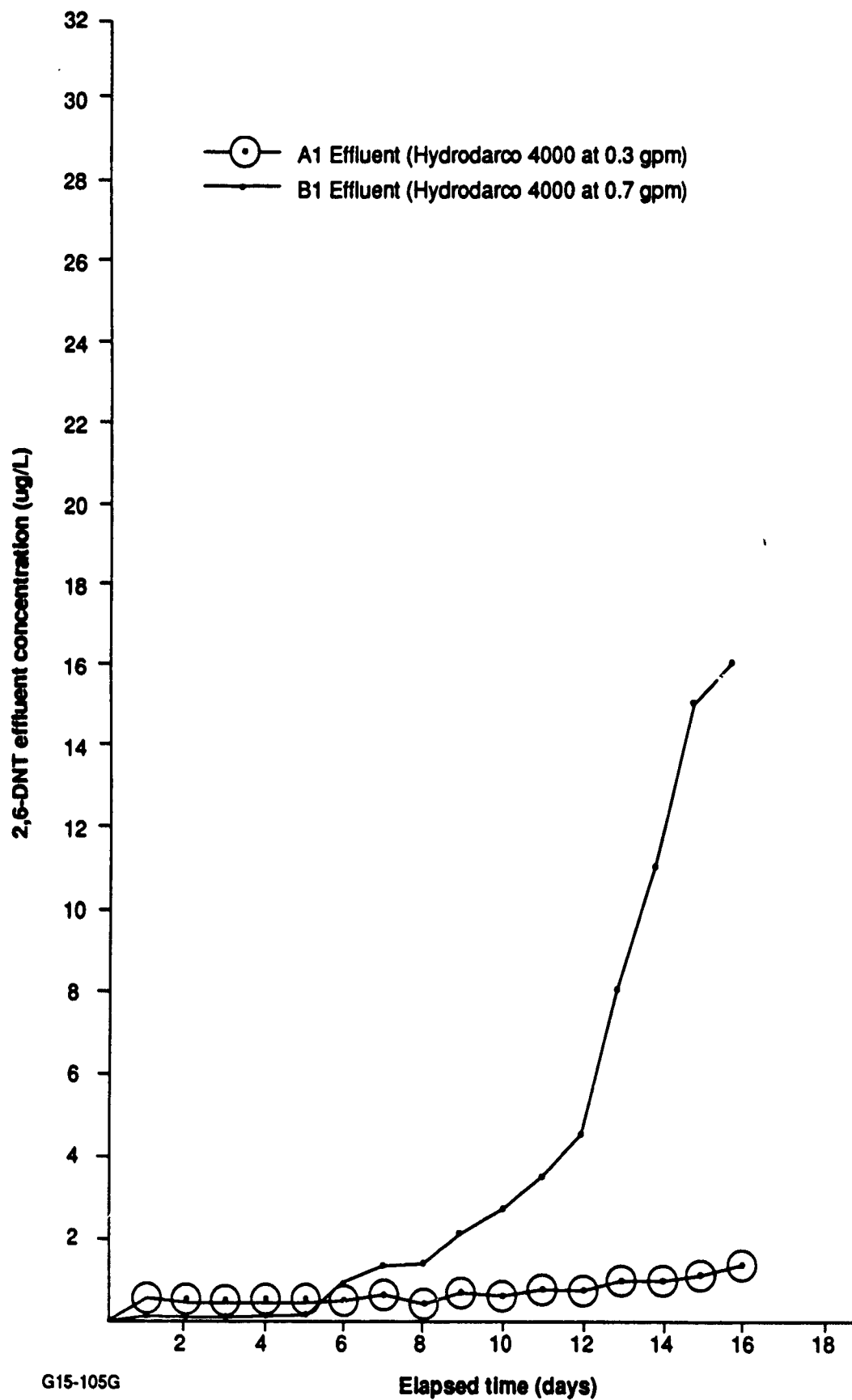
G-15-105C

Figure 5-5 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.



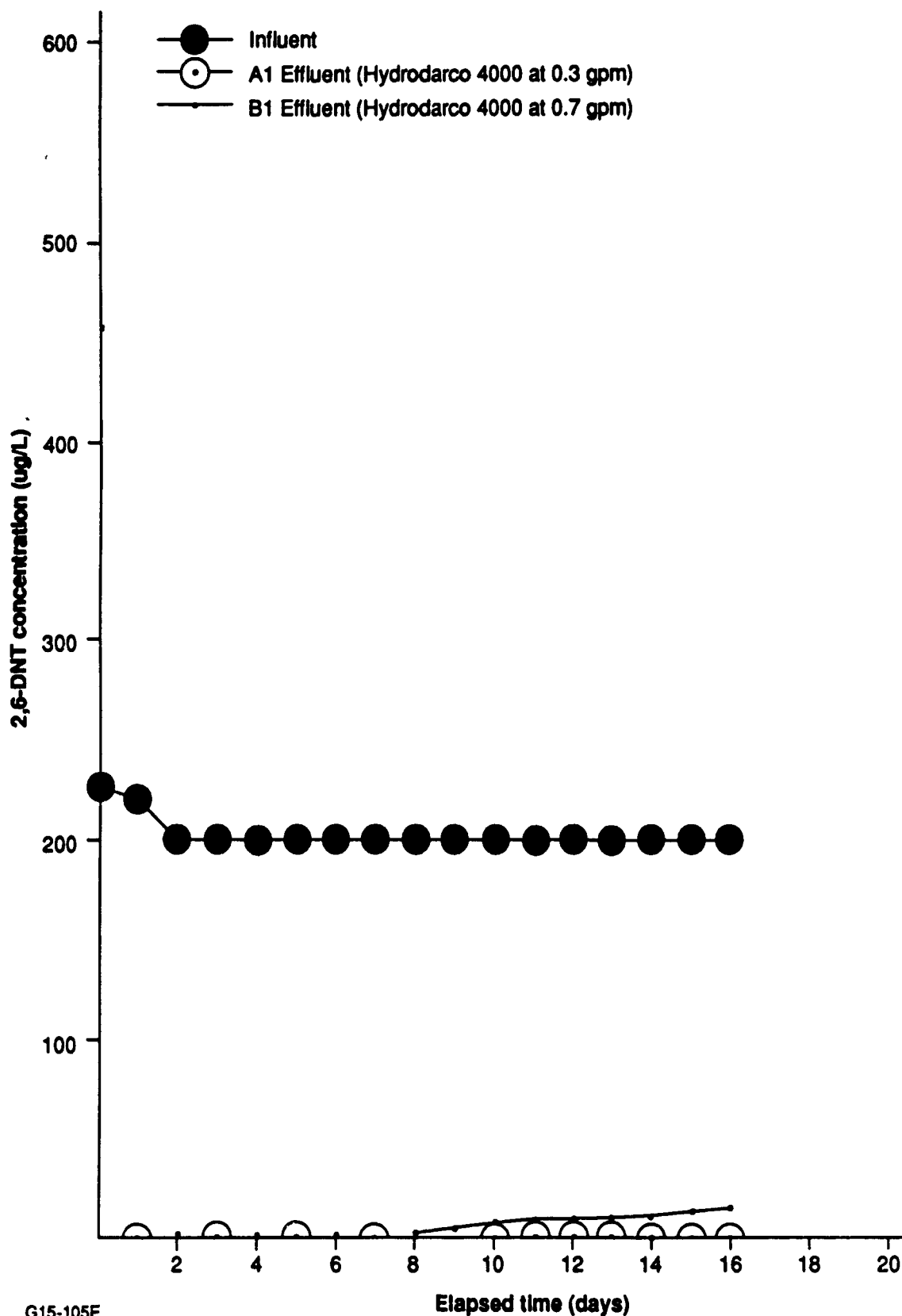
G15-105D

Figure 5-6 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.



G15-105G

Figure 5-7 2,6 DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.



G15-105E

Figure 5-8 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.

TABLE 5-7. WESTON'S ANALYTICS DIVISION RESULTS FOR
2,4-DNT AND 2,6-DNT FROM RUN ONE STARTING ON
15 FEBRUARY 1989 AT BAAP

Sample ID	Concentrations in µg/L	
	2,4-DNT	2,6-DNT
Column A1 (Calgon Filtrasorb 300)		
15 Feb. 1989 - 10:00 AM ^a	<0.458	<0.017 [0.013(j)] ^b
16 Feb. 1989 - 10:00 AM	<0.458	0.048
17 Feb. 1989 - 10:00 AM	<0.458	0.200
Column B1 (Hydrodarco 4000)		
15 Feb. 1989 - 10:00 AM ^a	c	c
16 Feb. 1989 - 10:00 AM	<0.458	0.102
17 Feb. 1989 - 10:00 AM	<0.458	0.063

^a15 Feb. 10:00 AM - 6 hr. into GAC Test

16 Feb. 10:00 AM - 30 hr. into GAC Test

17 Feb. 10:00 AM - 54 hr. into GAC Test

^b<0.017 is USATHAMA certified lower detection limit, however can detect lower and 0.013(j) represents the estimated value.

^cSample bottle was accidentally broken by the laboratory during extraction procedure.

TABLE 5-8. WESTON'S ANALYTICS DIVISION RESULTS FOR
2,4-DNT AND 2,6-DNT FROM RUN TWO STARTING ON
8 MARCH 1989 AT BAAP

Sample ID	Hours	Concentration in $\mu\text{g/L}$	
	into Test	2,4-DNT	2,6-DNT
Column A1 (Hydrodarco 4000 at 0.3 gpm)			
8 March 1989 - 16:00 P.M.	2	18.1	9.8
9 March 1989 - 16:00 P.M.	26	<0.46	0.30
10 March 1989 - 16:00 P.M.	50	<0.46	0.27
11 March 1989 - 16:00 P.M.	74	<0.46	0.26
12 March 1989 - 16:00 P.M.	98	<0.46	0.20
Column B1 (Hydrodarco 4000 at 0.7 gpm)			
8 March 1989 - 16:00 P.M.	2	0.50	0.19
9 March 1989 - 4:00 A.M.	14	<0.46	0.14
9 March 1989 - 16:00 P.M.	26	<0.46	0.08
10 March 1989 - 4:00 A.M.	38	<0.46	0.07
10 March 1989 - 16:00 P.M.	50	<0.46	0.06
11 March 1989 - 4:00 A.M.	62	<0.46	0.05
11 March 1989 - 16:00 P.M.	74	<0.46	0.05
12 March 1989 - 4:00 A.M.	86	<0.46	0.05
12 March 1989 - 4:00 P.M.	98	<0.46	0.04

TABLE 5-9. WESTON'S ANALYTICS DIVISION
TOTAL ORGANIC CARBON DATA FROM RUN ONE
STARTING ON 15 FEBRUARY 1989 AT BAAP

Sample ID	Hours into Test	<u>Concentration in mg/L</u> TOC
Column A1 (Hydrodarco 4000 at 0.5 gpm)		
27 February 1989 - 16:00 P.M.	300	1.3
27 February 1989 - 24:00 P.M.	308	0.52
28 February 1989 - 8:00 A.M.	316	0.71
28 February 1989 - 16:00 P.M.	324	1.1
28 February 1989 - 24:00 P.M.	332	0.81
1 March 1989 - 8:00 A.M.	340	1.7
1 March 1989 - 16:00 P.M.	348	9.8
1 March 1989 - 24:00 P.M.	356	2.5
2 March 1989 - 8:00 A.M.	364	1.3
Column B1 (Calgon Filtrasorb 300 at 0.5 gpm)		
27 February 1989 - 16:00 P.M.	300	1.1
27 February 1989 - 24:00 P.M.	308	0.52
28 February 1989 - 8:00 A.M.	316	0.62
28 February 1989 - 16:00 P.M.	324	1.1
28 February 1989 - 24:00 P.M.	332	0.81
1 March 1989 - 8:00 A.M.	340	9.3
1 March 1989 - 16:00 P.M.	348	10.1
1 March 1989 - 24:00 P.M.	356	2.6
2 March 1989 - 8:00 A.M.	364	1.3

TABLE 5-10. WESTON'S ANALYTICS DIVISION RESULTS
TOTAL ORGANIC CARBON DATA FROM RUN TWO
STARTING ON 8 MARCH 1989 AT BAAP

Sample ID	Hours into Test	<u>Concentration in mg/L</u> TOC
Column A1 (Hydrotarco 4000 at 0.3 gpm)		
12 March 1989 - 22:00 P.M.	104	1.2
13 March 1989 - 6:00 A.M.	112	2.6
13 March 1989 - 22:00 P.M.	128	0.97
14 March 1989 - 6:00 A.M.	136	1.7
14 March 1989 - 14:00 P.M.	144	0.5u*
14 March 1989 - 22:00 P.M.	152	0.5u
15 March 1989 - 6:00 A.M.	160	0.5u
15 March 1989 - 14:00 P.M.	168	0.5u
16 March 1989 - 6:00 A.M.	184	0.5u
Column B1 (Hydrotarco 4000 at 0.7 gpm)		
12 March 1989 - 22:00 P.M.	104	1.5
13 March 1989 - 6:00 A.M.	112	3.2
13 March 1989 - 14:00 P.M.	120	2.0
13 March 1989 - 22:00 P.M.	128	1.2
14 March 1989 - 6:00 A.M.	136	1.9
14 March 1989 - 14:00 P.M.	144	0.5u
14 March 1989 - 22:00 P.M.	152	0.5u
15 March 1989 - 6:00 A.M.	160	0.5u
15 March 1989 - 14:00 P.M.	168	2.7
15 March 1989 - 22:00 P.M.	176	2.1
16 March 1989 - 6:00 A.M.	184	0.5u

*Indicates that the parameter was not detected at or above the detection limit. The associated numerical value was the sample detection limit.

TABLE 5-11. WESTON'S ANALYTICS DIVISION GAC INFLUENT
VOLATILE ORGANICS DATA FROM RUN ONE
STARTING 15 FEBRUARY 1989 AT BAAP

Parameter	Sample Description		
	Before Air Stripper Bypass		After Air Stripper Bypass
	16 February 1989 µg/L	16 February 1989 µg/L	16 February 1989 µg/L
Carbon Tetrachloride	ND	ND	ND
Chloroform	2.4	2.5	ND
Trichloroethylene	ND	ND	1.9
1,1,1-Trichloroethane	ND	ND	ND

Notes: ND = Below detection limit.
Detection limit is 1.0 µg/L

B1). The influent temperature was measured every 4 hours. Temperature data (morning (0800) readings) are presented in Table 5-12). The pH was measured on all influent and effluent samples analyzed for 2,4-DNT and 2,6-DNT in the field laboratory. The pH of all samples was approximately 7.

TABLE 5-12. MORNING (0800) TEMPERATURE OF INFLUENT TO GAC COLUMNS
PILOT TREATMENT STUDY AT BAAP

Run One		Run Two	
Elapsed Time (Days)	Temperature (°F)	Elapsed Time (Days)	Temperature (°F)
1	61.3	1	56.1
2	62.0	2	60.4
3	61.1	3	61.6
4	62.5	4	60.6
5	64.9	5	64.0
6	63.2	6	59.5
7	63.3	7	63.4
8	61.8	8	63.9
9	58.4	9	59.9
10	58.2	10	63.3
11	60.2	11	63.6
12	60.5	12	62.9
13	59.8	13	63.4
14	61.4	14	63.4
15	59.9	15	62.8
16	59.5	16	62.3
17	58.8	17	64.8

6. DISCUSSION OF RESULTS

This section provides discussion and interpretation of the data presented in Section 5.

6.1 Air stripper test program.

6.1.1 Explosives emissions. As noted previously, the air stripper was used in this project primarily to remove volatile compounds from the raw groundwater, so that carbon adsorption of explosives could be evaluated. As an adjunct, however, the potential for discharge of explosives from an air stripper intended to remove volatiles was also to be evaluated.

The explosives emissions evaluation during this study consisted of three separate test runs during which exhaust gases from the stripper were sampled and analyzed. All three air stripper test runs were conducted during the second GAC test run (and therefore after the air stripper inlet nozzle was repaired). The emissions test procedures are discussed in Section 4. Data from all three test runs are presented in Table 5-1.

Table 5-1 indicates that explosives were detected in the air exhaust of the stripper. The feed rate to the stripper was approximately 4 gpm of explosives-contaminated water for each time period for each test; therefore, over a 4-hour period approximately 960 gallons of water were processed through the stripper. The contaminated water contained 0.18 mg/L of both 2,4-DNT and 2,6-DNT for runs one and two and 0.34 mg/L of 2,4-DNT and 0.19 mg/L of 2,6-DNT for run three. These input concentrations equate to 3.62×10^{-4} lb/hr for 2,4-DNT and 2,6-DNT for runs one and two, 6.84×10^{-4} lb/hr for 2,4-DNT run three, and 3.82×10^{-4} lb/hr for 2,6-DNT run three. Comparing input concentrations to output air emissions, on the average 99.8 percent of 2,4-DNT and 99.5 percent of 2,6-DNT remained in the liquid phase and did not exit through the stripper air exhaust.

The exhaust gas ductwork configuration, necessitated by site conditions, shown in Figure 4-1, required the use of a U-shaped connection between the descending and ascending exhaust gas ductwork. Although this low point was located downstream from the demister, the possibility existed for accumulation of moisture at this point. A sample tap was installed at this point to permit sampling and analysis of any collected moisture.

It was found that the "U" connector at the base of the stack did accumulate contaminated condensate through the course of each test run. This water was analyzed and found to contain almost identical levels of explosives as the feed water. These results were presented in Table 5-2. Therefore, it can be

assumed that this condensate is a result of mist carryover through the air stripper mist eliminator and that this water should be returned to the feed tank for reprocessing. This condensate was well above the USABRDL criteria of 0.2 ug/L 2,4-DNT and 0.007 ug/L 2,6-DNT.

Stack gases were near saturation at approximately 72 percent relative humidity for all three runs.

Air emission limits have not been established for 2,4-DNT and 2,6-DNT and are therefore not available for comparison to air stripper test results.

One sampling problem was encountered during the test program. A power failure occurred during run three and a 1.5-hour sampling delay was experienced. The air stripper was allowed to stabilize prior to the resumption of sample run three. All data presented are believed to be representative of process conditions encountered during the test program.

The air stripper exhaust was not characterized with respect to volatiles emissions. Their removal from the GAC influent was assessed during run one by sampling from the GAC influent tank. These data are presented in Section 5, and they indicate that the GAC influent contained very low concentrations of volatiles, as compared to the raw groundwater. Therefore, the air stripper was effective for its intended purpose of removing volatiles and minimizing their potential impact on the GAC test program.

It should, however, be noted that samples taken from the GAC influent tank represent a composite of the accumulated volume therein. In addition to this limitation, very low levels of volatile organic compounds concentration in the feed to the air stripper made it difficult to qualify the air stripper efficiency in removing the volatile organic compounds.

6.2 Continuous flow (pilot plant) activated carbon testing.

6.2.1 Effluent characteristics. Chronological data showing influent and effluent explosives concentrations for all test runs have been presented in Tables 5-3 through 5-6 and shown graphically in Figures 5-1 through 5-8. These data clearly show that the use of new granular activated carbon in continuous flow columns produced very low effluent explosives concentrations, generally in the low part per billion (ppb) range during the early portions of each run. The ability to treat the USABRDL criteria cannot be directly determined since neither the field lab results (represented by data in Tables 5-3 through 5-6) nor WESTON's Analytics Division results (represented by data in Tables 5-7 and 5-8) were certified to achieve such low detection limits.

These data show that in most test runs effluent explosives levels rose gradually through the duration of the experiment.

However, in no run did the effluent concentration of either 2,4-DNT or 2,6-DNT exceed 10 percent of the respective (average) influent concentration before it became necessary to terminate the run. In the first run, which examined both selected carbons at identical influent flow rates of 0.5 gpm, effluent levels of 2,4-DNT reached 40 ug/L (Filtrisorb 300) and 14 ug/L (Hydrodarco 4000) at the end of 16 days of operation. Effluent levels for 2,6-DNT at this point were 24 ug/L (Filtrisorb 300) and 15 ug/L (Hydrodarco 4000).

Based upon these results, it appeared that the time required for the operation to complete breakthrough at this loading rate might preclude additional runs. The determination was made to terminate these runs at this point.

The second run employed a higher flow rate through one column train (0.7 gpm). Since the output of monitor well PBN82-02C was limited to approximately 1.0 gpm, the other column train operated at 0.3 gpm. In this run, both column trains employed Hydrodarco 4000 carbon, which had provided the lower final effluent concentrations for both contaminants in run one. At the end of 16 days, effluent 2,4-DNT levels were 0.48 ug/L at 0.3 gpm, and 10 ug/L at 0.7 gpm. Effluent levels for 2,6-DNT were 0.12 ug/L and 1.6 ug/L, respectively. As with run one, complete breakthrough was not observed, and with the concurrence of USATHAMA run two was terminated at this point. The average, influent 2,4-DNT concentration for the second run was 50 percent lower than the first run. Similarly, the average, influent 2,6-DNT concentration for the second run was 33 percent lower than the first run.

It should be noted that a major contributing factor to the inability to obtain breakthrough within available time periods was the low influent concentration of the contaminants of concern, at approximately two orders of magnitude lower than anticipated during the preparation of the Test Plan.

Table 6-1 shows that generally good agreement was obtained between the mobile (field) laboratory analyses and those performed by WESTON's Analytics Division, particularly considering the difference in detection limits between the analytical methods.

TOC data from the two runs, shown in Tables 5-9 and 5-10, were relatively inclusive, with TOC concentrations generally in the low mg/L range, as compared to low ug/L concentration for the explosives. It might be noted that, particularly in run one, effluent TOC concentrations were quite similar in both columns even though they varied widely over time. This observation supports the possibility that these data represent relatively nonadsorbable species in the groundwater (as opposed to, for example, analytical interference or background). Since, however,

TABLE 6-1. WESTON'S ANALYTICS DIVISION RESULTS VS.
WESTON FIELD LABORATORY RESULTS FOR
RUN TWO AT BAAP

Sample ID	Hours into Test	Lionville Laboratory Results Concentration in ug/L		Field Laboratory Results Concentration in ug/L	
		2,4-DNT	2,6-DNT	2,4-DNT ^a	2,6-DNT
Column A1 (Hydrodarco 4000 at 0.3 gpm)					
8 March 1989 - 16:00 P.M.	2	18.10	9.80	0.7 ^b	0.6 ^b
9 March 1989 - 16:00 P.M.	26	<0.46	0.30	0.4	0.4
10 March 1989 - 16:00 P.M.	50	<0.46	0.27	—	—
11 March 1989 - 16:00 P.M.	74	<0.46	0.26	0.3	0.3
12 March 1989 - 16:00 P.M.	98	<0.46	0.20	0.25	0.25
Column B1 (Hydrodarco 4000 at 0.7 gpm)					
8 March 1989 - 16:00 P.M.	2	0.50	0.19	0.2 ^b	0.2 ^b
9 March 1989 - 4:00 A.M.	14	<0.46	0.14	NO ^c	0.1 ^c
9 March 1989 - 16:00 P.M.	26	<0.46	0.08	NO	0.1
10 March 1989 - 4:00 A.M.	38	<0.46	0.07	NO ^c	0.1 ^c
10 March 1989 - 16:00 P.M.	50	<0.46	0.06	—	—
11 March 1989 - 4:00 A.M.	62	<0.46	0.05	NO ^d	0.1 ^d
11 March 1989 - 16:00 P.M.	74	<0.46	0.05	NO	0.1
12 March 1989 - 4:00 A.M.	86	<0.46	0.05	NO ^d	0.1 ^d
12 March 1989 - 16:00 P.M.	98	<0.46	0.04	—	—

^aND = Below detection limit.

^bSample taken at 14:00 hours on 8 March 1989.

^cSamples taken at 6:00 hours.

^dSamples taken at 8:00 hours.

these data were quite variable, and DNT concentrations were so much lower than TOC values, it is not possible to attribute changes in TOC levels to adsorption of explosives.

6.2.2 Operating summary. Tables 6-2 and 6-3 summarize operating characteristics for runs one and two. Base upon the flow rate observed (average) influent concentrations, and total operating time, the total mass loading of each explosive to each column was calculated. Based upon the total amount of carbon in each column and the specific adsorption capacity of the carbon for the explosive (as determined from the isotherm tests) the total column capacity for each explosive was calculated. Finally, from the mass of explosive applied and the capacity of the column, the percent utilization of column capacity was calculated. As noted previously, the effluent (i.e., not adsorbed) fraction of the explosives did not exceed 10 percent and most of the time was substantially lower. Therefore, for this calculation the difference between the total mass of explosive applied and that adsorbed (as would be estimated by integration under the respective concentration curves in Figures 5-1 through 5-8) was considered minor.

Tables 6-2 shows that, after 16 days of operation at the indicated loading, relatively small fractions of each carbon's capacity for each explosive was utilized.

Table 6-3 suggests the same conclusions for all three loading rates using Hydrodarco 4000. It should be noted that, even though the maximum hydraulic loading in run two was higher than in run one, the explosives concentrations in the groundwater had fallen as compared to run one, resulting in a lower mass loading rate of explosives to the column.

TABLE 6-2. ACTIVATED CARBON COLUMN OPERATING AND
PERFORMANCE DATA FOR RUN ONE AT BAAP

Hydrodarco 4000 VS. Calgon Filtrasorb 300

Column outer diameter = 5 inches (0.42 ft)
Column inner diameter = 4.25 inches (0.35 ft)
Column area = 0.100 ft²
Bed Volume (at 2 ft. depth) = 0.200 ft³ (1.50 gallons)

	Hydrodarco 4000	Filtrasorb 300
Flow Rate	0.5 gpm	0.5 gpm
Surface Loading Rate	5.0 gpm/ft ²	5.0 gpm/ft ²
Contact Time	3.0 min.	3.0 min.
Hydraulic Loading	2.50 gpm/ft ³	2.50 gpm/ft ³
2,4-DNT Influent Concentration (avg.)	0.42 mg/L	0.42 mg/L
2,6-DNT Influent Concentration (avg.)	0.3 mg/L	0.3 mg/L
2,4-DNT Capacity (Rate)*	0.12 lb/lb	0.05 lb/lb
2,6-DNT Capacity (Rate)*	0.016 lb/lb	0.044 lb/lb
Weight of Carbon in Column	4.8 lb	5.8 lb
Column 2,4-DNT Capacity (wt)	0.576 lb	0.290 lb
Column 2,6-DNT Capacity (wt)	0.077 lb	0.255 lb
Total 2,4-DNT Loading to Column (lbs)	0.045	0.045
Total 2,6-DNT Loading to Column (lbs)	0.029	0.029
2,4-DNT Capacity Utilized	7.8%	15.5%
2,6-DNT Capacity Utilized	37.7%	11.4%
Run Time (days)	16	16

*From Isotherm Data.

TABLE 6-3. ACTIVATED CARBON COLUMN OPERATING AND
PERFORMANCE DATA FOR HYDRODARCO 4000 FROM RUNS ONE AND TWO AT BAAP

Column outer diameter = 5 inches (0.42 ft)
column inner diameter = 4.25 inches (0.35 ft)
Column area = 0.100 ft²
Bed Volume (at 2 ft. depth) = 0.200 ft³ (1.50 gallons)

Flow Rate	0.3 gpm (Run Two)	0.5 gpm (Run One)	0.7 gpm (Run Two)
Surface Loading Rate	3.0 gpm/ft ²	5.0 gpm/ft ²	7.0 gpm/ft ²
Contact Time	5.0 min.	3.0 min.	2.2 min.
Hydraulic Loading	1.50 gpm/ft ³	2.50 gpm/ft ³	3.50 gpm/ft ³
2,4-DNT Influent Concentration (avg.)	0.17 mg/L	0.42 mg/L	0.17 mg/L
2,6-DNT Influent Concentration (avg.)	0.2 mg/L	0.3 mg/L	0.2 mg/L
2,4-DNT Capacity (Rate)*	0.06 lb/lb	0.12 lb/lb	0.06 lb/lb
2,6-DNT Capacity (Rate)*	0.013 lb/lb	0.016 lb/lb	0.013 lb/lb
Weight of Carbon in Column	4.8 lb	4.8 lb	4.8 lb
Column 2,4-DNT Capacity (wt)	0.288 lb	0.576 lb	0.288 lb
Column 2,6-DNT Capacity (wt)	0.062 lb	0.077 lb	0.062 lb
Total 2,4-DNT Loading to Column (lbs)	0.0098	0.045	0.023
Total 2,6-DNT Loading to Column (lbs)	0.012	0.029	0.027
2,4-DNT Capacity Utilized	3.4%	7.8%	8.0%
2,6-DNT Capacity Utilized	19.4%	37.7%	43.5%
Run Time (days)	16	16	16

*From Isotherm Data.

7. DESIGN CONSIDERATIONS

7.1 General. The primary goal of this project was to evaluate the feasibility of using GAC to treat explosives-contaminated groundwater, particularly in light of recently published USABRDL criteria. From the data presented in this report, some preliminary conclusions can be drawn concerning design and operating parameters.

7.2 Process variables and parameters.

7.2.1 Influent and effluent. Influent characteristics and required effluent characteristics are primary factors to be considered in developing a GAC treatment system.

Influent explosives concentrations in the experimental phases of this project were found to be substantially lower than anticipated based upon previous data. The anticipated total explosives concentration (2,4-DNT and 2,6-DNT) used for planning purposes was approximately 13.8 mg/L (12). Total explosives concentration in the groundwater sample provided for isotherm testing was approximately 2.45 mg/L. Total explosives concentrations during pilot plant runs one and two were, on average, 0.9 mg/L and 0.4 mg/L respectively. As a result of these changes, design and operating information directly applicable to the anticipated influent concentrations are not available.

As previously discussed, the effective operating life of a GAC column is primarily determined by a defined effluent breakthrough concentration, this definition generally being based upon acceptable (or permitted) effluent concentrations. Since it is not currently possible to certify explosives analytical methods at the USABRDL criteria, it is inappropriate to use such values as effluent breakthrough criteria. Effluent permit limitations for a particular groundwater remediation would be determined by the appropriate regulatory agency on a site-specific basis. Thus, a general "breakthrough" criterion to evaluate performance is not available.

7.2.2 GAC column operating characteristics. Within the constraints discussed above, it can be concluded that, at average influent concentrations and influent surface loading rates of 3.0 to 7.0 gpm/ft² and influent hydraulic loading rates of 1.5 to 3.5 gpm/ft³, GAC columns employing either Filtrasorb 300 or Hydrodarco 4000 can provide run lengths of at least 16 days while providing 2,4-DNT and 2,6-DNT removals of greater than 90 percent. Under conditions employed in this study, explosives concentrations could be reduced below detection limits (in this study, approximately 0.46 ug/L for 2,4-DNT and 0.017 ug/L for 2,6-DNT) for approximately 98 hours at the highest loading rate for 2,4-DNT and approximately 6 hours at an intermediate loading rate for 2,6-DNT.

Longer activated carbon column contact times (which in this study did not exceed 5 minutes) may provide even longer column lives.

Based upon the data obtained in this study, the preferred carbon for removing 2,4-DNT and 2,6-DNT from pretreated groundwater at BAAP would be Hydrodarco 4000.

The design and operating conclusions discussed above strictly apply only to groundwater containing 2,4-DNT and 2,6-DNT, i.e., groundwater that did not contain other contaminants or from which other contaminants have previously been removed. In this study, an air stripper was employed to remove volatile contaminants so that adsorption of explosives alone could be evaluated. While it was not the intent of this study to evaluate the need for an air stripper in a full-scale system, one experimental run was planned to examine the concurrent removal of explosives and volatiles. However, the extension of the initial runs, made necessary by the unexpectedly low influent explosives concentrations, precluded completion of this experiment. Consequently no conclusions are drawn concerning the relative need for an air stripper in conjunction with GAC columns for treatment of BAAP groundwater.

8. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are drawn from this study:

- The concurrent removal of 2,4-DNT and 2,6-DNT from groundwater using continuous flow granular activated carbon columns is feasible. At influent explosives concentrations encountered in this study, removals of 90 percent or better were maintained for at least 16 days at surface loading rates of up to 7.0 gpm/ ft² and bed contact times of 3 to 5 minutes. Longer column lives could likely be achieved at higher bed contact times. This possibility should be explored in future tests.
- It was not possible to certify an analytical method for the quantification of 2,4-DNT and 2,6-DNT concentrations at USABRDL criteria for these contaminants. Consequently, verification of compliance with these criteria could not be achieved. Therefore, their use as regulatory criteria at the present time is not recommended.
- Since quantification of explosives at the levels of USABRDL criteria could not be achieved, the performance of GAC systems in meeting these criteria could not be strictly evaluated. In the absence of other effluent breakthrough criteria, potential bed lives in full-scale operating facilities could not be predicted.
- Based upon the isotherm tests performed in this study, the best performing carbons of the five studied were Calgon Filtrasorb 300 and Hydrodarco 4000. Subsequent testing of these two carbons in continuous flow column testing indicated that Hydrodarco 4000 performed slightly better than Filtrasorb 300, as judged by effluent explosives concentrations at comparable bed run lengths.
- Based upon testing performed in this study, there is little potential for airborne emissions of 2,4-DNT or 2,6-DNT in the exhaust of an air stripper used to remove volatile compounds. However, analysis of the condensate that collected in the downward leg of the air stripper exhaust indicated that entrained mist in the exhaust will exhibit essentially the same explosives concentrations as the air stripper influent. Therefore, careful attention should be paid to the efficiency of the demister used in such applications.

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CONTENTS (continued)

		<u>Page</u>
Paragraph 4.2	Activated carbon.....	4-9
4.2.1	Description of planned test program.	4-9
4.2.1.1	Test conditions and experimental variables.....	4-10
4.2.1.2	Operational monitoring.....	4-10
4.2.1.3	Evaluation criteria.....	4-12
4.2.2	Actual test program.....	4-13
4.2.2.1	Continuous flow column test conditions for run one.....	4-13
4.2.2.2	Continuous flow column test conditions for run two.....	4-14
4.2.3	Variance analysis.....	4-14
4.3	Analytical method development for 2,4-DNT and 2,6-DNT.....	4-15
4.3.1	Analytical procedures for explosives analysis in field laboratory.....	4-15
4.3.2	Analytical procedure for explosives analysis by WESTON's Analytics Division.....	4-15
4.3.3	Analytical procedures for volatile organics in water.....	4-15
4.3.4	Analytical procedure for total organic carbon in water.....	4-15
5	PRESENTATION OF EXPERIMENTAL RESULTS...	5-1
5.1	Air stripper.....	5-1
5.1.1	Explosives.....	5-1
5.2	Activated carbon.....	5-1
5.2.1	Explosives.....	5-1
5.2.1.1	Field lab results.....	5-1
5.2.1.2	WESTON's Analytics Division results.	5-9
5.2.2	Total organic carbon.....	5-9
5.2.3	Volatile organics.....	5-9
5.2.4	Temperature and pH.....	5-9
6	DISCUSSION OF RESULTS.....	6-1
6.1	Air stripper test program.....	6-1
6.1.1	Explosives emission.....	6-1
6.2	Continuous flow (pilot plant) acti- vated carbon testing.....	6-2
6.2.1	Effluent characteristics.....	6-2
6.2.2	Operating summary.....	6-5
7	DESIGN CONSIDERATIONS.....	7-1
7.1	General.....	7-1
7.2	Process variables and parameters....	7-1
7.2.1	Influent and effluent.....	7-1
7.2.2	GAC column operating characteristics	7-1
8	CONCLUSIONS AND RECOMMENDATIONS.....	8-1

APPENDIX A

**CERTIFICATION PACKAGE FOR WESTON'S LOW LEVEL
HPLC METHOD FOR DNT IN WATER**



208 WELSH POOL ROAD
PICKERING CREEK INDUSTRIAL PARK
LIONVILLE, PA 19353
PHONE: (215) 524-7360
TELEX: 83-5348

11 February 1989

Commander
US Army Toxic and Hazardous Materials Agency
CETHA-TE-A/D. Stevenson
Bldg E4460
Aberdeen Proving Ground, MD 21010-5401

Subject: Contract No. DAAA15-88-D-0010/Task Order 3
Certification for DNT's in Water

Dear Doug,

Enclosed is the data certification package for WESTON's low level HPLC method for DNT in Water performed in support of the above-referenced contract.

The following items were discussed with Doug Scarborough on 9 February 1989:

- o The high control spike for day 1 certification is slightly above the highest daily calibration standard. Since most of the method trial runs showed response close to 80% recovery, a 25% buffer on the high end of the calibration curve was not analyzed. In order to preserve the maximum analysis range, these data were used.
- o The full range tested included values five times lower than the optimum range chosen for certification. Reproducibility at these lower levels was not acceptable for certification. After talking to Doug, conversation with the analyst revealed that workup of the data at these levels was not saved. Since this data is not being used, it was not redone.
- o Calibration/certification statistics for a shorter range (i.e. to 20X rather than 100X) was saved, and is added at the end of the certification package.

I have also included a copy of the pre-certification package. I made a few corrections to the text and, after discussion with Les Brown, was able to get graphs from the IRPQAP. Both DNT compounds are included.

WESTON

USATHAMA DNT Certification

-2-

11 February 1989

Should you have any questions regarding these data or the corresponding method, please do not hesitate to contact me at (215) 524-7360.

Sincerely,

ROY F. WESTON, INC.

Dianne S. Therry
Dianne S. Therry
QA Coordinator

Enclosures

cc: Patricia Spaine (USATHAMA)
Walter Wujcik (WESTON)



208 WELSH POOL ROAD
PICKERING CREEK INDUSTRIAL PARK
LIONVILLE, PA 19353
PHONE: (215) 524-7360
TELEX: 83-5348

25 January 1989

Patricia Spaine
US Army Toxic and Hazardous Materials Agency
Bldg E4460, Room 200
Eeal Road
Aberdeen Proving Ground, MD 21010-5401

Subject: Contract No. DAAA15-88-D-0010/Task Order 3
Pre-Certification for DNT's in Water

Dear Patricia,

Enclosed are two copies of the pre-certification data package for WESTON's low level HPLC method for DNT in Water, performed in support of the above-referenced contract. Per Marty Stutz, this package was sent to Doug Stevenson.

This is a copy of what was sent on Monday, by overnight Federal Express. This package was delivered on Tuesday, 24 January 1989 at 10:37 a.m., per a trace done by Fed Ex. The package was signed for by M.Seigh.

Should you have any questions regarding these data or the corresponding method, please do not hesitate to contact me at (215) 524-7360.

Sincerely,

ROY F. WESTON, INC.

Dianne S. Therry
Dianne S. Therry
QA Coordinator

Enclosures

cc: W. Wujcik (WESTON)



238 WELSH POOL ROAD
FACKERING CREEK INDUSTRIAL PARK
LIONVILLE, PA 19353
PHONE: (215) 524-7360
TELEX: 83-5348

23 January 1989

Commander
US Army Toxic and Hazardous Materials Agency
AMXTH-TE/D. Stevenson
Bldg E4460
Aberdeen Proving Ground, MD 21010-5401

Subject: Contract No. DAAA15-88-D-0010/Task Order 3
Pre-Certification for DNT's in Water

Dear Doug,

Enclosed is the data pre-certification package for WESTON's low level HPLC method for DNT in Water performed in support of the above-referenced contract.

The following was resolved with Marty Stutz this afternoon in response to questions I had regarding this submittal:

- o Data are not linear at this low level. What needs to be submitted other than the QA Plan-specified information?
 1. The method write-up needs to state that a) the calibration is not linear, and that b) daily calibration must be a full initial calibration curve.
 2. The IRPQAP print-out will only be the first data page. Since the model is not linear, the program will not produce the graphs and the last print-out is identical to the first.
- o Check standards were not analyzed with the pre-certification runs; however, the initial stock solutions were verified against a stock prepared by a different analyst. Per Marty, this data has been provided in the pre-certification method, in Section IX.

Should you have any questions regarding these data or the corresponding method, please do not hesitate to contact me at (215) 524-7360.

Sincerely,

ROY F. WESTON, INC.

Dianne S. Therry
Dianne S. Therry
QA Coordinator

Enclosures

PRECERTIFICATION PERFORMANCE DATA PACKAGE CHECKLIST

Contract/Task No. DAAA15-88-D-0010 Installation BAAP
Task Order 3

The following items are included in this Precertification Performance Data Package for 2,6-DNT and 2,4-DNT (low level) in Water.
Analyte(s) Matrix

X Method written up in USATHAMA format.

Calibration:

X Calibration data and curves (plot of raw data).

X Documentation for Lack of Fit and Zero Intercept Tests.

Dianne S. Therry 1-25-89
Dianne S. Therry Date
Contractor QAC

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EXPLOSIVES IN WATER
Pre-Certification Method
for Low-Level DNT

I. SUMMARY

A. Analytes:

2,6-DNT	2,6-Dinitrotoluene
2,4-DNT	2,4-Dinitrotoluene

B. Matrix: WATER

C. General Method: A water sample is extracted by liquid/liquid apparatus and analyzed by GC with an electron capture detector.

II. APPLICATION

A. Calibration Range (extract concentration):

26DNT	0.0007 - 0.70 ug/mL
24DNT	0.010 - 10.0 ug/mL

B. Tested Concentration Range (water concentration):

26DNT	0.0007 - 0.70 ug/L
24DNT	0.010 - 10.0 ug/L

C. Sensitivity:

Peak Height in mm at an attenuation of 2^3

26DNT	24 mm for 0.007 ug/mL (extract concentration)
24DNT	118 mm for 0.100 ug/mL (extract concentration)

D. Interferences:

Any compound that is solvent extractable, gas chromatographs, responds to an electron captive detection and elutes at the same retention time as the dinitrotoluenes.

E. Safety Information:

Work in well-ventilated areas. Wear adequate protective clothing to avoid skin contact. Wash skin with soap and water thoroughly immediately after contact.

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III. APPARATUS AND CHEMICALS

A. Instrumentation

1. Hewlett-Packard 5890 Gas Chromatograph equipped with 7362A Autosampler HP 3396A Integrator, and Nickel-63 electron capture detector.
2. Analytical balance capable of weighing 0.001 g for standard preparation.

3. Parameters

a. Column:

6' x 1/4" OD x 2mm ID glass packed with 1.5% SP2250/1.95% SP 2401 on 100/120 mesh supelcoport.

b. Conditions.

Injection port - 200°C
Detection - 300°C
Oven - 120°C - 180°C at 40°C/min.
Hold at 180°C for two minutes.
Injection size - 3 uL
Flow Rate - 50 mL/minute 5% Methane/ 95% Argon.

c. Retention Times:

2,6-DNT	8.5 - 9.5 minutes
2,4-DNT	10.5 - 12.0 minutes

B. ANALYTES

1. Chemical Abstracts Registry Numbers

2,6-DNT	606-20-2
2,4-DNT	121-14-2

2. Chemical Reactions

None. Explosives are measured directly on the GC.

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3. Physical Properties:

	Formula	Mol. Wt.	M.P. (°C)	B.P. (°C)
26DNT	<chem>C7H6N2O4</chem>	182.14	66	---
24DNT	<chem>C7H6N2O4</chem>	182.14	71	300 (decomposes)

D. REAGENTS and SARMS.

1. Water : Glass Distilled
2. Hexane : UV Grade
3. Methylene Chloride : Distilled in Glass
4. Methanol : Distilled in Glass
5. Glass Wool: Baked at 400°C overnight.
6. Sodium Sulfate: granular anhydrous - ACS reagent grade
7. Sodium Chloride: ACS reagent grade
8. Nitrogen: Prepurified
9. 5% Methane/95% Argon: P-5 grade
10. Standard Analytical Reference Materials:
2,6-DNT SARM No. 1148
2,4-DNT SARM No. 1147

IV. PRECERTIFICATION CALIBRATION

A. Initial Calibration

1. Preparation of Standards:
 - a. Stock calibration solutions for each isomer (i.e. two separate solutions) containing approximately 5,000 mg/L of dinitrotoluene are prepared by accurately weighing ca. 50 mg of a SARM into a 12 mL vial and dissolving the dinitrotoluene in 10 mL toluene pipetted into bottle.

b. Intermediate Calibration Standards

1). Intermediate Calibration Standard A
(High Level):

Assuming a nominal concentration of 5,000 mg/L for the stock solutions, prepare the following intermediate calibration mix by diluting the indicated amounts of stock calibration standards to 5.0 mL in a volumetric flask with hexane. Seal in a vial with a Teflon-lined cap and store in the freezer at 0-4°C.

<u>Compound</u>	<u>uL of Stock Calib. Std.</u>	<u>Resulting Conc. (ug/mL)</u>
2,6-DNT	70	70
2,4-DNT	1,000	1,000

2). Intermediate Calibration Standard B:

Make a serial dilution (1:10) of Intermediate Calibration Standard A by diluting 1.0 mL to a final volume of 10 mL with hexane. Seal with a Teflon-lined cap and store in the freezer at 0-4°C. The resulting solution will have the following concentration:

<u>Compound</u>	<u>Resulting Conc.</u>
2,6-DNT	7.0 ug/mL
2,4-DNT	100. ug/mL

3. Intermediate Calibration Standard C:

Make a serial dilution (1:10) of Intermediate Calibration Standard B by diluting 1.0 mL to a final volume of 10 mL with hexane. Seal with a Teflon-lined cap and store in the freezer at 0-4°C. The resulting solution will have the following concentration:

<u>Compound</u>	<u>Resulting Conc.</u>
2,6-DNT	0.7 ug/mL
2,4-DNT	10.0 ug/mL

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c. Working Calibration Standards:

Using the following table, prepare a series of eleven working calibration standards. Store in a Teflon-capped vial in a freezer at 0-4°C.

WORKING CALIBRATION STANDARDS

RELATIVE CONC.	AMT. (uL) INTERMED. CAL. STD. TO ADD			FINAL VOLUME	RESULTING CONCENTRATION (ug/mL)	
	A	B	C		2,6-DNT	2,4-DNT
0	0	0	0	10 mL	0	0
0.1x	-	-	10	10 mL	0.0007	0.01
0.2x	-	-	20	10 mL	0.0014	0.02
0.5x	-	5	-	10 mL	0.0035	0.05
1.0x	-	10	-	10 mL	0.0070	0.10
2.0x	-	20	-	10 mL	0.0140	0.20
5.0x	5	-	-	10 mL	0.0350	0.50
10x	10	-	-	10 mL	0.0700	1.00
20x	20	-	-	10 mL	0.1400	2.00
50x	50	-	-	10 mL	0.3500	5.00
100x	100	-	-	10 mL	0.7000	10.00

2. Instrument Calibration

- Set up the instrument according to the manufacturer's recommendations.
- Hexane is analyzed as a blank to verify a stable baseline.
- Analyze the medium calibration standard (10x) to verify peak separation and retention times.
- Analyze the calibration standards prepared in Section IV.A.1.c.

3. Analysis of Calibration Data

- Tabulate the calibration standard concentration versus the peak height response for each calibration standard.
- Perform a quadratic regression analysis on the calibration data plotting peak height vs. concentration in ug/L.

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4. Calibration Checks

- a. After completion of analysis of samples, a calibration standard at the highest concentration is analyzed. The response must agree within 25% for that concentration compared to the daily initial curve. If it does not, the calibration standard will be re-analyzed. If the calibration fails this test, initial calibration must be performed, and all samples analyzed since the last acceptable calibration must be re-analyzed.
- b. No certified calibration check standards are available for these compounds; therefore, the analyst will prepare a calibration check standard at a concentration near the high end of the daily calibration curve. This standard will be prepared from a separate stock solution using the procedure outlined in Section IV.A.1. It agree within $\pm 25\%$ of the true value as outlined in the preceding Section IV.A.4.a.

V. PROCEDURE

A. Separations

1. Using a permanent marker, draw a line on the sample bottle at the meniscus of the sample. Transfer the entire liter of sample to a liquid/liquid extractor, which already contains ca. 200 mL methylene chloride. Rinse the sample container with ca. 60 mL methylene chloride, adding to the liquid/liquid extractor. Add additional methylene/chloride to the extractor so that the methylene chloride level is sufficient to distill over. Fit the liquid/liquid extractor with a 500 mL round bottom flask (containing several Teflon boiling chips) in a heating mantle and water cooled condenser. Distill the methylene chloride for 16 hours.
2. Shut off after 16 hours of distillation, allow to cool.
3. Fill a three inch funnel approximately one-half full of anhydrous sodium sulfate after plugging the outlet with glass wool. Filter extract (contents of 500 mL round) bottom through glass wool into Kuderna Danish (KD) apparatus.

WESTON

4. Fit KD apparatus with a 3-ball Snyder column and distill to ca. 10 mL.
 5. Add 60 mL hexane and distill to ca. 5 mL
 6. Concentrate to 1.0 mL using a gentle system of nitrogen and store in 1.8 mL autosampler vial at 0-4°C until analysis.
- B. Chemical Reactions: None. Compounds are read directly on the GC.
- C. Instrumental Analysis:
1. Set the chromatographic conditions as indicated in section III.A.3.
 2. Instrument performance is checked during daily calibration with evaluation of the medium (10x) calibration standard (section IV.A.2).
 3. Once good peak separation is obtained, introduce 3 uL of each working calibration standard, samples, spikes and final standards into the chromatographic system using the manual injection manufacturer's recommended procedure.

VI. CALIBRATIONS

Plot response vs. ug/mL using a quadratic equation best fit. Obtain ug/mL in the sample extract from the calibration curve and divide by sample volume as shown:

ug/mL = Target concentration in extract from quadratic equation.

V = Sample volume in L.

D = Dilution, if necessary.

ug/mL - V x D₁₀ = ug/L target concentration in sample.

VII. REFERENCES

Method 8090, "Nitroaromatics and Cyclic Ketones", US EPA SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, November 1986.

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VIII. DATA

- A. Response versus concentration data.
- B. Response versus concentration graphs (not applicable, data are not linear).
- C. LOF Tests
- D. ZI Tests: Not applicable. Method fails lack of fit, as it is not linear in this low concentration range. Quadratic equations will be used for all calibration and sample calculation.

IX. Calibration Check Standard Results.

Calibration check standards were not analyzed. However, the stock solutions for pre-certification were checked against stocks prepared by another analyst, with the following results:

<u>2.6-DNT</u>	<u>Response Factor</u>	<u>SD</u>
E0088*	8160	
E00119**	8466	4%
<u>2.4-DNT</u>		
E0089*	5271	
E00116**	5376	2%

* Prepared by Denise Heebner Skrzat on 03/88

** Prepared by Abul Siddiqui on 01/89

Stocks E00119 and E00116 were used to prepare the EM0062 mix used for this pre-certification.

Method Name: DNT IN WATER
Compound: 24DNT
Units of Measure: UGL

Laboratory: WN
Analysis Date: 01/18/99
Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
 $Y = (15658.24560) + (71.28280000)X$ $Y = (73.70246410)X$

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	7846321960	18	435906775.6	11878033100	19	625159636.3
Total Error:	13099005	10	1309900.500	13099005	10	1309900.500
Lack of Fit:	7833222955	8	979152869.4	11864934095	9	1318326011

LOF F-Ratio(F): 747.5017143

LOF F-Ratio(F): 1006.432176

Critical 95% F: 3.07

Critical 95% F: 3.02

Data Not Linear

Data Not Linear

ZERO INTERCEPT HYPOTHESIS

** Models not linear. Do not test Zero Intercept hypothesis.

Diagnose and correct analytical system before continuing.

TABLE OF DATA POINTS

Targets: 10

Measures per Target: 2

	Target Value	Instrument Values	
1:	10	1340	1482
2:	20	2748	2947
3:	50	6654	7101
4:	100	12815	13558
5:	200	24936	25015
6:	500	55494	56138
7:	1000	104584	103812
8:	2000	190549	192041
9:	5000	406425	408316
10:	10000	702383	706692

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*** END OF PRE-CERTIFICATION DATA TABLE ***

PREPARATION OF STOCK STANDARD (SINGLE COMPONENT)

ORD #	COMPOUND	SOURCE & LOT#	% PURITY	FINAL WT. (mg)	TARE WT. (mg)	NET WT. (mg)	PURITY ADJUSTED NET WT.	SOLVENT	TOTAL VOLUME (mL)	FINAL CONC.	UNITS	DATE/ANALYST
12	Cyanogen chloride	USA 11111111	97%			10.5mg	10.5mg	water	10mL	1.05mg/mL	mg/mL	2H 11/2/88
13	Penta Chlorophenol	Aldrich 92004 (87-8-5)	99%	11.73542	11.61887	125.65	125.05	Isopropanol	10mL	12.505mg	mg/mL	AS 12/27/88
14	2,4-DNT #1	3-88	-	11.51193	11.46340	50.57	-	Toluene	10mL	5.057mg	mg/mL	AS 11/9/87
15	2,4-DNT #2	3-88	-	11.51138	11.46390	47.98	-			4.798mg		
16	2,4-DNT #3	3-88	-	11.55627	11.48865	47.62	-			4.762mg		
17	2,6-DNT #1	3-88	-	11.50400	11.45113	47.07	-			4.707mg		
18	2,6-DNT #2	3-88	-	11.55323	11.50318	49.25	-			4.925mg		
19	2,6-DNT #3	3-88	-	11.55483	11.50458	50.25	-			5.025		

PREPARATION OF STOCK STANDARD (SINGLE COMPONENT)

[illegible]

#4 1/10,000 E0089
in Heran
2.4 TNT

0.03

0.19

1.57

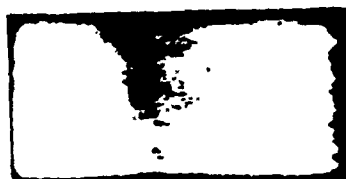
IF RUN # 4
BOTTLE # 4
HEH %

JUN/09/89

TIME 19:03:30

RT	HEH	HEH %
0.22	27	0.001
0.42	113300	2.147
0.55	2344	0.006
1.12	768	0.005
1.24	114	0.002
1.53	1010	0.003
1.95	72	0.002
2.23	273	0.005
2.35	138	0.003
2.59	63	0.001
2.75	28	0.001
3.25	1005	0.004
3.30	39	0.001
3.83	105600	2.001
5.19	657	0.012
7.57	5050000	95.699

UTL FRICTION: 1.0000 E+ 0



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7 1/10,000 E0088 in Hexan
2.6 DNT

3.22
3.22
3.22

5.02

7.45
8.37
10.15
11.47
13.18
13.58
14.54

IT RUN # 8
SUTILE 8
FREQ %

JUN/09/89

TIME 20:16:26

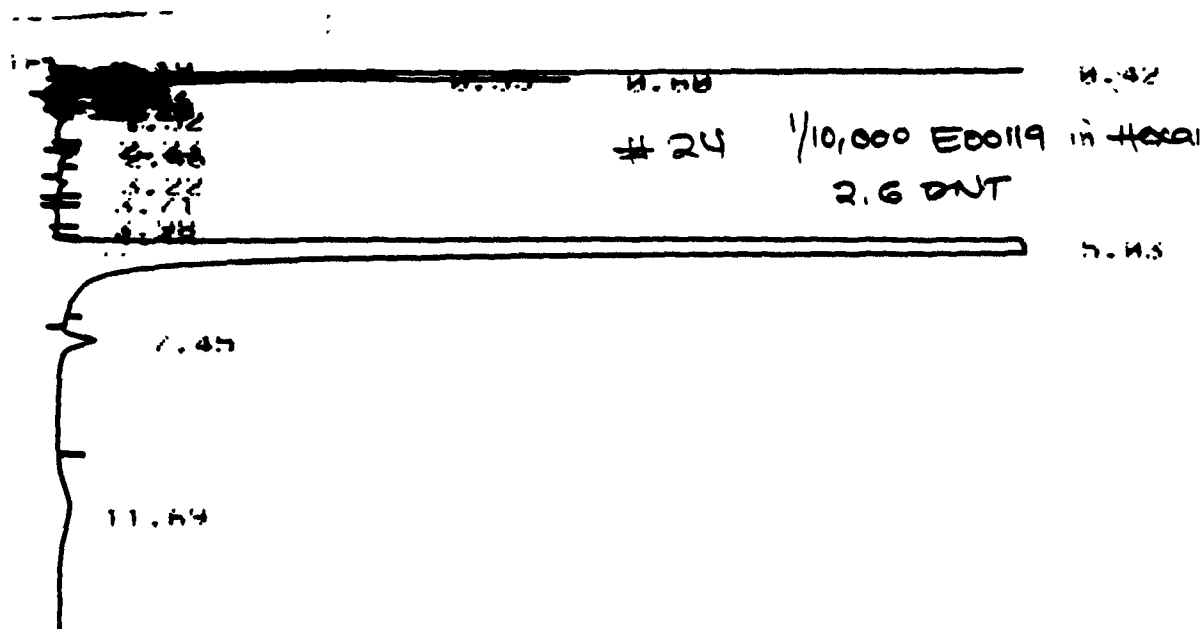
IT	FREQ	FREQ %
0.00	27	0.000
0.42	114100	1.538
0.80	4374	0.059
1.16	26	0.000
1.24	75	0.001
1.52	1596	0.022
2.08	41	0.001
2.21	114	0.002
2.45	4877	0.055
3.22	1629	0.022
4.07	17	0.000
5.02	7262000	97.905
7.45	26298	0.361
8.44	27	0.000
8.67	248	0.003
10.15	119	0.002
11.47	268	0.004
13.18	74	0.001
13.58	14	0.000
14.54	325	0.004

01E FREQ: 1.0000 E+ 0



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STWRT



HP WITH # 24
BUTLE 24
HREN %

JUN/10/89

TIME 02:16:46

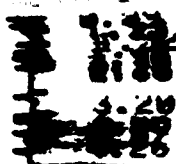
HP WITH # 24
BUTLE 24
HREN %

HP	HREN	HREN %
0.14	15	0.000
0.42	115100	2.501
0.55	4752	0.107
0.93	72	0.002
1.13	194	0.004
1.23	117	0.003
1.52	5954	0.089
2.23	288	0.007
2.45	2096	0.047
3.22	1621	0.037
3.98	93	0.002
5.03	4254000	96.141
7.45	13030	0.294
11.69	29410	0.665

OIL FACTOR: 1.000 E+ 0



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27 4/10,000 E00116 in Hexa
2.4 DNT

6.20

5.03

7.39

12.29

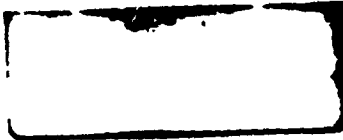
HP RUN # 27
BUTLE 27
AREA %

JAN/10/89

TIME 03:10:25

RT	AREA	AREA %
0.42	111700	4.031
0.55	5722	0.207
0.89	104	0.004
1.13	215	0.008
1.23	271	0.010
1.52	2149	0.078
1.71	106	0.004
1.95	20	0.001
2.23	332	0.012
3.20	1767	0.064
3.63	34	0.001
3.75	44	0.002
4.07	26	0.001
5.03	82380	2.973
6.20	296	0.011
7.39	2560000	92.394
12.29	5585	0.202

01L PHOTON: 1.0000 E+ 0



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CASE NARRATIVE

Samples have been prepared and analyzed according to USATHAMA Method UH18.

The following QA/QC control samples have been analyzed concurrently with each extraction batch. Abbreviations noted below have been used in the data summary.

Abbreviation

Description

Blank - USATHAMA standard matrix (soil or water) analyzed to provide an indication of lab contamination and it's effect on reported analytical data.

Samples (soil or water) are spiked with target compounds to provide precision and accuracy data.

SS - USATHAMA standard matrix spiked with target compound.

SSD - USATHAMA standard matrix spiked with target compound in duplicate.

D - Indicates duplicate analysis of a sample.

NS - Not spiked.

DL - Diluted below calibration range.

G - Indicates elevated detection limit due to sample interference.

J - Present below certified reporting limit.

NR - Not reported.

NOTE: Spikes have been reported as result (% recovery).

NOTE: Soil results are reported in a dry weight basis.

Data Qualifiers:

< - Less than

> - Greater than

Analysis Summary:

Weston Analytical Batch: 8902L479
Samples Collected: 02-16-89; 02-17-89
Samples Prepared: 02-21-89
Samples Analyzed: 02-27-89

APPROVED BY

George Perry
George Perry
HPLC Unit Leader
Lionville Analytical Laboratories

WESTON ANALYTICS
WATER EXPLOSIVES DATA

RFW Batch Number: 8902L479

CLIENT: USATHAMA-BAAP

Page: 1

Sample Information

Client	21689	21689	21789	21789	----
ID :	1000/A1	1000/B1	1000/A1	1000/B1	
RFW#:	001	002	012	013	BLANK
D.F.:	1	1	1	1	1
Units:	ug/L	ug/L	ug/L	ug/L	ug/L

2,6-DNT.....	0.048	0.102	0.200	0.063	< 0.018
2,4-DNT.....	< 0.458	< 0.458	< 0.458	< 0.458	< 0.458

Sample Information

Client	----	----	----
ID :	2XSS	10XSS	10XSSD
RFW#:	1	1	1
D.F.:	1	1	1
Units:	ug/L	ug/L	ug/L

2,6-DNT.....	0.013J(36.1%)	0.171(95.0%)	0.168(93.3%)
2,4-DNT.....	0.537(58.6%)	4.28(93.4%)	4.26(93.0%)

CASE NARRATIVE

Samples have been prepared and analyzed according to USATHAMA Method UH18.

The following QA/QC control samples have been analyzed concurrently with each extraction batch. Abbreviations noted below have been used in the data summary.

Abbreviation

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Blank - USATHAMA standard matrix (soil or water) analyzed to provide an indication of lab contamination and it's effect on reported analytical data.

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SSD - USATHAMA standard matrix spiked with target compound in duplicate.

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G - Indicates elevated detection limit due to sample interference.

J - Present below certified reporting limit.

NR - Not reported.

NOTE: Spikes have been reported as result (% recovery).

NOTE: Soil results are reported in a dry weight basis.

Data Qualifiers:

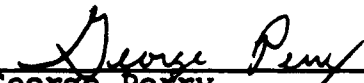
< - Less than

> - Greater than

Analysis Summary:

Weston Analytical Batch: 8902L460
Samples Collected: 02-16-89
Samples Prepared: 02-21-89
Samples Analyzed: 02-27-89

APPROVED BY


George Perry
HPLC Unit Leader
Lionville Analytical Laboratories

WESTON ANALYTICS
WATER EXPLOSIVES DATA

RFW Batch Number: 8902L460

CLIENT: USATHAMA-BAAP

Page: 1

Sample
Information

Client 21509
ID : 1000/A1
RFW#: 001
D.F.: 1
Units: ug/L

2,6-DNT..... 0.013J
2,4-DNT..... < 0.458