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GRANULAR ACTIVATED CARBON (GAC) SYSTEM PERFORMANCE CAPABILITIES AND OPTIMIZATION

MRI Project No. 8182-S, Final Report

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Prepared for
COMMANDER, U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
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Performance tests were conducted to determine the capability of granular activated carbon (GAC) to adequately treat pink water (munitions wastewater) from Army ammunition plants (AAPs). Comparative isotherm tests were conducted with five GACs to recommend an optimized grade for pink water treatment and to study temperature and compositional effects. Target effluent criteria of 0.04 mg/L for trinitrotoluene (TNT), 0.03 mg/L for cyclotrimethylenetrinitramine (RDX) or cyclotetramethylenetetranitramine (HMX), and 0.0007 mg/L for 2,4-dinitrotoluene (2,4-DNT) were achieved in the isotherm tests. Pilot scale multiple column tests were conducted at Iowa AAP to determine GAC capabilities under typical operating conditions. The effluent criteria were generally met for RDX, HMX, and 2,4-DNT but not for TNT.

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PREFACE

This report was prepared for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAK11-84-C-0070 by Mr. Gary Hinshaw, Ms. Cindy Fanska, Mr. Douglas Fiscus, and Mr. Scot Sorensen of Midwest Research Institute. Other Midwest Research Institute personnel who assisted in this project are Ms. Audrey Sanford, Mr. Steve Cummins, Mr. David Griffin, Mr. Christopher Bowles, and Mr. Randy Nelson. Mr. Hinshaw was the project leader, under the direction of Mr. Fiscus. Ms. Fanska led the analytical chemistry operations.

This report lists the results of tests of granular activated carbon (GAC) in reducing nitrobodies in U.S. Army ammunition plant wastewaters and discusses the suitability of granular activated carbon in achieving low nitrobody concentrations in effluent discharges.

Pilot scale column tests were conducted at Iowa Army Ammunition Plant, which is contractor-operated by Mason & Hanger - Silas Mason, Inc. Mason & Hanger personnel who assisted MRI included Mr. Elmer Pollpeter, Mr. Gail Allen, and Mr. Leon Shahan. The cooperation, efforts, and suggestions of these and other Mason & Hanger and Army personnel are gratefully acknowledged.

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1. SUMMARY

Recommended interim water quality criteria for the munition compounds trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), and 2,4-dinitrotoluene (2,4-DNT) are several orders of magnitude lower than present discharge standards. Using these values (0.04 mg/L for TNT, 0.03 mg/L for RDX or HMX, and 0.0007 mg/L for 2,4-DNT) as point source effluent criteria, performance tests were conducted to determine the capability of granular activated carbon (GAC) to adequately treat pink water (munitions wastewater) from Army ammunition plants (AAPs). Comparative isotherm tests were conducted with five GACs to recommend an optimized grade for pink water treatment and to study temperature and compositional effects. The effluent criteria were achieved in the isotherm tests, and were generally achieved in preliminary column tests conducted in the laboratory. Pilot scale multiple column tests were then conducted at Iowa AAP to determine GAC capabilities under typical operating conditions (e.g., 6 gpm/ft^2 hydraulic loading rate and 8 min contact time). The effluent criteria were generally met for RDX, HMX, and 2,4-DNT but not for TNT.

2. INTRODUCTION

2.1 BACKGROUND

Granular activated carbon (GAC) columns are employed at Army ammunition plants (AAPs) to remove nitrobodies from pink water (wastewater from the manufacture, handling, and packaging of munitions) prior to discharge into the environment. The nitrobodies of greatest concern are TNT (2,4,6-trinitrotoluene), RDX (cyclotrimethylenetrinitramine), HMX (cyclotetramethylenetetranitramine), and 2,4-DNT (2,4-dinitrotoluene). Allowable nitrobody concentrations in the effluent discharge after GAC treatment are presently regulated by the various state pollution control agencies. There is a concern that these regulations may become more stringent in the future.

2.2 EFFLUENT DISCHARGE REGULATIONS

2.2.1 Present Regulations

It is beyond the scope of this project to list all effluent discharge regulations at all AAPs. Table 2-1 lists 1984 regulations at six AAPs which are believed to be typical of current discharge standards. The regulations may be written for TNT, RDX, a combination, or total nitrobodies. The allowable discharge levels range from 0.3 to 25 mg/L, or 0.3 to 15.0 mg/L where GAC treatment is used.

Because no serious operational problems are documented, the conclusion is reached that current GAC columns have the capacity to meet the type of discharge limits listed in Table 2-1.

2.2.2 Future Regulations

Interim environmental criteria were developed by the U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) to anticipate future effluent limitations for munition compounds. These criteria are used by USATHAMA to assess current pollution abatement technologies and where current technologies are inadequate to identify areas where research is needed to meet the proposed effluent criteria.

Based on available toxicology studies and methodologies proposed by the U.S. Environmental Protection Agency (Federal Register, 43, 21506-21518, 1978; and Federal Register, 44, 15926-15981), the following interim criteria for munition compounds were recommended for the protection of human health:

Nitrobody munition compound	Recommended interim criteria (mg/L)
TNT	0.04
RDX	0.03
HMX	0.03
2,4-DNT	0.0007

In this study, these values were used as the point source effluent criteria.

For individual compounds, the recommended criteria are an order of magnitude lower than present standards. Also, the total of all four proposed nitrobody concentrations is only 0.1007 mg/L, which in most cases is an order of magnitude lower than the present single compound standards. Therefore, recommended interim criteria could severely challenge GAC capability.

2.3 RESEARCH NEED

While much is known about the capabilities of GAC, gaps were found in the data on the removal efficiency of unique military contaminants by a GAC column. The capability of GAC to reduce nitrobody concentration has been reported[3,21] to be as low a level as 0.1 mg/L. Data on TNT only[21] indicates that a TNT concentration of 0.04 mg/L can be achieved. However, there is no supportive literature to indicate that levels of 0.03 mg/L for RDX and HMX, and 0.0007 mg/L for 2,4-DNT can be achieved. Also, while some work has been done on competitive adsorption when more than one nitrobody is present in pink water, investigations[3] have not been conducted at levels below 0.2 mg/L.

The net result is that uncertainty exists concerning the capability of GAC to achieve proposed effluent discharge limits well below what has previously been measured. This uncertainty presents a serious problem should the allowable discharge limits for nitrobodies become more stringent, resulting in the need for a research program aimed at evaluating and optimizing the performance of GAC columns in treating pink water.

2.4 OBJECTIVES

In general, the objective of this program was to perform research studies which will provide quantitative data on the capability of GAC to remove the nitrobodies TNT, 2,4-DNT, RDX, and HMX from pink water under conditions found at AAPs. AAPs tend to use single GAC columns or in some cases two columns in series. It has been theorized that four columns in series is necessary to achieve the more stringent proposed effluent nitrobody levels and to achieve maximum GAC usage. While the main thrust of the program was the development of the four columns in series system, tests were also conducted on a single GAC column. These tests aided in the design of the columns in series system and provided comparative data to current AAP column practice. Bench or pilot scale equipment was scaled down allowing test results to be readily extrapolated to actual AAP conditions.

Comparative tests with carbons currently in use at the AAPs and other selected grades of commercially available carbon were done so that an optimized grade of activated carbon for pink water treatment could be recommended. Based on these results, further efforts were made to optimize system configuration and operational modes and to determine the economic impact of the optimized conditions.

The best estimate of the concentrations of munition nitrobodies in pink water found at AAPs and the reduction required to meet possible future effluent discharge limits are as follows.

Nitrobody	Pink water concentration (mg/L)	Possible or proposed allowable effluent discharge concentration (mg/L)	(μg/L)	Reduction required (%)
TNT	100	0.04	40	99.96
RDX	30	0.03	30	99.90
HMX	10	0.03	30	99.70
2,4-DNT	1	0.0007	0.7	99.93

Pink water is a generic term for munition wastewater produced at load, assemble, and pack (LAP) facilities and projectile washout facilities. The coloration arises from photolysis of α-TNT or hydrolysis in the presence of alkali.[17,23] However, pink water may also contain varying levels of RDX and HMX, depending on the particular formulation being handled. The nitrobody 2,4-DNT is not strictly an explosive munitions compound, but is a byproduct in the manufacture of TNT and is normally present in pink water at low levels. Acetylated decomposition derivatives of RDX and HMX are other impurities normally present.[4,21]

Depending on the munition formulations handled at a particular AAP, pink water may contain all four nitrobodies of interest, or only TNT and 2,4-DNT, or only RDX and HMX.

Specifically, the objective of this program was to provide an answer to the following questions:

- For typical pink water occurring at AAPs, can GAC achieve effluent concentrations equal to or below the possibly more stringent limitations listed above?

  If so, then:

- What are the optimum operating parameters for a four column in series GAC treatment system, and

- What are the economics of constructing and operating such systems?

TABLE 2-1. Pink Water Discharge Regulations.[a]

Facility		Discharge designation	Discharge limit, mg/L				Present treatment method
AAP	State		Total nitrobodies	TNT/RDX	TNT	RDX	
Iowa	Iowa	Daily average	-	1.0	-	-	GAC
Kansas	Kansas	Average	-	-	-	0.5	GAC
		Maximum	-	-	-	1.0	GAC
Lone Star	Texas	Daily average	-	-	0.3	-	GAC
		Maximum	-	-	15.0	-	GAC
Louisiana	Louisiana	Average	-	-	2.0	-	GAC
		Maximum	-	-	5.0	-	GAC
McAlester	Oklahoma	Average	-	-	0.3	15	Lagoon
		Maximum	-	-	1.0	25	Lagoon
Milan	Tennessee	Monthly average	1.0	-	-	-	GAC
		Maximum	1.5	-	-	-	GAC

NOTE: - = None specified.

[a] Existing regulations in 1984.

3. GAC ADSORPTION THEORY

3.1 GENERAL THEORY OF GAC ADSORPTION

Adsorption is a mass transfer process wherein components of a fluid are deposited on the surface of an adsorbent by surface forces. GAC has been found to be an excellent adsorbent for organics. Adsorption theory is that organic molecules are attracted to a carbon surface by Van der Waals (non-bonded) forces. The Langmuir equation which describes monomolecular adsorption is:

$$q_e = \frac{Q^{\circ}bC_e}{(1+bC_e)}$$

q_e = weight (or number of moles) of solute adsorbed per unit weight of carbon
C_e = concentration of pollutant left in solution (residual or equilibrium concentration)
Q° = weight (or number of moles) of solute adsorbed per unit weight of carbon to form a complete monolayer on the carbon surface (i.e., to completely saturate the adsorption capacity of the carbon)
b = constant related to the energy or net enthalpy or adsorption

Because the GAC effective surface area gradually decreases as the solute is adsorbed, considerably more GAC must be provided than that required for startup. To normalize various GAC bed configurations, GAC rating data are usually given in terms of the weight of solute per unit weight of GAC (q_e).

3.2 ISOTHERM THEORY

An adsorption isotherm test is a batch adsorption test used to determine the maximum adsorption capability of GAC. An adsorption test is actually a series of individual batch tests performed in the laboratory under standardized conditions and is of course valid only for the temperature at which the tests were conducted. In the isotherm tests all conditions are kept the same except for varying the carbon dosage (grams of carbon/gram of solute).

While the Langmuir equation is an expression of adsorption theory, an empirical model is commonly used in isotherm wastewater treatability studies because of the convenience of use in determing q_e from laboratory batch isotherm tests.

A model of isothermal adsorption is the Freundlich equation which relates the amount of pollutant in a solution to the amount adsorbed. The Freundlich equation is:

$$q_e = \frac{x}{m} = K\,C_e^{1/n}$$

q_e = weight of solute adsorbed per unit weight of carbon
x = weight of solute adsorbed per unit volume = $C_o - C_e$
m = weight of carbon per unit volume
K = constant (sometimes expressed as K_F for Freundlich constant)
n = constant
C_e = concentration of pollutant left in solution (residual or equilibrium concentration)
C_o = initial concentration in solution before contacting GAC (used to calculate m)

In logarithmic form the equation becomes $\log q_e = \log \frac{x}{m} = \log K + \frac{1}{n} \log C_e$, where 1/n is the slope of the straight line isotherm. By varying m and measuring C_e, x is determined ($C_o - C_e$) and a plot of log q_e versus log C_e is easily obtained for as many different GAC dosages (m) as desired. With the isotherm line slope known, the q_e for any desired C_e can be determined.

The Frendlich equation assumes a linear relationship between log q_e and log C_e. This may not always be the case, especially when more than one solute compound is present and competitive adsorption takes place. However, the modeling approach of the Freundlich equation can still be used. The equation of q_e and C_e can be derived by computerized least squares curve fit methods for a variety of curvilinear relationships, allowing q_e to be predicted for any desired C_e.

The advantage of isotherms is that various GACs can be tested relatively quickly in the laboratory for performance in adsorbing a particular compound and the GAC with the best performance selected. Also, the effects of temperature, and influent solution composition can be readily tested.

3.3 COLUMN THEORY

Adsorption theory applies to a column as well as to a batch isotherm test. But a column is a dynamic system with fresh solution always being presented to the GAC. Thus, the concept of GAC in equilibrium with a solution concentration does not apply. The three important concepts that govern GAC column operation are breakthrough, hydraulic loading, and pressure drop. These are discussed next.

3.3.1 Breakthrough

The most important parameter for a continuous flow column is the operating line or breakthrough curve for the column. The operating line is a measure of the effluent concentration (C_f) versus the weight of solute per weight of GAC (q_e). For a given column diameter, bed depth, and packing density, the weight of carbon is fixed. As flow continues in time, the weight of adsorbed solute increases and q_e increases. Solute adsorption continues, at a rate unique to the GAC used and the solute concentration, until the adsorptive capacity of the GAC is reached, at which time the effluent concentration equals the influent concentration (C_o). This is termed breakthrough.

$$\text{Breakthrough:} \quad q_e \text{ when } C_f = C_o$$

The operating line is an expression of q_e versus C_f for a continuous flow column, while an isotherm is an expression of q_e versus C_e for a batch system. An equilibrium curve can be plotted from the isotherm data by plotting the equilibrium concentration (C_e) corresponding to an adsorbed concentration q_e measured in the isotherm tests. However, the measure of C_f versus q_e for a dynamic system will be different than the measure of C_e

versus q_e for a static system. Thus for a given q_e, the actual effluent concentration will be greater than that predicted from isotherm data, or:

$$C_f > C_e \text{ for a given } q_e$$

Knowledge of breakthrough is very important for maximizing GAC usage. In a multiple column wastewater treatment facility it is important to maximize GAC usage so as not to waste GAC. Operating the first column in a series until breakthrough occurs insures that the GAC in the first column has achieved its maximum adsorption capability. Knowledge of q_e at breakthrough is necessary to predict when the first column in a series needs to be changed.

3.3.2 Hydraulic Loading

Aqueous flow to a carbon adsorption column is expressed as hydraulic loading, which is the gallons per minute (gpm) of flow per unit cross-sectional area (ft^2) of the carbon column. This expression is equivalent to velocity as follows:

Hydraulic loading:

$$\text{gpm/ft}^2 \text{ of column} = \frac{(\text{gal})(\text{ft}^3)}{(\text{min})(\text{gal})(\text{ft}^2 \text{ of column})} = \text{ft/min} = \text{face (superficial) velocity}$$

Thus, for any given hydraulic loading, the velocity of the fluid impacting the carbon column surface is independent of column diameter. Therefore, results for a specific hydraulic loading can be directly transferred from one column diameter to another, such as from a laboratory bench scale test to a full scale unit.

For a given GAC, as hydraulic loading increases the pressure drop increases. Obviously, lower pressure drops are desired because of the resulting lower operating costs. It has been found, however, that there are practical limits to hydraulic loading due to GAC adsorption characteristics. At low hydraulic loadings (below 2 gpm/ft^2), a stagnant film can surround the individual GAC particles. The solute in this film is depleted more rapidly than it can be replaced by diffusion from the balance of the solution in the system. In this situation, the diffusional resistance across the film is the controlling factor, not the rate of GAC adsorption.

At high hydraulic loadings (above 10 gpm/ft^2), the solution is moving past the individual GAC particles faster than the ability of the GAC to adsorb the solute. Adsorption is essentially a monolayer phenomenon. At high hydraulic loadings, the monolayer does not have time to form properly.

It has been found[15] that for most organics, hydraulic loading within the range of 2 to 10 gpm/ft^2 is not a limiting factor to GAC adsorption.

3.3.3 Pressure Drop

Pressure drop per unit length of bed depth is a function of hydraulic loading and GAC particle size. The basic expression of pressure drop is:

$$\Delta P = \frac{KvVL_c}{(D_p)^2 D_c}$$

where ΔP = pressure drop (inches of water)
K = constant
v = viscosity (centipose)
V = flow rate (gpm)
L_c = GAC bed depth (ft)
D_p = mean GAC particle diameter (mm)
D_c = column diameter (ft)
Pressure drop ratio = $\Delta P/L_c$
LD ratio = L_c/D_c

Within the range of 2 to 10 gpm/ft^2, the pressure drop ratio can be expected to range from 0.4 to 11 in.H_2O/ft for commercial grades of GAC.[15]

4. SELECTION OF CANDIDATE GACs

4.1 DEFINITION OF GAC PROPERTIES

GAC is characterized by several physical and chemical properties which are useful in determining an initial selection. Table 4-1 lists the usual properties described for GAC and their definitions.

One of the most important properties is surface area. Adsorption is essentially a monolayer surface phenomenon. The GAC manufacturing processes results in a highly developed pore structure within GAC particles. The walls of these pores provide an internal surface area orders of magnitude larger than that provided by the outer surface of the GAC granule. Including the outer surface and the internal pore structure, the specific surface area is normally 500 to 1,500 m^2/g, which accounts for the high adsorption capability of GAC. In selecting a GAC, all other properties being equal, the highest specific surface area is desired.

Another important property is pore size. The internal pore structure of GAC is a maze of interconnecting channels, each channel being large at the particle surface and terminating in very small channels in the particle interior. Conventional GAC terminology classifies pore sizes into three groups as follows.

Pore diameter, Å	Classification
< 100	Micropores
100 to 1,000	Transitional pores or meso pores
> 1,000	Macropores

Most of the adsorption process takes place in the micropores. There is no direct measure of pore size, although a standard test is used to measure pore volume. High pore volume is desirable based on the assumption that it also results in a high specific surface area. The closest measures of pore diameter are iodine and molasses numbers. The iodine number is an indication of GAC ability to absorb low molecular weight molecules and assumably measures micropores of < 40 Å diameter. The molasses number is an indicator of the ability of GAC to adsorb higher molecular weight molecules and assumably measures micropores of diameter > 40 Å and meso pores of diameter 100 to 1,000 Å. For AAP purposes, munitions are higher molecular weight molecules (168-296); thus, a higher molasses number is desirable. Also, the ability to remove taste and odor (phenol number) is a desirable quality since pink water may be discharged to rivers and streams after clean-up by GAC.

GAC granular size is expressed by a variety of measures such as mean particle diameter, effective size, and uniformity coefficient. However, most GACs are defined by the manufacturer by the sieve sizes through which most of the GAC passes and is retained. For example, the sieve designation 8 x 30 means that the majority of the GAC passes a No. 8 sieve but will not pass a No. 30 sieve. The primary importance of granular size is that the smaller sizes generally pack tighter in a column and have higher column pressure drops. For example, a 12 x 40 sieve designation GAC would be expected to have a higher pressure drop than an 8 x 30 GAC, all other things being equal. The larger granular sizes are preferred because lower pressure drops mean lower operating costs. However, it is generally believed that in a GAC column, GACs with smaller mean particle diameters will remove impurities to lower levels. This does not necessarily mean that the adsorption of the individual GAC particles is better, but that the total column operates better. Thus, a dichotomy exists in that large sieve size is desirable for low pressure drop, but small particle size and thus small sieve size is desirable for pollutant removal to low effluent concentrations.

GAC density can be measured in a variety of ways. The most meaningful measure is bulk density, backwashed and drained, as this measures the actual GAC column volume needed. Higher density results in smaller columns for the same weight of GAC, resulting in lower capital costs.

Obviously low moisture and ash is desired. Also, high resistance to degradation during handling (abrasion number) is desirable.

4.2 GAC MANUFACTURERS

There are a relatively large number of sources of supply for activated carbon. The 1983 Thomas Register lists 43 different firms that sell activated carbon. It is unknown if all of these firms actually manufacture activated carbon that they sell and how many of these firms actually sell GAC that would be suitable for treating pink water. Such a survey is beyond the scope of this study.

Discussions with personnel from the following four AAPs revealed that the majority, if not all, AAPs use Calgon Filtrasorb 300 GAC.

- Radford AAP
- Louisiana AAP
- Iowa AAP
- Kansas AAP

However, one AAP representative recommended that Calgon Filtrasorb 200 be investigated because it is lower in cost than Filtrasorb 300. Filtrasorb 200 is expected to have lower adsorption capacity than Filtrasorb 300, but in theory, the lower cost would more than offset the lower adsorption capacity.

In addition to Calgon, three other GAC manufacturers were identified from the literature.[14,15] Telephone contacts verified the firms' familiarity with pink water treatment, and their GACs were judged to be candidates for AAP use. These firms are:

- ICI Americas
- Westvaco
- Witco

Other firms may produce equally suitable GACs, but to seek them out would be a lengthy process that is not within the scope of this project.

4.3 PUBLISHED GAC PROPERTIES

ICI, Westvaco, and Witco all produce a GAC similar to Calgon Filtrasorb 300 in that they are all 8 x 30 sieve size. Table 4-2 lists the properties of Calgon Filtrasorb 200 and 300 and the GACs similar to Filtrasorb 300 produced by the other three manufacturers. Data are available from the manufacturers' product data bulletins or literature references on all GAC properties except phenol number; however, no single GAC has information available for all other properties. Properties are generally similar, although for the important property of surface area, Hydrodarco 3000 and Filtrasorb 200 have lower surface areas than the other three GACs.

The primary objective of this study was to determine the ultimate capability of GAC in removing nitrobodies from pink water to very low levels ranging from 0.7 to 40 ppb. Because it is desired that final concentrations be in this low ppb range, ultimate adsorption capability takes precedence over other considerations such as pressure drop. When asked which GAC would provide the best pink water adsorption performance, all four manufacturers were unanimous in recommending GACs different from those shown in Table 4-2. Their recommendations are:

Manufacturer	Recommended GAC for pink water	Mesh size
Calgon	Filtrasorb 400	12 x 40
ICI	Darco H 85	8 x 30
Westvaco	WV-G	12 x 40
Witco	Witcarb 950	18 x 40

Table 4-3 lists the properties of these GACs. As in the case of Table 4-2, some data are available on all GAC properties, but no individual GAC has specifications for all the properties listed.

Filtrasorb 400 has the highest listed surface area of any GAC, although the range listed overlaps the other two GACs.

Figure 4-1 shows the pressure drops of the GACs listed in Tables 4-2 and 4-3 in the recommended hydraulic loading range of 2 to 10 gpm/ft^2. As would be expected, the pressure drop ratios of the larger GACs are all lower than the smaller sized GACs with the exception of Westvaco Nuchar WV-G. All manufacturers list temperature for the rated pressure drop ratio. These temperatures are also shown in Figure 4-1.

As expected, GAC costs are similar among manufacturers. Table 4-4 lists costs of truckload lots and the minimum weight definition of a truckload lot, which varies from 24,000 to 32,000 lb depending on the manufacturer. Truckload lots in actual practice would generally be heavier than these minimums, but Table 4-4 lists the minimum purchase necessary to receive the truckload lot price. All cost comparisons are made using the Table 4-4 truckload lot prices, which are the lowest manufacturer's published prices as of January 1985. These prices do not take into account any price reductions for extremely large volumes, long term purchasing agreements, etc., that might be negotiated in individual AAP purchasing contracts.

For less than truckload lots, prices are higher and the price classification by weight category is different for each manufacturer. Included as background information are the various less than truckload lot prices (Table 4-5).

4.4 SELECTION OF FIVE GACs FOR ISOTHERM TESTS

The test plan calls for selection of five GACs for isotherm tests.

Criteria for selection are:

- Adsorption - GACs with the best adsorption capability
- Popular use - GACs most often used at AAPs

- Pressure drop - lowest Δp GACs
- Cost - lowest priced GACs

Pink water adsorption was unknown prior to conducting the isotherm tests. However, the various GACs can be ranked according to their published adsorption properties (Tables 4-2 and 4-3) providing some insight as to expected adsorption characteristics. Also, cost (Table 4-4) and pressure drop data (Figure 4-1) are known. Table 4-6 ranks the various GACs according to all their published properties and costs.

Calgon Filtrasorb 400 ranks first in surface area and second in pore volume, iodine number, and particle diameter. Assuming that these properties indicate high adsorption capability, then Filtrasorb 400 is an obvious choice for a high ranked adsorption capability GAC. Filtrasorb 400 ranks seventh in pressure drop ratio and last in cost (with one other GAC). However, based on the assumption that high adsorption capability takes precedence over low price and pressure drop, then Filtrasorb 400 is an obvious choice for a candidate test GAC.

Westvaco WV-G and Witco Witcarb 950 rank second in surface area and first in iodine number. Neither have pore volume data available. WV-G ranks third in particle diameter, but Witcarb 950 does not have particle diameter data available. WVG ranks second in pressure drop along with Filtrasorb 300 and is third in cost. Therefore, Westvaco WV-G is an obvious second choice for a candidate GAC because of good adsorption properties, pressure drop ratio, and cost. The Witcarb 950 is last in pressure drop and seventh in cost. However, it is selected as a candidate GAC because it ranks second with WV-G in surface area and iodine number and is recommended by the manufacturer for pink water treatment.

The fourth GAC selected is Calgon Filtrasorb 300 because it is the GAC now in use by AAPs and test data on this GAC will provide a base line of comparison of laboratory GAC results to AAP operating experience. Table 4-6 shows that Filtrasorb 300 ranks third in surface area and pore volume, fourth in iodine number, fifth in mean particle diameter, second in pressure drop, and sixth in cost.

The fifth GAC selected for testing is Calgon Filtrasorb 200. While Filtrasorb 200 ranks first in particle diameter, there is no pore volume data available and it ranks next to last in surface area, iodine number, and pressure drop. Also it is only medium priced. However, as previously discussed, it is included as a candidate test GAC because of an AAP's recommendation that a Calgon GAC that is lower priced than the currently used Filtrasorb 300 be tested.

Property data from manufacturers and literature references were obtained for nine different GACs that potentially could be used to treat pink water. The five selected for isotherm tests and their property rankings are listed in Table 4-7.

This selection is based on available data. However, phenol number, molasses number, and carbon tetrachloride activity were not used because not enough GACs have these properties listed to allow a meaningful comparison. Also, of the five selected GACs, only two had pore volume data and one did not have particle diameter data. The use of iodine number as a selection criterion can also be questioned because iodine number is considered to be an indicator of low molecular weight material adsorption, and the pink water nitrobodies are higher molecular weights. Molasses number is a better indicator, but manufacturers reported molasses numbers for only two of the nine GACs.

The one adsorption criterion for which there were data available for all GACs is surface area, and four of the GACs selected rank first, second, and third using the highest published surface area value. Filtrasorb 200 ranks fifth in surface area, but it is included to provide comparison of a lower cost Calgon product to Filtrasorb 300.

In summary, five GACs were selected for isotherm tests based upon adsorption criteria (surface area, pore volume, iodine number, and mean particle diameter), popular use, pressure drop, cost, and manufacturers' recommendations. Those GACs are Calgon Filtrasorb 200, 300, and 400; Westvaco Nuchar WV-G; and Witco Witcarb 950.

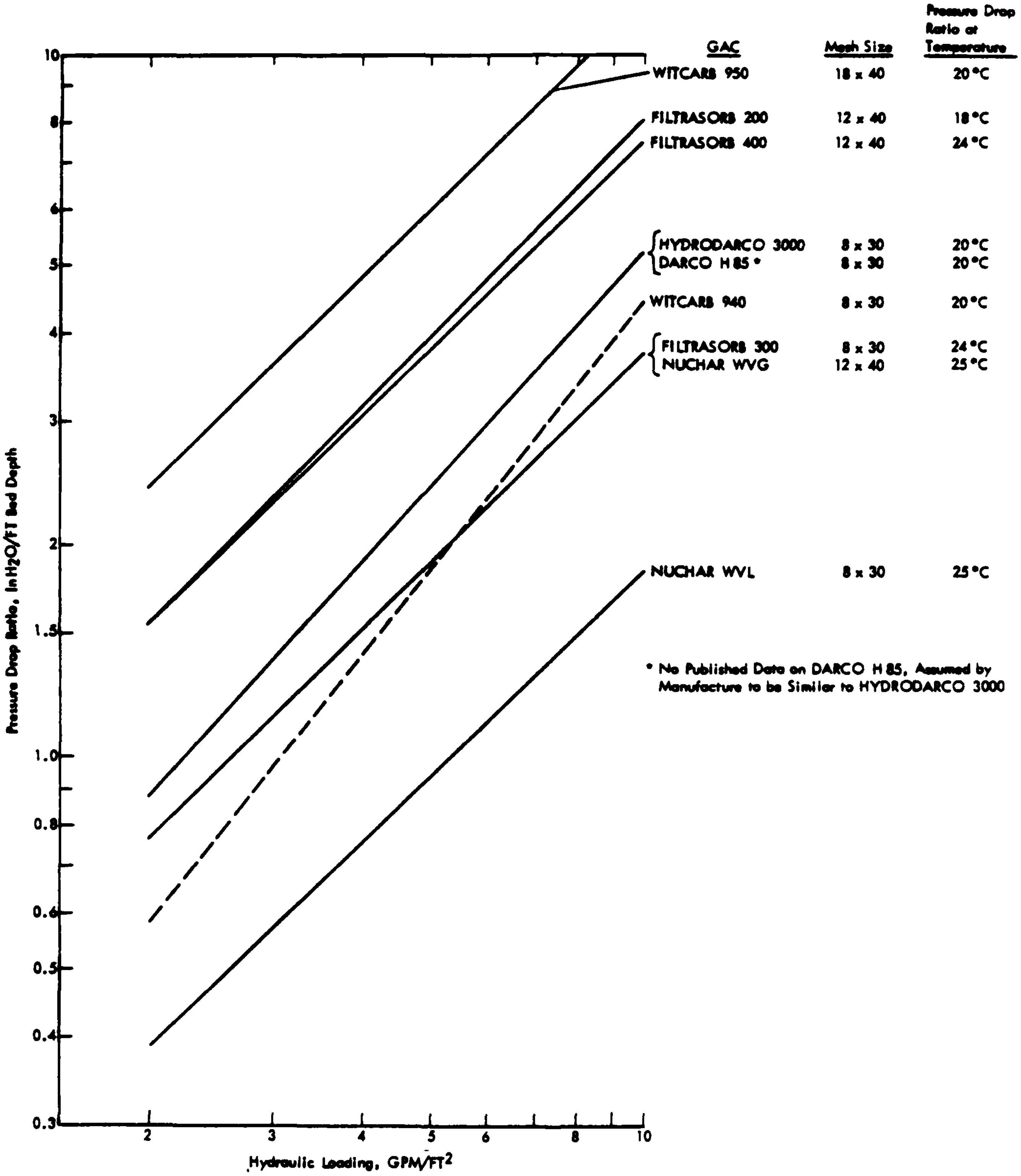

Figure 4-1. Manufacturers' published GAC pressure drop ratios.

TABLE 4-1. Properties Used to Define GAC.

Adsorption properties	Units	Description	Desired value for use with pink water
Specific surface area	m^2/g	Surface area measured by N_2 gas adsorption by Brunauer, Emmett and Teller (BET) method.	High
Pore volume	cm^3/g	Difference in volumetric displacement in mercury and in helium.	High
Phenol number	-	Index of ability to remove taste and odors.	High
Iodine number	-	Ability to adsorb low molecular weight substances. Believed to correlate to micropores < 40 Å diameter.	-
Molasses number	-	Ability to adsorb higher molecular weight substances. Believed to correlate to micropores and mesopores from 40 to 1000 Å diameter.	High
Carbon tetrachloride activity	%	Wt. % of carbon tetrachloride adsorbed at 25°C from dry air saturated with carbon tetrachloride at 0°C. Value is a relative indication of GAC adsorptive capability.	High
Mean particle diameter	mm	Mean particle size from screening tests using an appropriate sieve set. Smaller sized GACs have generally proven best for pollutant removal to very low effluent concentrations.	Small
Material Handling and Process Flow Properties			
Sieve size range	% by wt	% by wt passing the larger sieve size and retained by the smaller sieve size (U.S. Standard Sieve). Larger sieve sizes usually result in lower column ΔP.	Large

TABLE 4-1. Concluded.

	Units	Description	Desired value for use with pink water
Effective size	mm	Sieve opening passing 10% by wt of the GAC.	-
Uniformity coefficient	-	Sieve size passing 60% of the GAC divided by the sieve size passing 10% of the GAC.	< 2.1
Abrasion number	-	Resistance to degradation in handling, measured by resistance to breakage by steel balls in a Ro-Tap machine.	High
Apparent density	g/cm^3	Weight/unit volume of GAC uniformly packed in a 100 mL column.	-
Particle density	g/cm^3	Weight/unit volume of the total GAC particles.	-
Real density	g/cm^3	Density of the skeleton of a GAC particle determined by helium displacement.	-
Bulk density, backwashed and drained	lb/ft^3	Weight/unit volume of GAC that has been wetted, washed, and drained. Measures the actual space needed for GAC in an operating column.	High
Manufacturing Quality Properties			
Ash	% by wt	Residual left after all carbon is burned in a standard ash test. Ash does not aid adsorption and low ash is desired for GAC.	Low
Moisture, as packed	% by wt	Moisture content as sold. Since GAC is sold by weight, low moisture is desired.	Low

TABLE 4-2. Properties of Currently Used Filtrasorb 300 and Similar GACs.

Sieve size	Calgon Filtrasorb 200	Calgon Filtrasorb 300	ICI Americas Hydrodarco 3000	Westvaco Nuchar WV-L	Witco Witcarb 940
Designation	12 x 40	8 x 30	8 x 30	8 x 30	8 x 30
> No. 8, % by wt		15	8	8	-
> No. 12, % by wt	5				
< No. 30, % by wt		4	5	5	-
< No. 40, % by wt	5				
Adsorption Properties					
Specific surface area, m^2/g	850-900	950-1,050^{a}	550-650	1,000	900-1,000
Pore volume, cm^3/g	-	0.85^{a}	1.0	0.85^{a}	-
Iodine number	850	900	550	950	-
Molasses number	-	-	90	-	-
Carbon tetrachloride activity, %	-	-	-	-	40-50
Mean particle diameter, mm	0.8-1.0	1.5-1.7	1.4-1.6	1.4-1.7	-
Material Handling and Process Flow Properties					
Effective size, mm	0.55-0.65	0.8-0.9	0.8-0.9	0.85-1.05	-
Uniformity coefficient	1.7	≤ 1.9^{a}	≤ 1.9	1.8	-
Abrasion number	70	75	-	70	-
Apparent density, g/cm^3	-	0.48^{a}	0.43^{a}	0.47-0.50	0.53-0.57
Particle density, g/cm^3	1.4-1.5	1.3-1.4^{a}	1.3-1.4	1.35-1.45	-
Real density, g/cm^3	-	2.1^{a}	2.0^{a}	2.1^{a}	-
Bulk density, backwashed and drained, lb/ft^3	30	26^{a}	23-24	25-27	
Manufacturing Quality Properties					
Ash, % by wt	8.0	0.5	18	1.0	< 1.0
Moisture as packed, % by wt	2.0	2.0	9	2.0	< 1.0

NOTE: - = No data available.

[a] Information from References 14 and 15. All other data from manufacturers' product bulletins.

TABLE 4-3. Properties of GACs Recommended by Manufacturers for Pink Water Treatment.

Sieve size	Calgon Filtrasorb 400	ICI Americas Darco H 85	Westvaco Nuchar WV-G	Witco Witcarb 950
Designation	12 x 40	8 x 30	12 x 40	18 x 40
> No. 8, % by wt	-	15	-	-
> No. 12, % by wt	5	-	8	-
< No. 30, % by wt	-	4	-	-
< No. 40, % by wt	4	-	5	-
Adsorption Properties				
Specific surface area, m^2/g	1,000-1,200[a]	1,000	1,100	1,000-1,100
Pore volume, cm^3/g	0.94[a]	-	-	-
Phenol number	-	-	-	27
Iodine number	1,000	900	1,050	1,050
Molasses number	-	200	-	-
Carbon tetrachloride activity, %	-	-	-	50-60
Mean particle diameter, mm	0.9-1.1	1.5-1.7	0.9-1.20	-
Material Handling and Process Flow Properties				
Effective size, mm	0.55-0.65	-	0.55-0.75	-
Uniformity coefficient	≦ 1.9[a]	-	1.8	-
Abrasion number	75	75	75	95
Apparent density, g/cm^3	0.44[a]	-	0.43-0.47	0.46-0.53
Particle density, g/cm^3	1.3-1.4[a]	-	1.3-1.4	-
Real density, g/cm^3	2.1	-	-	-
Bulk density, backwashed and drained, lb/ft^3	25[a]	24-32	24-26	-
Manufacturing Quality Properties				
Ash, % by wt	0.5	-	1.0	< 1.0
Moisture as packed, % by wt	2.0	2.0	2.0	< 1.0

NOTE: - = No data available.

[a] Information from References 14 and 15. All other data from manufacturers' product bulletins.

TABLE 4-4. GAC Truckload Lot Costs.

GAC	FOB Location	Mesh size	Minimum weight lb	Cost as of January 1985 $/lb
Calgon Filtrasorb 200	Catlettsburg, KY	12 x 40	30,000	0.83
Calgon Filtrasorb 300	Catlettsburg, KY	8 x 30	30,000	0.89
Calgon Filtrasorb 400	Catlettsburg, KY	12 x 40	30,000	0.96
ICI Americas Hydrodarco 3,000	Marshall, TX	8 x 30	24,000	0.96
ICI Americas Darco H 85	Marshall, TX	8 x 30	24,000	0.865
Westvaco Nuchar WV-L	Corrington, VA	8 x 30	32,000	0.76
Westvaco Nuchar WV-G	Corrington, VA	12 x 40	32,000	0.81
Witco Witcarb 940	Petrolia, PA	8 x 30	30,000	0.70
Witco Witcarb 950	Petrolia, PA	18 x 40	30,000	0.91

TABLE 4-5. GAC Less Than Truckload Lot Costs.[a]

	Calgon			ICI Americas		Westvaco		Witco	
	FOB, Catlettsburg, KY			FOB, Marshall TX		FOB, Covington, VA		FOB, Petrolia, PA	
Weight category, lb	Filtrasorb 200	Filtrasorb 300	Filtrasorb 400	Hydrodarco 3000	Darco H 85	Nuchar WV-L	Nuchar WV-G	Witcarb 940	Witcarb 950
100	-	-	-	2.085	1.99	-	-	-	-
< 500	1.27	1.35	1.44	-	-	-	-	-	-
200 to < 2,000	-	-	-	-	-	-	-	0.93	1.18
500 to < 2,000	1.07	1.14	1.22	-	-	-	-	-	-
1,200 to 3,600	-	-	-	1.085	-	-	-	-	-
2,000 to 4,000	-	-	-	-	0.99	-	-	-	-
2,000 to 8,000	-	-	-	-	-	1.06	1.13	-	-
2,000 to < 10,000	0.98	1.05	1.12	-	-	-	-	0.79	1.00
4,800 to 7,200	-	-	-	1.05	-	-	-	-	-
6,000 to 8,000	-	-	-	-	0.955	-	-	-	-
10,000 to 18,000	-	-	-	-	-	0.95	1.01	-	-
10,000 to < 30,000	0.93	0.99	1.06	-	-	-	-	0.74	0.95
20,000 to 30,000	-	-	-	-	-	0.87	0.93	-	-

NOTE: - = No data available.

[a] All mesh sizes same as Table 4-4.

TABLE 4-6. Ranking of GAC Adsorption Properties, Pressure Drop, and Cost.

Legend

Carbon	Size	Legend Term
Calgon Filtrasorb 200	12 x 40	F200
Calgon Filtrasorb 300	8 x 30	F300
Calgon Filtrasorb 400	12 x 40	F400
ICI Americas Hydrodarco 3000	8 x 30	H3000
ICI Americas Darco H 85	8 x 30	H85
Westvaco Nuchar WV-L	8 x 30	WVL
Westvaco Nuchar WV-G	12 x 40	WVG
Witco Witcarb 940	8 x 30	W940
Witco Witcarb 950	18 x 40	W950

Ranking

Specific[a] surface area	Pore[a] volume	Iodine[a] number	Mean[b] particle diameter	Pressure[b] drop ratio	Cost[b]
F400	H3000	WVG, W950	F200	WVL	W940, WVL
WVG, W950	F400	F400	F400	F300, WVG	WVG
F300,	F300, WVL	WVL	WVG	W940	F200
WVL, H85, W940		F300, H85	H3000	H3000, H85	H85, F300
F200		F200	F300, WVL, H85	F400	W950
H3000		H3000		F200	F400, H3000
				W950	

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[a] Ranking from highest to lowest values.

[b] Ranking from smallest to largest particle diameter and lowest to highest pressure drop and cost.

TABLE 4-7. Five GACs Selected for Isotherm Tests.

	Ranking of GACs[a]				
Adsorption criteria	Calgon Filtrasorb 400	Westvaco Nuchar WV-G	Witco Witcarb 950	Calgon Filtrasorb 300	Calgon Filtrasorb 200
Surface area	1	2	2	3	5
Pore volume	2	No data	No data	3	No data
Iodine number	2	1	1	4	5
Mean particle diameter	2	3	-	5	1
Other criteria					
Popular use	Not used	Not used	Not used	1	Not used
Pressure drop	5	2	7	2	6
Cost	6	3	5	4	3
Recommended by manufacturer as best for pink water treatment	Yes	Yes	Yes	-	-

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NOTE: - = No data available.

[a] Rank position from Table 4-6; highest to lowest ranking from left to right.

5. ISOTHERM TESTS

5.1 INTRODUCTION

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 of interest. The tests are run at a specified constant temperature; hence, the name "isotherm." The resulting data are then interpreted by comparing the weight of pollutant adsorbed per unit weight of GAC (q_e) to the weight of pollutant remaining in a unit weight or volume of solution (C_e).

There were several objectives behind the isotherm tests conducted in this program. The first objective was to determine if the desired low effluent nitrobody concentrations could be achieved under ideal equilibrium conditions with any of the GACs selected for testing. Because of these low concentrations, it was necessary to use relatively high dosages of GAC in the isotherm tests (discussed in Section 5.4.3.2) and also to develop extremely sensitive analytical procedures (described in Appendix A).

A second objective was to rank the five GACs selected for testing to determine which GAC performs the best for pink water containing all four nitrobodies. Isotherm tests were conducted with each GAC using nearly identical test conditions. The GAC producing the highest q_e values at the C_e values of interest was considered the best performing GAC.

A third objective was to determine if variations in temperature over the range normally expected for operating AAPs (i.e., just above freezing to a hot summer day) would have a significant impact on GAC performance. Although AAP operating experience has indicated there are few or no temperature effects on GAC performance, this experience needed to be verified in the laboratory under carefully controlled conditions. Tests were conducted using cold, ambient, and hot water baths to examine temperature effects in a laboratory situation.

A final objective was to examine effects on GAC performance arising from variations in solution composition. Three types of comparisons were made. First, GAC performance with a four-component pink water solution was compared to GAC performance with two-component solutions containing either the nitroamines only (RDX and HMX) or the nitroaromatics only (TNT and 2,4-DNT). These tests showed whether or not preferential adsorption occurs; that is, whether one or more compounds are adsorbed in preference to others when all four are in solution, or if total adsorption performance decreases. Second, a test was run on actual pink water collected from an AAP to compare results with those obtained from synthetic pink water prepared in the laboratory. Finally, the effect of having a polar solvent (acetone) present in the pink water was examined to determine if acetone-based stock solutions could be used to make up synthetic pink water for the column tests.

5.2 TEST MATRIX

A summary of the test matrix followed in conducting the isotherm tests is given in Table 5-1. A test time of 20 hr was used in all tests. Studies reported in the literature have indicated that 20 hr is more than adequate to attain equilibrium when the GAC is finely powdered, as was the case in these tests. The same four-component pink water solution was used in all but the two tests involving two-component solutions. Ambient room temperature was used except when the temperature was deliberately varied. Once the best-performing GAC was selected, it was used in all the remaining tests except as noted otherwise.

5.3 MATERIALS

5.3.1 GACs

The five GACs selected for isotherm tests were specified in Section 4.4. They are listed again below, with additional information on carbon source provided.

Manufacturer	Trade Name	Grade	Mesh Size	Carbon Source
Calgon	Filtrasorb	200	Not available	Bituminous coal
Calgon	Filtrasorb	300	8 x 30	Bituminous coal
Calgon	Filtrasorb	400	12 x 40	Bituminous coal
Westvaco	Nuchar	WV-G	12 x 40	Bituminous coal
Witco	Witcarb	950	18 x 40	Petroleum coke

5.3.2 Nitrobodies

Four different nitrobody compounds were used to produce synthetic pink water. Only 2,4-DNT, classified as a nonexplosive, was available as a stock laboratory chemical. The explosive nitrobody compounds were obtained from Goex, Inc., in Cambden, Arkansas. Both RDX and HMX were shipped and stored wet with an antifreeze solution of water and propanol. The TNT was shipped and stored dry. All three explosive compounds were stored in a freezer located in a designated explosion-proof facility.

The nitrobodies were not assayed for purity although it is known that RDX may be contaminated with HMX and vice versa, and that TNT may contain traces of 2,4-DNT or other dinitrotoluenes. However, characterization of the prepared pink water solution by chemical analysis was sufficient for purposes of this program.

Additional information on the four nitrobodies used in the isotherm tests is given below.

Nitrobody munition compound	Manufacturer or Source	Classification	Production Code
TNT	Goex, Inc.	Type 1 (80.26°C m.p.)	Lot 8
RDX	Goex, Inc.	Type 2, Grade 5	4R851-38
HMX	Goex, Inc.	Grade B	HDL709-1
2,4-DNT	Pfaltz and Bauer	Stock No. D48050	Not available

5.3.3 Actual AAP Pink Water

During the course of this project, uncertainties arose as to the authenticity or reliability of using laboratory data resulting from tests on synthetic pink water in order to scale up to wastewater treatment systems handling actual pink water. Accordingly, comparative isotherm studies were performed on both synthetic pink water and actual pink water from an operating AAP.

Samples of actual pink water were obtained March 12, 1985 at Kansas Army Ammunition Plant (KAAP) near Parsons, Kansas. Two 5-gal. samples were collected from a settling tank at the 1100 production site, near Building 1127. Cyclotol, a mixture of 70% RDX and 30% TNT, was being produced and poured at this site.

5.4 PROCEDURES

5.4.1 Preparation of GACs

The GACs were used in a powdered state for the isotherm tests. This assured that equilibrium conditions would be obtained in tests conducted overnight. Grinding GAC to a powdered state does not significantly increase the total surface area of the active sites, but it does decrease the time required for organic molecules to diffuse to the active sites.

A starting weight of about 20 g was used for each of the five GACs. The weighed carbon was ground either in a porcelain mortar and pestle or in a motor-operated laboratory grinder with a spinning blade in an enclosed cup.

The ground carbon was then sieved through a 325 mesh brass screen (No. 325 U.S. standard sieve). The fraction passing through the sieve was dried in an oven at 150°C (302°F) for at least 3 hr, then cooled in a dessicator. The jars containing the powdered carbon were kept tightly sealed except when dosages for isotherm tests were being weighed out.

5.4.2 Preparation of Synthetic Pink Water

5.4.2.1 Four-component solution. A single 20-L batch of synthetic pink water was used for all of the isotherm tests requiring a four-component synthetic pink water. This solution was prepared using the apparatus shown in Figure 5-1. The tank was prefilled with 20 L of deionized water.

Suitable quantities of wet munition compounds were weighed (according to expected dry weight) and placed on the glass fiber filter inside the dissolving assembly. Each compound was placed in its own dissolving assembly. A short length of plastic hose from each filter pointed upwards maintained a minimum water level in each funnel. This ensured that the explosives would not dry if power to the pump should fail. Samples from the tank were analyzed as the recirculation continued to determine if desired concentrations were achieved. The water from the tank was circulated over the filters for 3 days in order to dissolve as much as possible of each munition compound. At the end of this period, the filters and any undissolved compounds were disposed by appropriate means. The tank, pump, and piping were all of plastic construction. There were no analytical chemistry problems encountered due to possible leaching of materials from the tank, pump, and piping. Fresh pink water solutions prepared as above did not show any significant impurity peaks in the HPLC chromatograms.

5.4.2.2 Two-component solutions. Only single tests were run using either of the two-component solutions; thus, much less solution volume was required. In each case, the required quantities of wet munition compounds were added to 1.6 L of hot (about 85°C) deionized water in a 2 L beaker placed on a combination heating/stirring plate. Additional deionized water was added to make 1.8 L of solution, and the solution was magnetically stirred while it slowly cooled for several hours. This preparation method was much more rapid and trouble-free than the method described above for the four-component solution.

5.4.2.3 Summary of pink water concentrations. The concentrations of each of the four nitrobodies of interest in the three types of synthetic pink water and the AAP pink water are summarized below. The values given are based upon initial analysis, except as noted. The concentration of each compound generally decreased with time as decomposition occurred. The pH of the synthetically prepared solutions ranged from 5.5 to 5.7, whereas the pH of the actual pink water was 7.0.

Pink water type	Concentrations, mg/L			
	TNT	RDX	HMX	2,4-DNT
Synthetic 4-component	73.4	27.7	5.76	0.939
(final analysis after aging 3 months)	59.0	23.1	4.53	0.763
Actual AAP pink water	49.4	22.0	4.02	0.0663
Synthetic 2-component	-	22.6	4.42	-
Synthetic 2-component	110	-	-	1.29

5.4.3 Conducting Isotherm Tests

5.4.3.1 Temperature control. A shaker table (Eberbach Corporation, Model 5900) with the capacity to hold six 500-mL flasks simultaneously provided agitation during the isotherm tests. The flasks were kept partially submerged in a water bath to maintain them all at the same temperature. The ambient temperature tests were conducted at room temperature which varied from 20° to 25°C. In all tests, the bath temperature was monitored using a thermocouple and digital temperature monitor with a strip-chart recorder. The fluctuations in ambient temperature were within ±2-3°C for each test.

For the high temperature test (nominally 49°C), temperature control was provided by built-in electric resistance heaters in the water bath that were controlled by a thermostat. A separate laboratory vapor compression chiller provided temperature control for the low temperature test (nominally 4°C). Water from the separate chiller bath was circulated through heat exchanger coils in the shaker table bath. Temperature fluctuations for both the high and the low temperature test were within about ±1°C.

5.4.3.2 General procedure. For conducting the isotherm tests, 500 mL glass Erlenmeyer flasks were used, stoppered with rubber stoppers wrapped in aluminum foil. Before each test, the flasks were washed in laboratory cleaning solution, rinsed with deionized water, then allowed to dry and final rinsed with pesticide-grade acetone. The foil used to wrap the stoppers was also rinsed with acetone. Similar cleaning procedures were used for filtering funnels, sample bottles, and other glassware. The sample bottle lids used Teflon cap liners.

The carbon dosages, preweighed to the nearest milligram using a top-loading electronic balance, were placed into tared plastic weigh boats. Final weights were obtained using an analytical-grade balance, weighing to ±0.01 mg. The weigh boat was weighed before and after dumping the powdered carbon into a clean, empty 500 mL flask. Five different carbon dosages were used for each isotherm test. A sixth flask without carbon served as a blank. The nominal dosages ranged from 10 to 5,000 mg/L solution. Although the largest carbon dosages were higher than what is generally used in similar isotherm tests, they were necessary to ensure that the equilibrium concentrations were lower than the proposed discharge standards, which represent much lower target values than is generally the case. The nominal weights of carbon used in each flask ranged from 0.025 to 1.25 g. The actual weights used for each test and the solution volumes are given in Appendix D.

After the carbon dosages were added, the same volume (generally 250 mL) of test solution was poured into each flask and tightly stoppered. A pH reading of the test solution was also taken at this time. After clamping the flasks onto the shaker table, the motor was turned on. The speed was adjusted to about 2 cycles/sec, with each cycle being a back-and-forth oscillation of the shaker table. The temperature was controlled as needed and was recorded throughout each test. The test was conducted for 20 hr.

At the end of the test, the shaker table was turned off. Each flask was vacuum filtered through a glass fiber filter (Whatman GF/F) into a clean filter flask. The filtered solution was then poured into a labeled sample bottle. The filter containing the powdered carbon was disposed of by appropriate means. In some cases, it was necessary to filter the solutions using the highest carbon dosages two or more times to remove most of the fine carbon particles. The filter paper has a 98% retention efficiency for particle sizes of 0.7 μm and greater in liquids. The samples were then analyzed according to procedures given in Appendix A.

5.5 RESULTS AND DISCUSSION

5.5.1 GAC Selection

5.5.1.1 Results. Parallel isotherm tests were run on the five GACs selected for experimental work, using equivalent test conditions. Those conditions were ambient temperature (approximately 22°C), a 20-hr test time, and the same four-component synthetic pink water solution. The same nominal carbon dosages were also used for all of the tests in this series. These dosages were 10, 50, 200, 1,000, and 5,000 mg/L. The solution volume was fixed at 250 mL. The test results from each type of GAC are given in Tables 5-2 through 5-6. Results include the carbon dosages (M), the equilibrium concentrations (C_e) for each compound, and the carbon loading (q_e) for each compound. The same carbon dosages apply for each compound for a given GAC test. Not shown in these tables are the values of X used in calculating q_e.

$$X = C_o - C_e; \; q_e = X/M$$

Plots were made of log q_e versus log C_e for each nitrobody and for each GAC. In order to rank the various GACs, isotherm plots were made by combining data from all five GACs for a given compound. These plots are shown in Figures 5-2 through 5-5.

For a given C_e, the greater the q_e value, the better is that GAC in adsorbing a particular compound out of solution. Thus, for these figures, the best performing GAC may be readily indicated by the line closest to the top of the graph.

There are several instances in these figures where an arrow points from a data point to the upper left-hand quadrant of the graph. This is due to analysis providing a "less than the minimum detectable level" result, as noted in the data tables. The benefit of including this point on the graph is to demonstrate that the equilibrium concentration was less than the desired low effluent concentration, although the exact value is unknown.

5.5.1.2 Discussion. The results clearly indicate that the consistently best performing GAC was Witcarb 950. The second or third best GAC is more difficult to determine. In order to provide some quantitation to the ranking method, q_e values from each carbon for a given nitrobody were compared at selected C_e values. The relative rankings of the GACs at various C_e values are shown in Table 5-7. The rankings specific to each nitrobody are given for several C_e values, and an estimate of the overall ranking throughout the range of C_e values is provided. The best estimate of ranked order of performance for all four nitrobodies is, from best to worst, Witcarb 950, Nuchar WV-G, Filtrasorb 400, Filtrasorb 300, and Filtrasorb 200.

Accordingly, Witcarb 950 was selected for conducting the balance of the isotherm tests.* The manufacturer-supplied sample used for these tests had an identification number of AC-9611. A graphical presentation of the performance of this GAC showing results for all four of the nitrobodies is provided in Figure 5-6. Using this four-component pink water solution, Witcarb 950 most efficiently adsorbed TNT from solution, followed by RDX, then HMX,

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* Witco Chemical Corporation stopped production of all activated carbon in late 1985. (Witco Press Release No. 85-126, "Witco to Modernize Petrolia, Pennsylvania Facility; Shuts Down Activated Carbon Operations," October 31, 1985.)

then 2,4-DNT, as the q_e levels indicate. Of course, testing was in a static situation where equilibrium could be attained. It is probably less than coincidental that the order of q_e is also the order of starting concentrations for the four nitrobodies.

In addition to ranking the tested GACs, several other observations can be made from the isotherm results. First, it was learned that all of the GACs tested are capable of achieving the desired effluent levels for all four nitrobodies, given a high enough carbon dosage (i.e., ≥ 1,000 mg/L). In some cases, this was demonstrated by noting the absence of a detectable level of a given compound in the filtrate samples.

Another observation involves the projected maximum q_e values for each compound and each GAC. During the operation of a carbon column, as the carbon approaches exhaustion, the effluent concentration approaches the influent concentration. The GAC generally is at the maximum q_e value at this point. When isotherm data are linear, the maximum q_e value may be approximated by extrapolating the data to the original concentration (C_o) and reading the q_e value at that point. When the data form a nonlinear plot, however, this approach is misleading, as would be the case with the data from this study.

The maximum saturation capacities from the experimental data may be approximated by the q_e values resulting from the lowest carbon dosages (10 or 20 mg/L). In these instances, the change in concentration is fairly low (i.e., < 10%) and C_e is near C_o. As an example, the q_e values representing maximum saturation capacity for Witcarb 950 GAC are shown below.

Saturation Capacities at Minimum Carbon Dosage
for Witcarb 950

Nitrobody	q_e at M_{min}
TNT	0.56
RDX	0.066
HMX	0.024
2,4-DNT	0.017

5.5.2 Temperature Effects

5.5.2.1 Results. In order to examine the effect of varying temperature on adsorption by GAC, isotherm tests were conducted on Witcarb 950 at three temperatures, representing normal variation expected at AAPs. The temperatures used were 4°C (39°F)--low, 22°C (72°F)--ambient, and 49°C (120°F)--high. The results from the ambient test were given previously in Table 5-6. Isotherm results for the low and high temperature tests are provided in Tables 5-8 and 5-9, respectively.

Temperature effects for each nitrobody were examined by plotting the isotherms on the same graph. Because the large number of data points was confusing on a single graph, the data were separated into two sets. RDX and HMX results are shown in Figure 5-7, and 2,4-DNT and TNT results are shown in Figure 5-8.

5.5.2.2 Discussion. Shifts in q_e due to temperature variations over the range tested were quite small. However, the results do indicate two general tendencies. First, better performance (higher q_e) for both RDX and HMX is achieved as the temperature decreases. Second, better performance for TNT and, to a lesser extent, for 2,4-DNT is achieved as the temperature increases. Competitive adsorption, which is discussed below, undoubtedly is a cofactor with temperature effects when all four compounds are present.

5.5.3 Composition Effects

5.5.3.1 Results. The effects of varying composition and associated adsorption interferences were examined by conducting additional isotherm tests using two-component solutions on Witcarb 950. Isotherm test results for a solution containing only RDX and HMX at levels approximating those used in prior tests are given in Table 5-10. The results for a solution containing only 2,4-DNT and TNT are given in Table 5-11. For appropriate comparisons, the reader is referred to Table 5-6 where test results from the four-component solution are shown. All of these tests were conducted at ambient temperature (70°F). Graphical comparisons of solution effects were made by plotting isotherms simultaneously from both two-component and four-component solutions. The results for RDX and HMX are shown in Figure 5-9, and the results for DNT and TNT are shown in Figure 5-10.

5.5.3.2 Discussion. The effects on GAC performance of removing two compounds from solution depends on the type of compound. There was only a slight improvement in performance for both TNT and DNT by removing RDX and HMX from solution. Furthermore, the isotherms remained roughly parallel. In contrast, a large improvement in performance (i.e., a large increase in q_e) was achieved for both RDX and HMX when the TNT and DNT were removed from solution. In this case, however, the comparison isotherms were not parallel. The major shift in q_e was for low carbon dosages, or as C_e approached C_o. In other words, the isotherms "straightened out" closer to a linear form when TNT and DNT were not present to compete with the other compounds. These data suggest that GAC in a dynamic system that is becoming increasingly saturated with nitrobodies would remove TNT and DNT more efficiently than RDX and HMX. Such projections must be approached cautiously, however, due to the many differences between isotherm tests and continuous column operation.

The carbon dosage required to remove each pollutant by a given amount is also helpful in assessing performance capabilities. Removal efficiencies as a function of carbon dosage were determined for each nitrobody in both the two-component and the four-component pink water, as shown in Figure 5-11. For a given carbon dosage, the removal efficiencies for RDX and HMX are much lower if TNT and DNT are also present. For a four-component solution, a dosage of about 500 mg GAC/L is required to remove 90% of each nitrobody, while a dosage of 1,000 mg/L is required to remove over 99% of each nitrobody.

5.5.4 Comparison of Synthetic to Actual Pink Water

5.5.4.1 Results. An isotherm test was conducted on a sample of actual pink water from an AAP so that test results could be compared to results from using synthetic pink water. The results from the AAP pink water are given in Table 5-12. The reader is referred to Table 5-6 for results from synthetic water. Both tests were run at ambient temperature using Witcarb 950.

The two sets of test results are compared graphically in Figure 5-12. As stated previously, the starting concentrations of the two types of pink water were very similar, except for 2,4-DNT. This is indicated by the data points at the minimum carbon dosage (far right-hand points) for each compound.

5.5.4.2 Discussion. The results from the KAAP pink water were virtually identical to the results from the synthetic pink water for HMX, RDX, and TNT. The starting concentrations for these compounds were similar.

Test results for 2,4-DNT were quite different, with much poorer GAC performance using the actual AAP pink water. The starting concentration for 2,4-DNT varied considerably, over an order of magnitude, which would seem to explain the difference in performance.

These data indicate that laboratory isotherm data using synthetic pink water can be reproduced using AAP pink water as long as the concentrations are roughly equivalent, in spite of any contaminants expected in actual pink water. This also suggests that column data from synthetic pink water could be scaled up and still apply for actual pink water.

5.5.5 Solvent Effects

5.5.5.1 Results. To determine if an organic polar solvent such as acetone would affect the GAC adsorption process for munition compounds, parallel tests were run using Filtrasorb 300 at ambient temperature. In one case, acetone was added to the test solution at a concentration of 2% by volume. This level was arrived at by conservatively estimating the amount of solvent necessary to use acetone-based stock solutions of each individual nitrobody in order to make up a synthetic pink water solution. The advantages of using stock solutions would be that the explosives could be more safely handled and that the solution process could be hastened.

The test results from the acetone-spiked pink water are given in Table 5-13. A graphical comparison of these data with the normal synthetic pink water is shown in Figure 5-13. Fewer data points are shown for the acetone-spiked solution because one of the samples was lost prior to analysis (the flask broke during the isotherm test).

5.5.5.2 Discussion. Adding acetone at the 2% level does not have much effect on adsorption of either DNT or TNT. However, there was a significant loss in adsorption performance for both RDX and HMX when acetone was added. The q_e values for a given C_e generally shifted downward about half an order of magnitude when the acetone was present.

These results indicate that acetone or a similar solvent could be used as an aid in solubilizing TNT and DNT. If this approach is used for solubilizing RDX or HMX, however, the results will require close examination.

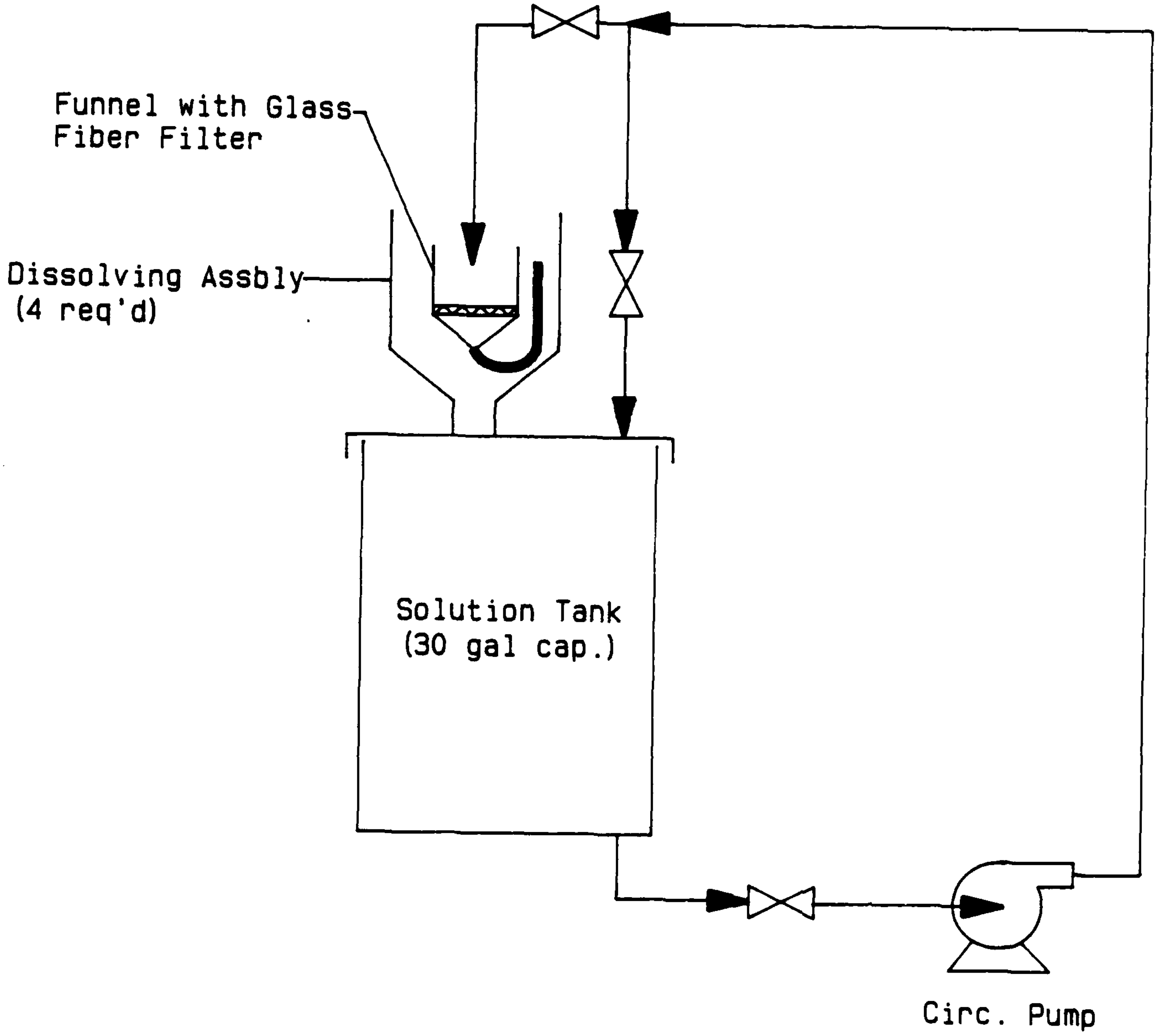

Figure 5-1. Schematic diagram of solution tank with dissolving assembly.

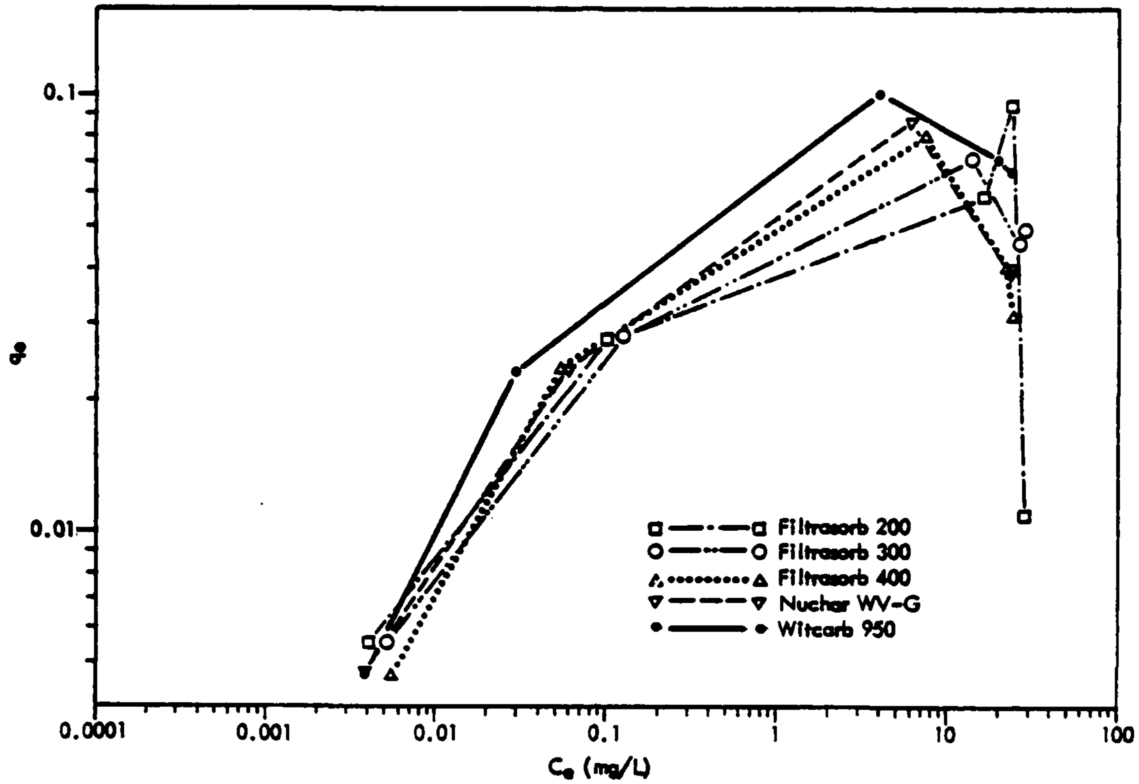

Figure 5-2. RDX isotherms for five GACs using four-component pink water.

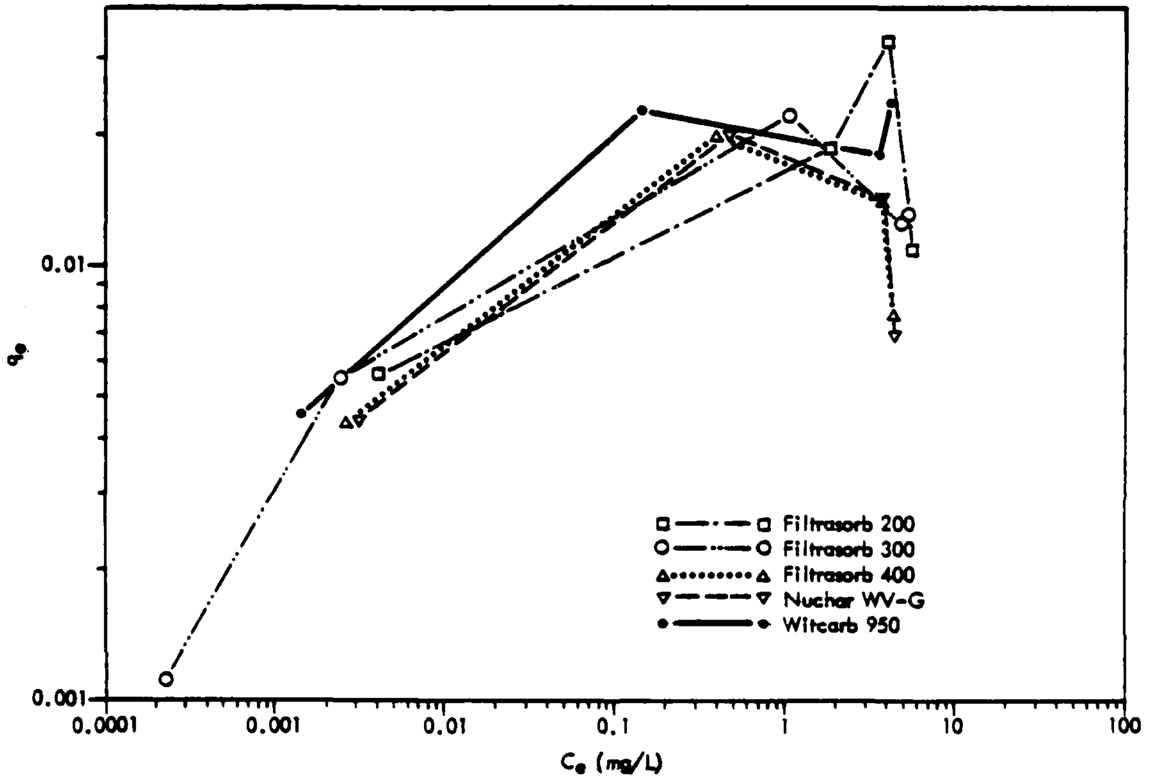

Figure 5-3. HMX isotherms for five GACs using four-component pink water.

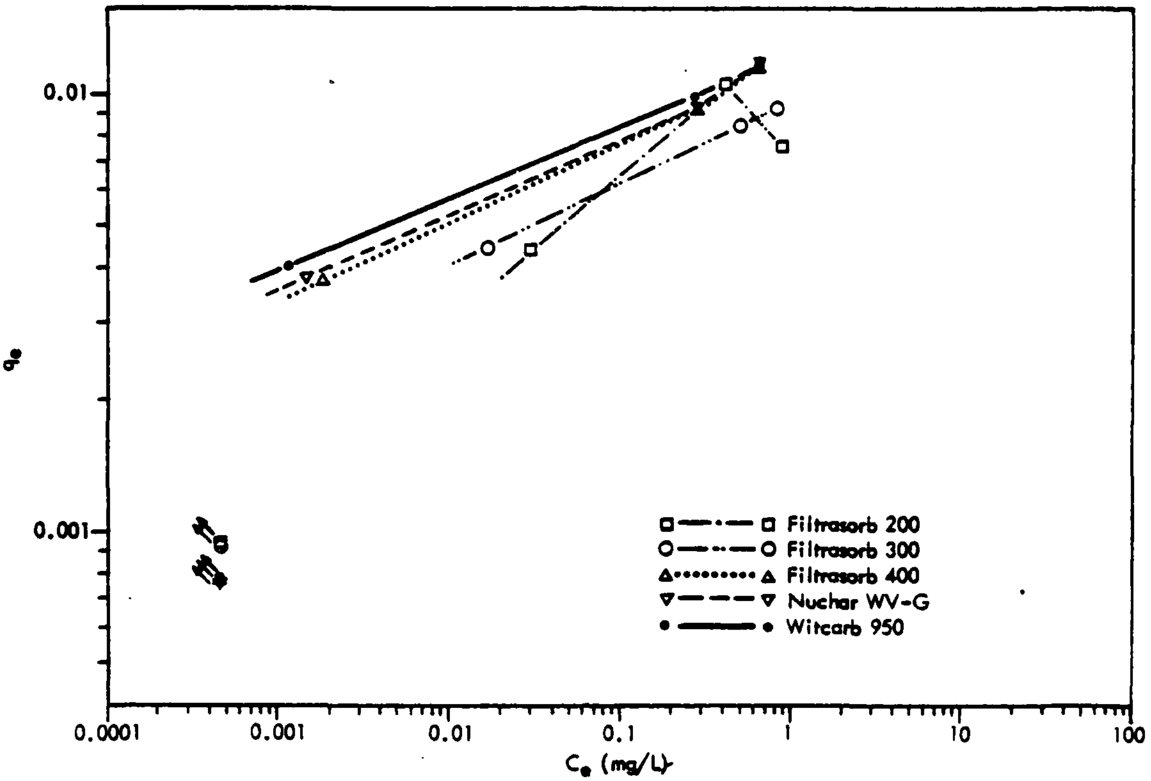

Figure 5-4. 2,4-DNT isotherms for five GACs using four-component pink water.

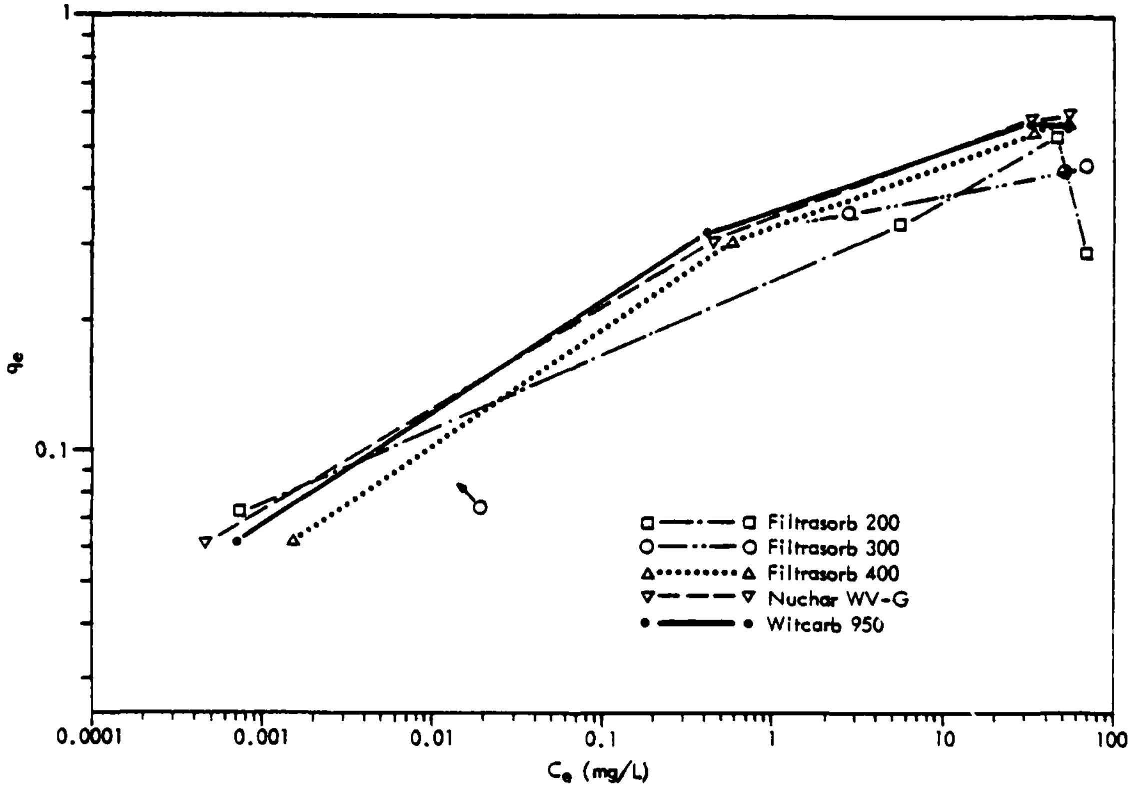

Figure 5-5. TNT isotherms for five GACs using four-component pink water.

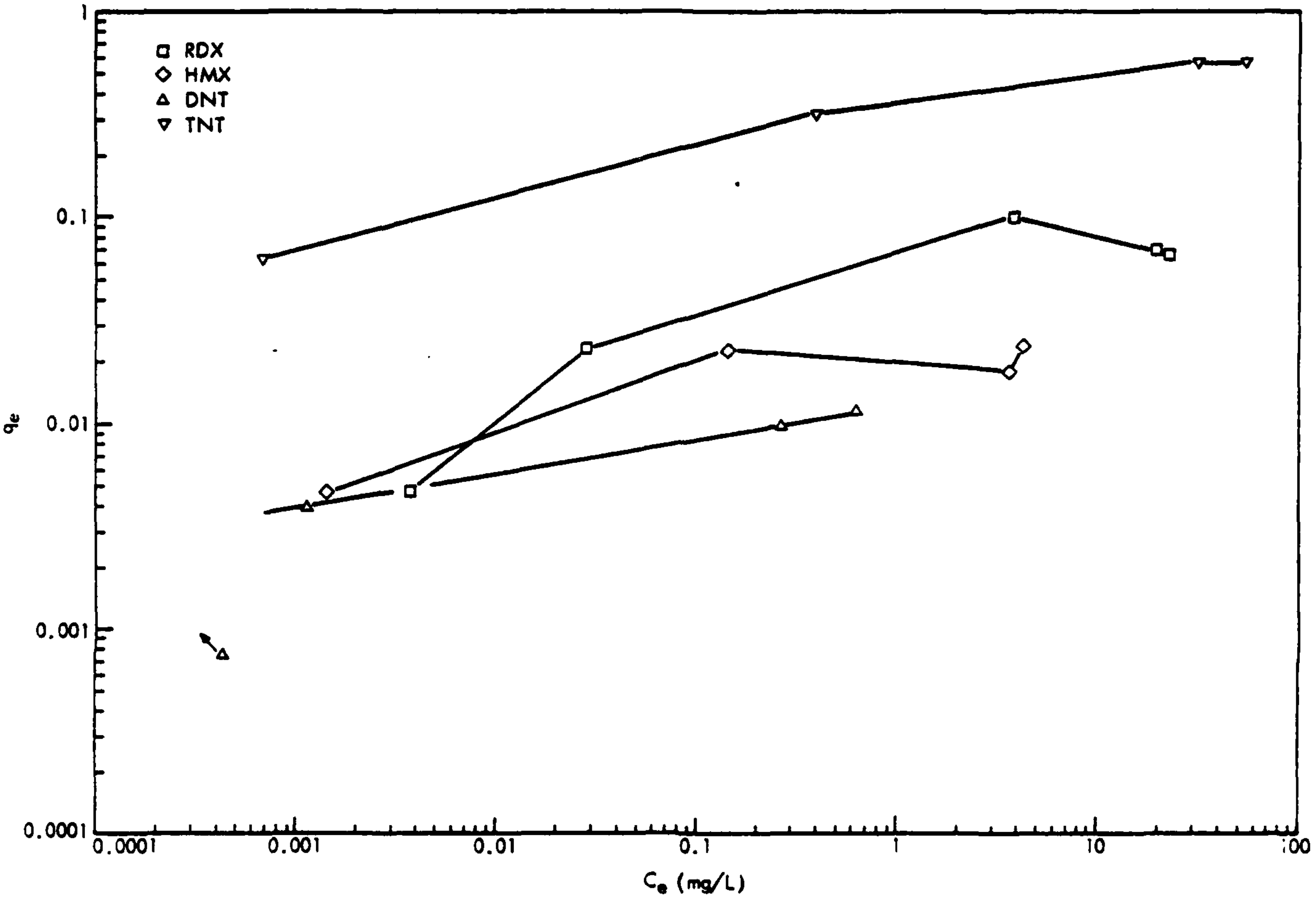

Figure 5-6. Isotherms for Witcarb 950 using four-component pink water.

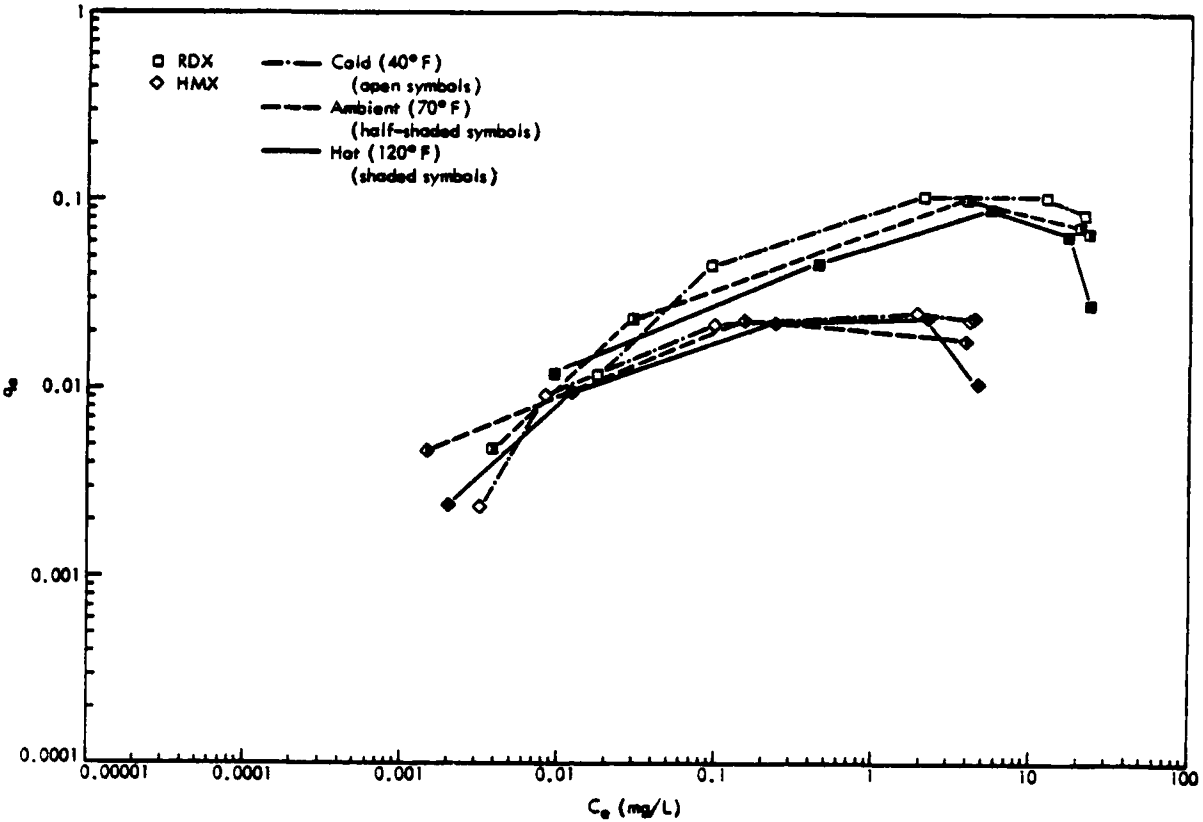

Figure 5-7. Witcarb 950 isotherms showing effects of varying temperature (RDX and HMX).

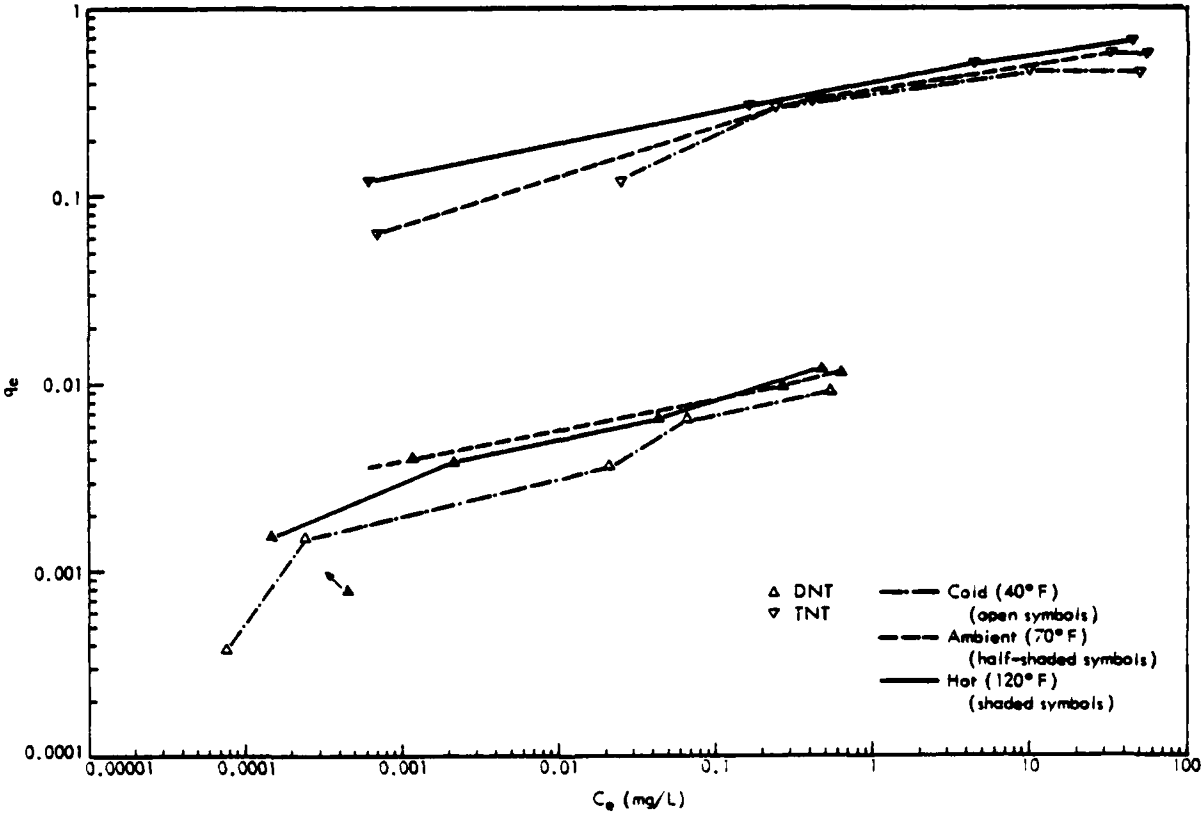

Figure 5-8. Witcarb 950 isotherms showing effects of varying temperature (DNT and TNT).

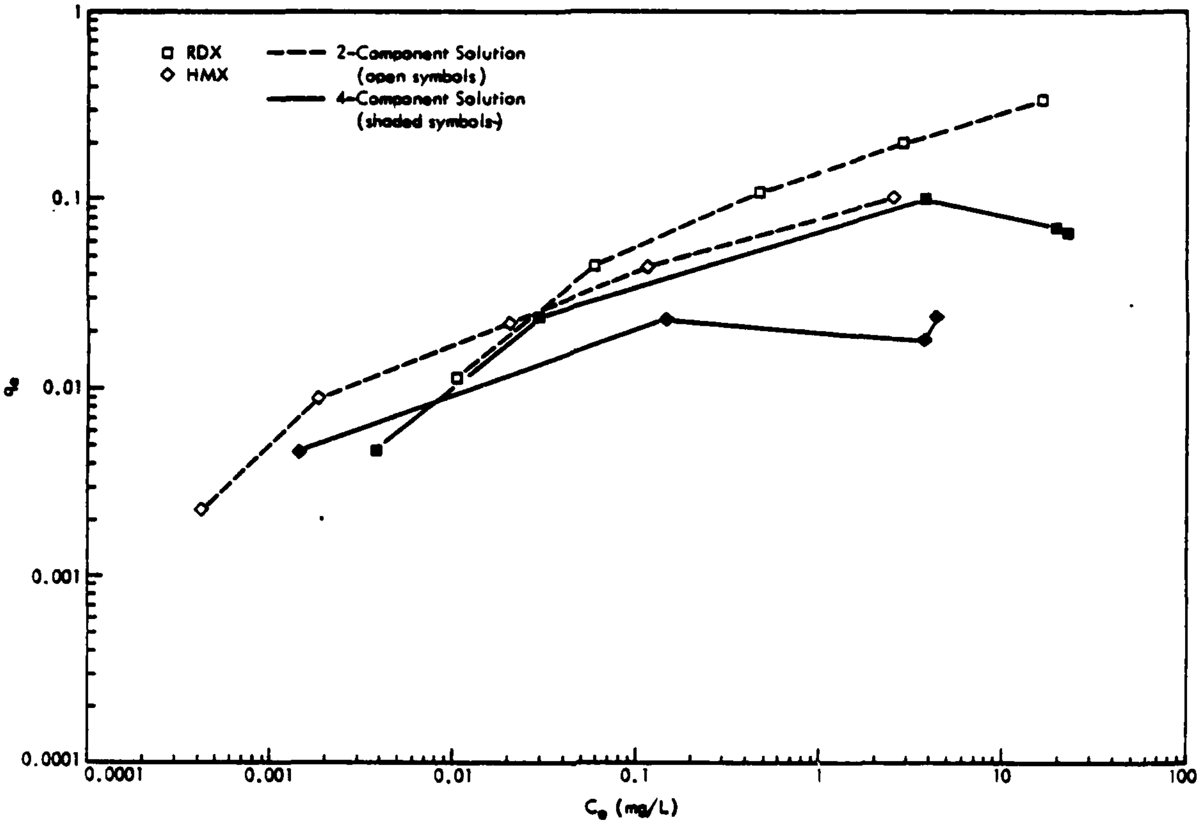

Figure 5-9. Witcarb 950 isotherms showing effects of varying solution composition (RDX and HMX).

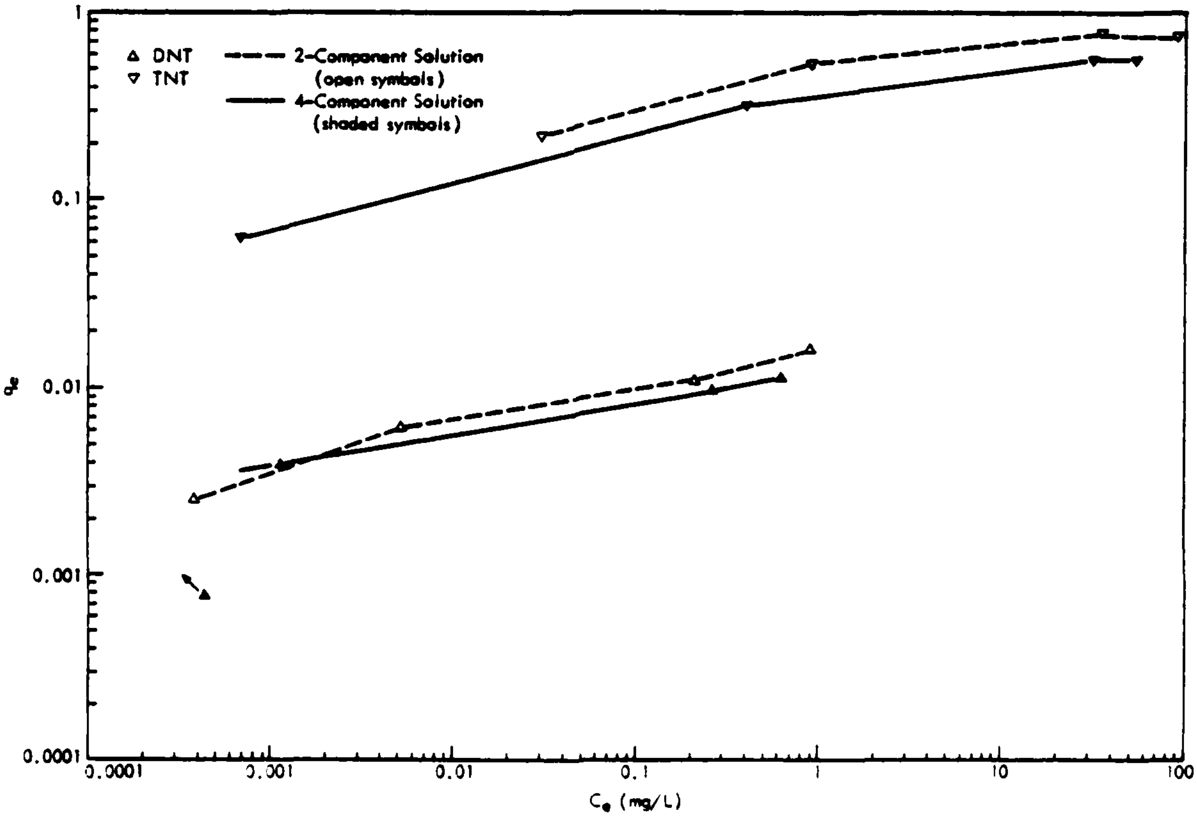

Figure 5-10. Witcarb 950 isotherms showing effects of varying solution composition (DNT and TNT).

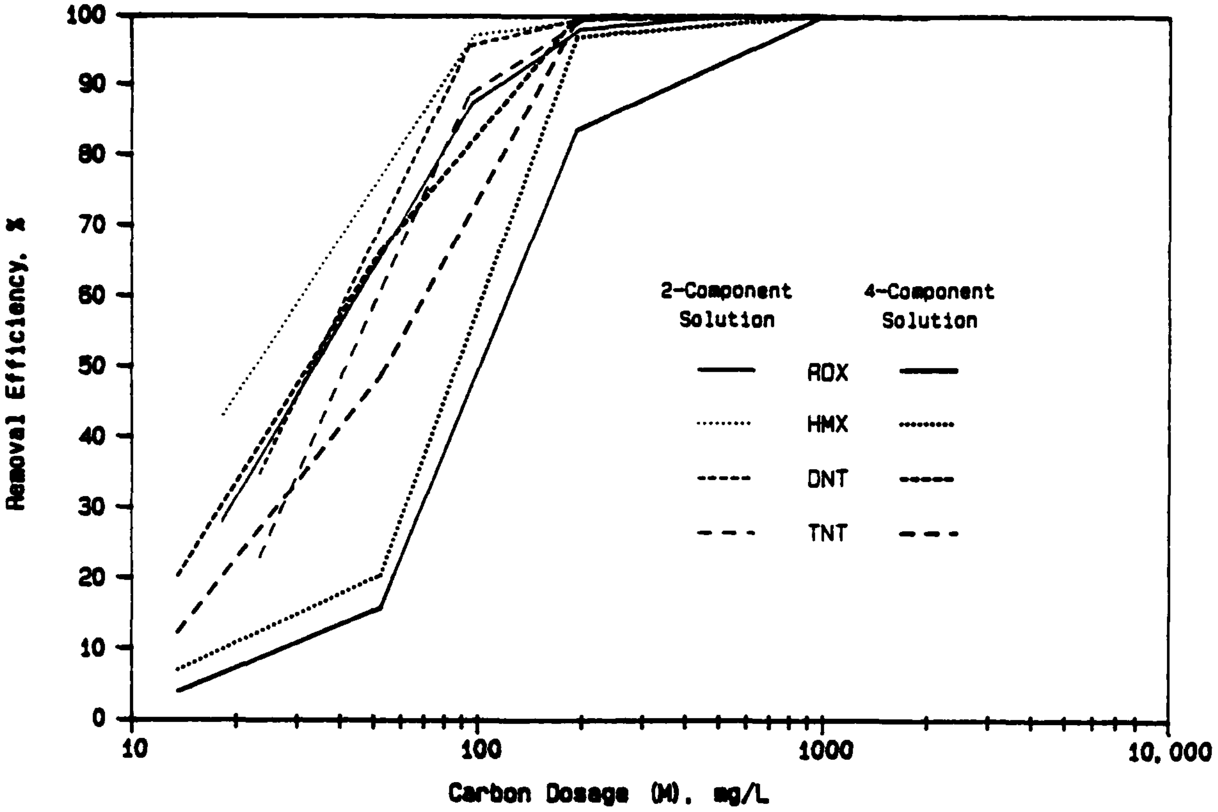

Figure 5-11. Nitrobody removal efficiencies as a function of carbon dosage.

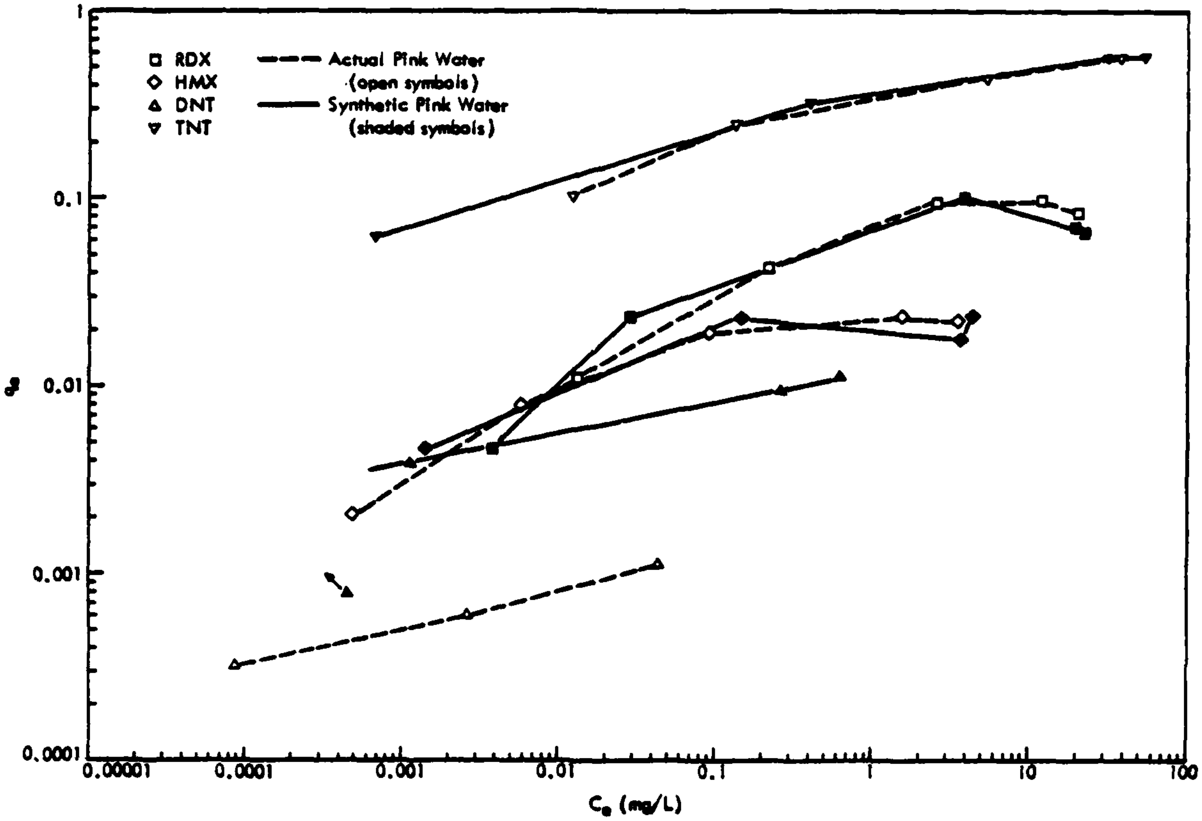

Figure 5-12. Comparison of isotherm test data for actual pink water with synthetic pink water.

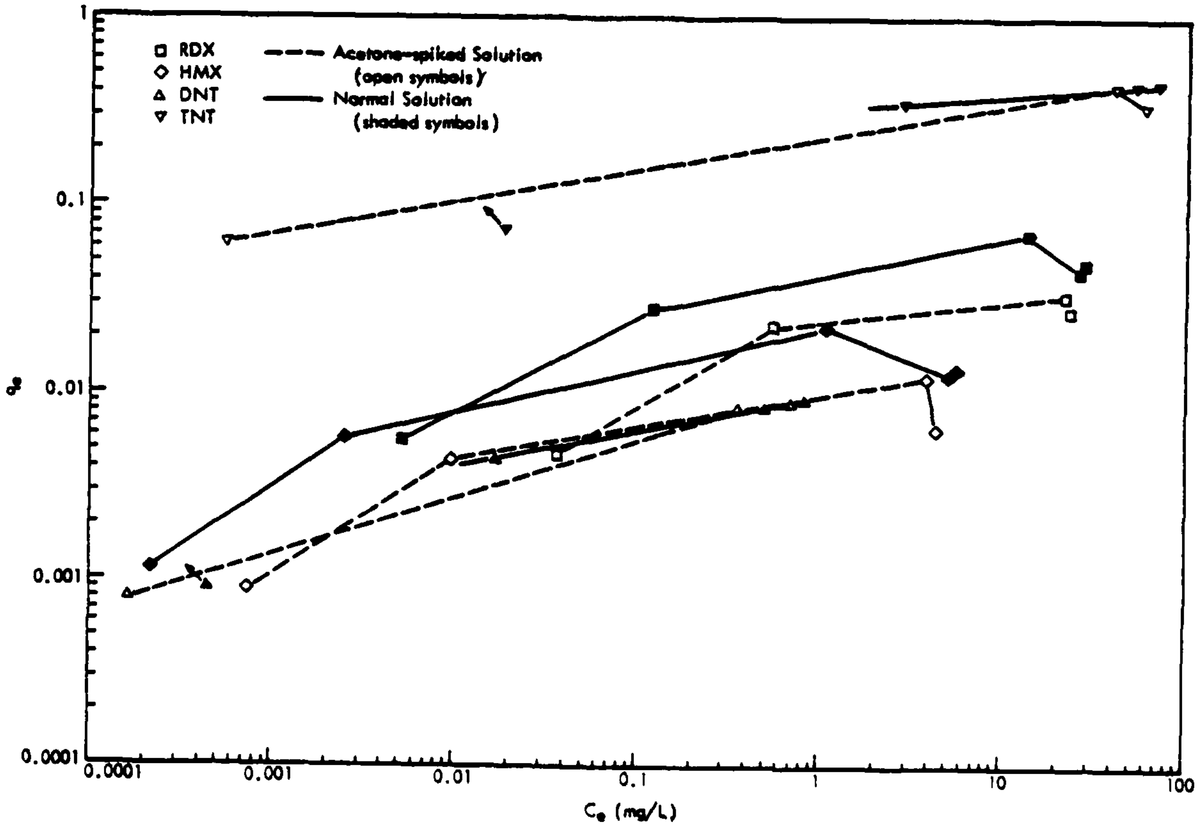

Figure 5-13. Isotherm test results showing effects of acetone present in solution.

TABLE 5-1. Isotherm Test Matrix.

20-hr Isotherm tests	Samples	No. of variables
Isotherm tests to select best-performing GAC. Witcarb 950 was selected and used throughout balance of tests (except as noted).	30	5 GACs 1 Temperature 1 Solution 6 GAC dosages[a]
Isotherm tests to determine effect of temperature	12	1 GAC 2 Temperatures 1 Solution 6 GAC dosages[a]
Isotherm tests to determine competitive adsorption effect by changing solution composition	12	1 GAC 1 Temperature 2 Solutions 6 GAC dosages[a]
Isotherm tests to compare synthetic pink water to actual AAP pink water	6	1 GAC 1 Temperature 1 Solution 6 GAC dosages[a]
Isotherm tests to determine solvent (acetone) effect on nitrobody adsorption	6	1 GAC[b] 1 Temperature 1 Solution 6 GAC dosages[a]
Total of five comparative studies	Total of 66 samples	Total studied: 5 GACs 3 Temperatures 5 Solutions[c] 6 GAC dosages[a]

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[a] Five varying GAC dosages plus one blank (no GAC).
[b] Used Filtrasorb 300 (ran test prior to GAC ranking).
[c] Including acetone-spiked solution.

TABLE 5-2. Isotherm Test Results for Calgon Filtrasorb 200.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	27.7	N/A	5.71	N/A	0.925	N/A	72.8	N/A
9.2	27.6	0.0109	5.61	0.0109	0.855	0.0076	70.2	0.283
50.2	22.9	0.0957	4.06	0.0329	0.395	0.0106	46.5	0.524
203	15.9	0.0582	1.91	0.0187	0.0295	0.0044	5.56	0.332
1,001	0.0990	0.0276	0.00412[a]	0.0057	< MDL[a]	> 0.0009	0.000735[a]	0.0727
4,997	0.00400[a]	0.0055	ND[a]	N/A	ND[a]	N/A	ND[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

TABLE 5-3. Isotherm Test Results for Calgon Filtrasorb 300.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	28.0	N/A	5.61	N/A	0.915	N/A	73.7	N/A
12.0	27.4	0.0500	5.45	0.0133	0.802	0.0094	68.3	0.450
50.9	25.7	0.0452	4.98	0.0124	0.484	0.0085	51.3	0.440
201	13.5	0.0720	1.07	0.0226	0.0166	0.0045	2.74	0.353
1,000	0.120	0.0279	0.00248	0.0056	< MDL[a]	> 0.0009	< 0.0185	> 0.0737
5,001	0.00508[a]	0.0056	0.000216[a,b]	0.0011	ND[a]	N/A	< MDL[a]	N/A

N/A = Not applicable

ND = Not detected

MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

TABLE 5-4. Isotherm Test Results for Calgon Filtrasorb 400.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.7	N/A	4.45	N/A	0.769	N/A	62.7	N/A
12.8	23.3	0.0312	4.35	0.0078	0.619	0.0117	55.3	0.578
52.7	21.6	0.0398	3.70	0.0142	0.279	0.0093	34.0	0.544
203	7.29	0.0810	0.402	0.0200	0.00178[a]	0.0038	0.581	0.307
997	0.0521	0.0237	0.00270[a]	0.0045	< MDL[a]	> 0.0008	0.00155[a]	0.0629
5,001	0.00528[a]	0.0047	< MDL[a]	N/A	ND[a]	N/A	< MDL[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

TABLE 5-5. Isotherm Test Results for Westvaco Nuchar WV-G.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.3	N/A	4.52	N/A	0.763	N/A	61.6	N/A
10.2	22.9	0.0392	4.45	0.0069	0.643	0.0118	55.5	0.598
50.4	21.3	0.0397	3.80	0.0143	0.287	0.0094	32.3	0.581
200	5.91	0.0868	0.473	0.0202	0.00144[a]	0.0038	0.445	0.305
1,000	0.0553	0.0232	0.00317[a]	0.0045	< MDL[a]	> 0.0008	0.000470[a]	0.0616
5,001	0.00373[a]	0.0047	ND[a]	N/A	ND[a]	N/A	< MDL[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

TABLE 5-6. Isotherm Test Results for Witco Witcarb 950.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.3	N/A	4.58	N/A	0.779	N/A	61.8	N/A
13.6	22.4	0.0662	4.26	0.0235	0.621	0.0116	54.2	0.559
52.6	19.6	0.0703	3.64	0.0179	0.261	0.0098	31.7	0.572
194	3.79	0.1006	0.144	0.0229	0.00113[a]	0.0040	0.399	0.317
1,004	0.0284	0.0232	0.00142[a]	0.0046	< MDL[a]	> 0.0008	0.000687[a]	0.0615
5,008	0.00375[a]	0.0047	ND[a]	N/A	ND[a]	N/A	ND[a]	0.0123

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

TABLE 5-7. Ranking of GACs at Various C_e's and Overall Rankings.

Ranking order (best to worst)

Nitrobody	C_e (mg/L) 0.01	0.03	0.1	1	10	Overall
RDX	W950	W950	W950	W950	W950	W950
	F200	WVG, F400	F400	WVG	F300, F400	WVG, F400
	WVG	F200	F200	F400	WVG	F200
	F300	F300	WVG	F300	F200	F300
	F400		F300	F200		

Nitrobody	C_e (mg/L) 0.01	0.03	0.1	1	Overall
HMX	W950	W950	W950	F300	W950
	F300	F300	F400	W950	F300
	F200	F400	F300	WVG	F400
	F400	WVG	WVG	F400	WVG
	WVG	F200	F200	F200	F200

Nitrobody	C_e (mg/L) 0.01	0.1	Overall
2,4-DNT	W950	W950	W950
	WVG	WVG	WVG
	F400	F400	F400
	F300[a]	F200	F200, F300[a]
	F200[a]	F300	

Nitrobody	C_e (mg/L) 0.01	0.04	0.1	1	10	Overall
TNT	WVG	W950	W950	W950	W950	W950
	W950	WVG	WVG	WVG	WVG	WVG
	F200	F400	F400	F400	F400	F400
	F400	F200	F200	F300[a]	F300	F200
	F300[a]	F300[a]	F300[a]	F200	F200	F300[a]

Note: W950 = Witco Witcarb 950
WVG = Nuchar WV-G
F400 = Calgon Filtrasorb 400
F300 = Calgon Filtrasorb 300
F200 = Calgon Filtrasorb 200

[a] Exact ranking for this GAC is questionable due to limited analytical data.

TABLE 5-8. Isotherm Results for Low Temperature (40°F) Test of Witcarb 950.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.1	N/A	4.53	N/A	0.763	N/A	59.0	N/A
25.3	21.0	0.0831	3.95	0.0230	0.525	0.0094	47.9	0.439
109	12.0	0.1016	1.81	0.0249	0.0642	0.0064	9.63	0.452
204	1.99	0.1036	0.0929	0.0218	0.0203	0.0036	0.234	0.289
509	0.0888	0.0452	0.00782[a]	0.0089	0.000238[a]	0.0015	0.0240	0.116
2,004	0.0170[a]	0.0115	0.00304[a]	0.0023	0.0000736[a,b]	0.0004	ND[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

TABLE 5-9. Isotherm Results for High Temperature (120°F) Test of Witcarb 950.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.7	N/A	4.71	N/A	0.773	N/A	59.7	N/A
25.3	23.0	0.0277	4.45	0.0103	0.467	0.0121	43.3	0.649
111	16.5	0.0646	2.07	0.0237	0.0420	0.0066	4.30	0.497
204	5.30	0.0903	0.229	0.0220	0.00211[a]	0.0038	0.158	0.292
508	0.429	0.0458	0.0116[a]	0.0092	0.000147[a,b]	0.0015	0.000600[a]	0.118
2,020	0.000904[a]	0.0117	0.00193[a]	0.0023	ND[a]	N/A	ND[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

TABLE 5-10. Isotherm Test Results for Two-Component Solution (RDX and HMX) Using Witcarb 950.

Carbon dosage (M), mg/L	RDX Equil. conc. (C_e), mg/L	RDX q_e	HMX Equil. conc. (C_e), mg/L	HMX q_e
Blank (0)	22.6	N/A	4.42	N/A
18.5	16.3	0.341	2.50	0.104
97.9	2.83	0.202	0.114	0.0440
201	0.473	0.110	0.0200	0.0219
502	0.0594	0.0449	0.00181[a]	0.0088
1,998	0.0103[a]	0.0113	0.000416[a]	0.0022

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX

[a] Indicates analysis by trace enrichment method.

TABLE 5-11. Isotherm Test Results for Two-Component Solution (2,4-DNT and TNT) Using Witcarb 950.

	2,4-DNT		TNT	
Carbon dosage (M), mg/L	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	1.29	N/A	110	N/A
23.7	0.901	0.0164	92.3	0.746
95.7	0.213	0.0113	35.2	0.782
204	0.00522	0.0063	0.911	0.535
500	0.000389[a,b]	0.0026	0.0309	0.220
2,011	ND[a]	N/A	ND[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

TABLE 5-12. Isotherm Test Results for Pink Water from KAAP Using Witcarb 950.

Carbon dosage (M), mg/L	RDX		HMX		2,4-DNT		TNT	
	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	22.0	N/A	4.02	N/A	0.0663	N/A	49.4	N/A
20.0	20.3	0.0848	3.57	0.0225	0.0430	0.0012	37.9	0.574
101	12.0	0.0989	1.54	0.0245	0.00264[a]	0.0006	5.40	0.435
201	2.56	0.0966	0.0910	0.0195	0.0000893[a,b]	0.0003	0.137	0.245
500	0.218	0.0436	0.00591[a]	0.0080	ND[a]	N/A	0.0120[a]	0.0989
1,998	0.0132[a]	0.0110	0.000491[a]	0.0020	ND[a]	N/A	< MDL[a]	N/A

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

TABLE 5-13. Isotherm Test Results for Acetone-Spiked Pink Water Using Filtrasorb 300.

	RDX		HMX		2,4-DNT		TNT	
Carbon dosage (M), mg/L	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e	Equil. conc. (C_e), mg/L	q_e
Blank (0)	23.1	N/A	4.35	N/A	0.776	N/A	61.3	N/A
11.0	22.8	0.0274	4.28	0.0064	0.677	0.0090	57.6	0.338
50.7	21.4	0.0335	3.74	0.0120	0.350	0.0084	39.3	0.434
200	Lost	N/A	Lost	N/A	Lost	N/A	Lost	N/A
1,001	0.548	0.0225	0.00962[a]	0.0043	0.000163[a,b]	0.0008	0.00055[a]	0.0613
5,003	0.0363	0.0046	0.000732[a]	0.0009	ND[a]	0.0002	< MDL[a]	0.0123

N/A = Not applicable
ND = Not detected
MDL = Minimum detection level (concentration at lowest level standard) using trace enrichment analysis
MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for 2,4-DNT
MDL = 0.000370 mg/L for TNT

[a] Indicates analysis by trace enrichment method.

[b] < MDL, but quantitated.

6. PRELIMINARY COLUMN TESTS

6.1 INTRODUCTION

Several preliminary column tests were conducted on a small laboratory scale in order to gain enough column operating data to plan and design equipment for the multiple column tests. The primary information sought was (a) the time (or wastewater volume) required to reach breakthrough above the discharge limits; and (b) the time (or wastewater volume) required to reach near-complete saturation of the carbon. The ratio of item "b" to item "a" above is essentially the minimum number of columns required in a multiple column system.

Three preliminary tests were run. Tests 1 and 2 were single column tests with a "short" and "long" bed depth, respectively. Test 3 used a more refined design, based upon results obtained from the first two tests as well as isotherm test results. It consisted of two columns in series -- a "short" column intended for determining carbon saturation time, followed by a "long" column intended for determining breakthrough time for the discharge limits.

6.2 MATERIALS

Two different types of GACs were used for these tests. The first two tests were conducted prior to completion of the isotherm tests and were conducted with Calgon Filtrasorb 300 carbon, which represents the industry standard. The third test was conducted after the five GACs were ranked based upon isotherm test results. Therefore, Witco Witcarb 950 was the carbon used for this test.

The same nitrobody materials were used to generate pink water for these tests as were used for the isotherm tests.

6.3 PROCEDURES

6.3.1 Preparation of Synthetic Pink Water

Four-component pink water was synthetically prepared for the preliminary column tests using the same nominal concentrations as used for the isotherm tests. However, one important procedural difference should be noted. The nitrobodies were dissolved in acetone to make stock solutions, and the acetone stock solutions were used to spike deionized water. This procedure simplified pink water preparation but created two problems. First, some of the nitrobodies precipitated out of solution when the water was spiked (TNT could be seen), and crystals that did not dissolve had to be removed by recirculating the pink water and filtering it as it passed through the tubing. The second problem was related to the solvent's effect on RDX and HMX adsorption (see Section 5.5.5.2 on isotherm test results). The results of this preliminary column test were sufficient for the purpose of planning more carefully controlled tests. However, the results should not be used to predict performance in actual full-scale systems due to the effects of the presence of acetone.

All four nitrobodies were dissolved in a single aliquot of acetone to make the pink water used for Test 1. The amount of acetone added to the water was kept to a minimum this way, representing just the amount needed to dissolve all four compounds. The resulting acetone level in the pink water was only 0.20% on a volume basis.

A separate pink water solution was used for both Tests 2 and 3. This time, individual acetone stock solutions of each nitrobody were made up and added individually to 100 L of deionized water. The resulting level of acetone was 0.44% on a volume basis. Both batches of pink water contained considerably less acetone than was present in the isotherm tests (2% was used then) reported in Section 5.5.5.

The concentration of each of the four nitrobodies in the two batches of pink water used for the preliminary column tests are given below. The values represent initial analysis of the pink water.

Pink water batch	Concentration, mg/L TNT	RDX	HMX	2,4-DNT
Test 1	67.4	18.3	6.97	1.23
Tests 2 and 3	79.1	26.7	6.33	0.946

6.3.2 General Test Procedures

The desired quantity of GAC was weighed for each test. The GAC was degassed by being set under water several hours. Then the GAC/water slurry was loaded into a glass column fitted with glass wool on either end of the carbon bed. Glass beads were used to eliminate excess "dead" volume. The ends of the glass tube were fitted with one-hole rubber stoppers and a short length of glass tubing. (Note: In Test 2, a deviation from the above packing procedure was used. The GAC was packed dry; then deionized water was pumped through the column to degas the carbon.)

The carbon column(s) for each test was (were) connected to a pump, a calibrated flowmeter, and appropriate sampling ports. The pink water was pumped at a constant flow rate, and carbon column effluent samples were taken at varying time intervals. A sample of the influent was taken at the beginning and end of each test. The tests were all conducted at ambient temperature.

6.3.3 Test Conditions

Both measured and calculated test conditions for all three preliminary column tests are summarized in Table 6-1. These tests were range-finding tests, with conditions selected partly by trial and error. The desired results were not always achieved, but the tests did indicate some of the operational problems to be expected in larger, multiple column tests.

The glass column inner diameter was relatively small (2.3 and 1.75 cm), which may have introduced errors due to channeling or surface effects. Ordinarily, the smallest acceptable column diameter for such tests is in the 5- to 8-cm range. Thus, these results should not be used directly to predict performance of full-scale columns. However, conducting these tests did provide enough information to plan for the multiple column tests and to design appropriate equipment.

6.4 RESULTS AND DISCUSSION

6.4.1 Preliminary Column Test 1

The first column test was run on Filtrasorb 300 GAC using the conditions described in Table 6-1. The test period was approximately 37 hr, during which time the storage reservoir was emptied. The results of HPLC analysis performed on the collected samples are provided in Table 6-2. The cumulative test time is given for each sample. The number of bed volumes of wastewater passed through the column is also provided. This is generally a more descriptive parameter than is test time. Normalized breakthrough values are also given for each nitrobody. Normalized breakthrough is defined as the ratio of the effluent concentration to the influent concentration. Thus, a value of 0.0 represents complete removal and a value of 1.0 represents no removal. If a normalized breakthrough of 1.0 is reached for any nitrobody, the carbon column is saturated with respect to that compound, and the column is effectively exhausted. Implications for a multiple column operation in series are that when penetration in the first column in series approaches 1 (a value of 0.8 may be appropriate), that column should be taken out of operation.

A plot of normalized breakthrough as a function of both time and total number of bed volumes is shown in Figure 6-1. In this test, effluent levels approached influent levels (normalized breakthrough approached 1.0) for RDX and HMX much more rapidly than for 2,4-DNT and TNT. In fact, by plotting normalized results, it can be seen that the response for RDX is very similar to the response for HMX, and the response for 2,4-DNT is very similar to the response for TNT. The highest normalized breakthrough at the end of the test was 0.76 for RDX.

The effluent concentrations for all four nitrobodies exceeded the discharge limits immediately upon startup. To investigate the time to breakthrough at these levels, a second column test was planned using a much greater bed depth.

It is suspected that channeling occurred during the first column test, which may either explain or partially explain the relatively high effluent levels upon startup.

6.4.2 Preliminary Column Test 2

The second column test was run using the same size glass column, the same wastewater flow rate, and the same GAC (Filtrasorb 300) as were used in the first test. This time, however, the bed depth was greatly extended in order to watch for breakthrough above the discharge levels. One major problem complicated this test. When carbon was packed dry and then wetted by pumping deionized water through it, apparently not all of the air was removed prior to startup. As a result, the effective surface area available for adsorption may have been limited until the carbon was sufficiently wetted. The results of this test are given in Table 6-3. Normalized breakthrough levels are not included because it was absolute concentrations that were of concern in this test, rather than extent of carbon saturation.

As results shown in Table 6-3 indicate, the effluent concentrations notably dropped during the first hour of operation and may have continued to drop during the test. This may have been due to an improper carbon packing procedure as described above. Insufficient sample volumes were taken to allow for trace enrichment analysis. However, a composite was made of three samples. The test was terminated at approximately 6 hr. TNT concentrations were running near the effluent criterion, but concentrations of the other three compounds were still well below the specific effluent criterion.

Assuming that channeling was responsible for high initial concentration, this test indicates that the target effluent criteria can be achieved.

6.4.3 Preliminary Column Test 3

The third column test was planned following completion of the isotherm tests. Witcarb 950 was selected as the best ranking GAC for subsequent testing. The purpose of the third column test was to acquire as much useful performance information as possible from a laboratory column test using Witcarb 950. Two columns in series were used. Column A, with a bed depth of 11 cm, was expected to yield data on saturation of the carbon bed with one or more nitrobodies. Column B, with a bed depth of 45 cm, which made a combined bed depth of 56 cm for the series of Columns A and B, was expected to yield data on breakthrough above the low discharge limits. Sampling the effluent from each of these columns was analogous to sampling the effluent from the first and the last columns of a five in series column operation.

Analytical results are given for Column A in Table 6-4 and for Column B in Table 6-5. All samples from Column A were analyzed by the direct injection method of analysis. All Column B samples were also analyzed by direct injection, but results were all "not detected." The last several samples from Column B were also analyzed by trace enrichment analysis, as noted in Table 6-5.

Normalized breakthrough values are provided for the Column A results, as the primary interest was the time (or volume) required for carbon saturation. These values are plotted in Figure 6-2. This indicates that the carbon was almost completely saturated (penetration > 0.9) with RDX and HMX by the end of the test. By using normalized breakthrough data, it can be seen that RDX and HMX were adsorbed almost identically.

Since effluent levels of RDX and HMX approach influent levels more rapidly than with TNT and DNT, it is expected that the GAC is adsorbing more TNT and DNT, owing to differences in overall magnitude of concentration.

The cumulative carbon loading of all four nitrobodies during this test was calculated by multiplying the difference between influent and effluent concentration by the volumetric flow rate to obtain the mass loading rates onto the GAC, then multiplying this by the time interval between sampling to obtain the mass loaded onto the carbon during each interval of time. The cumulative masses were then summed for each sampling time and the sum divided by the mass of GAC used. This relationship is shown graphically in Figure 6-3. It can be seen that the bulk of nitrobodies adsorbed during this test consisted of TNT. Lesser quantities of RDX were adsorbed, followed by HMX and then DNT. This order also represents decreasing concentration in the influent. Column A was exhausted with respect to removal of RDX and HMX, even though it apparently had capacity to adsorb additional TNT. The carbon loadings reached by the end of the test were generally of the same magnitude as the maximum q_e values from the isotherm tests.

Nitrobody levels from the effluent of Column B did not exceed the effluent criteria during this test. In fact, 2,4-DNT could not be detected in any of the samples even when using trace enrichment analysis. A plot of concentration versus time or number of bed volumes is shown in Figure 6-4. The number of bed volumes is based upon Columns A and B combined.

Ignoring differences in GACs, the combined column test results indicate that the effluent criteria can be achieved at a shorter contact time than in Test 2. This may be due to the higher column loading rate and shorter mass transfer zone (refer to Section 7.6.3).

The results from this test were used for planning the multiple series column tests. Information obtained from this test included an indication of the number of bed volumes of pink water necessary to (a) exceed the discharge levels, and (b) saturate the column. Also, these results indicate that a 5:1 ratio for total bed volume to the first bed volume is higher than necessary. Thus, a four in series column operation may be practical, and this configuration was used for the larger scale column tests.

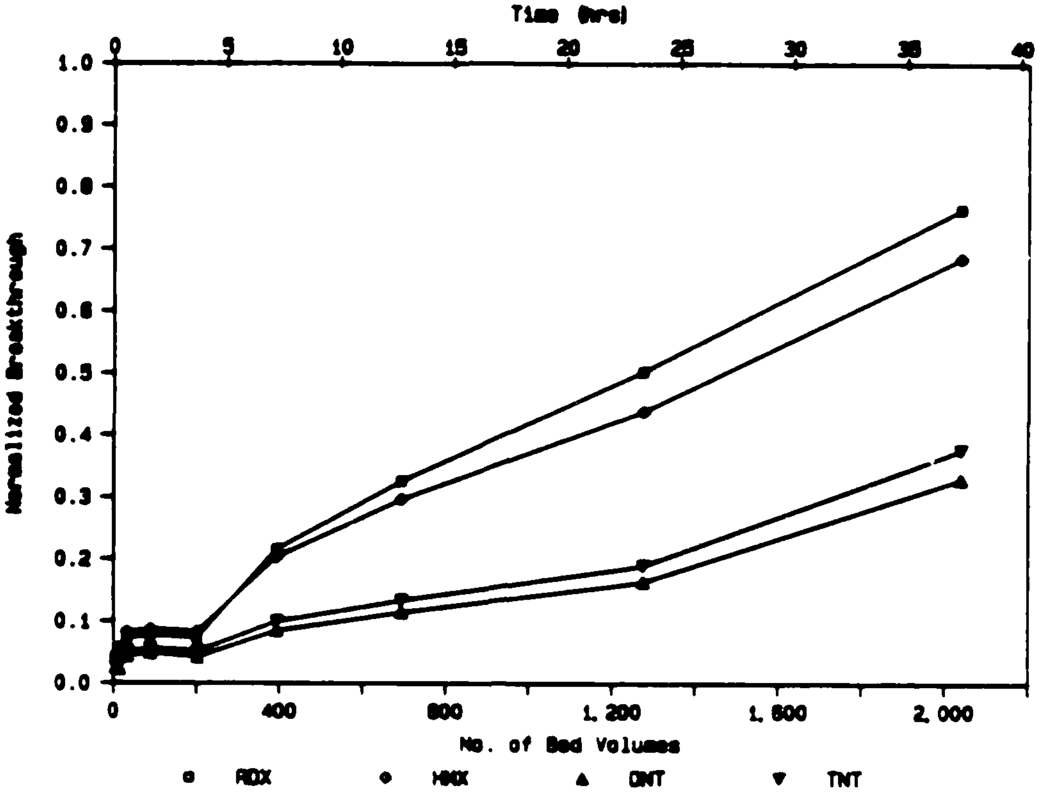

Figure 6-1. Breakthrough curve for preliminary column test No. 1.

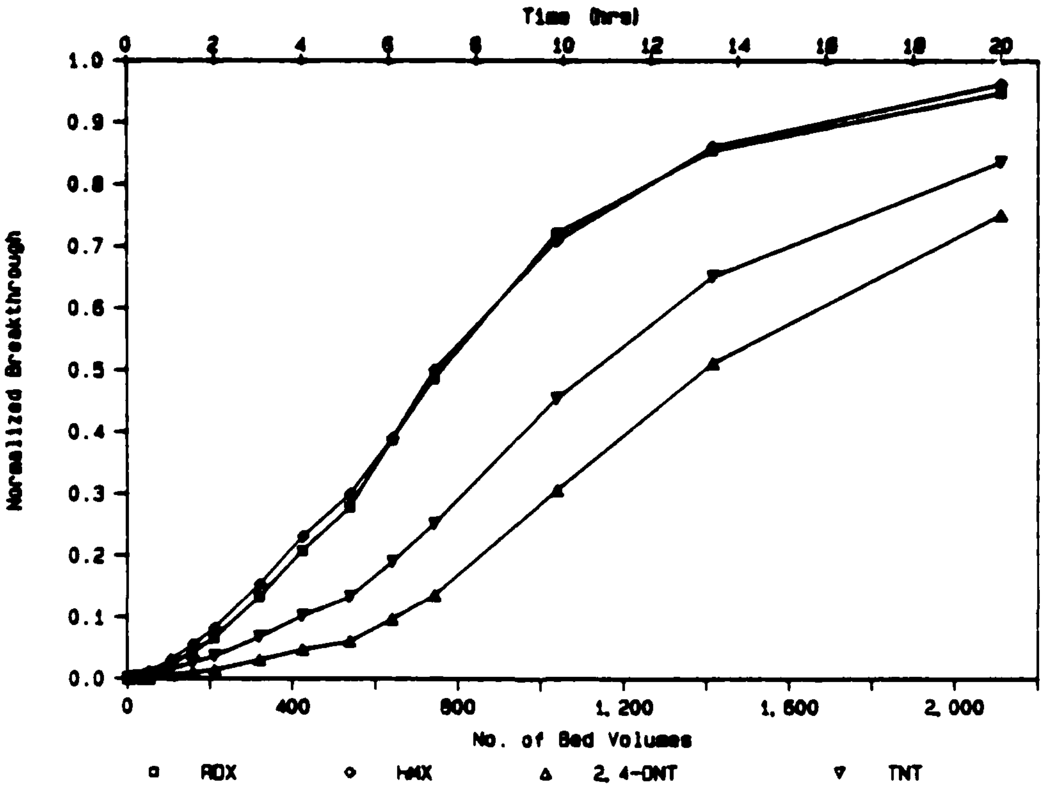

Figure 6-2. Breakthrough curve for preliminary column test No. 3 (column A effluent).

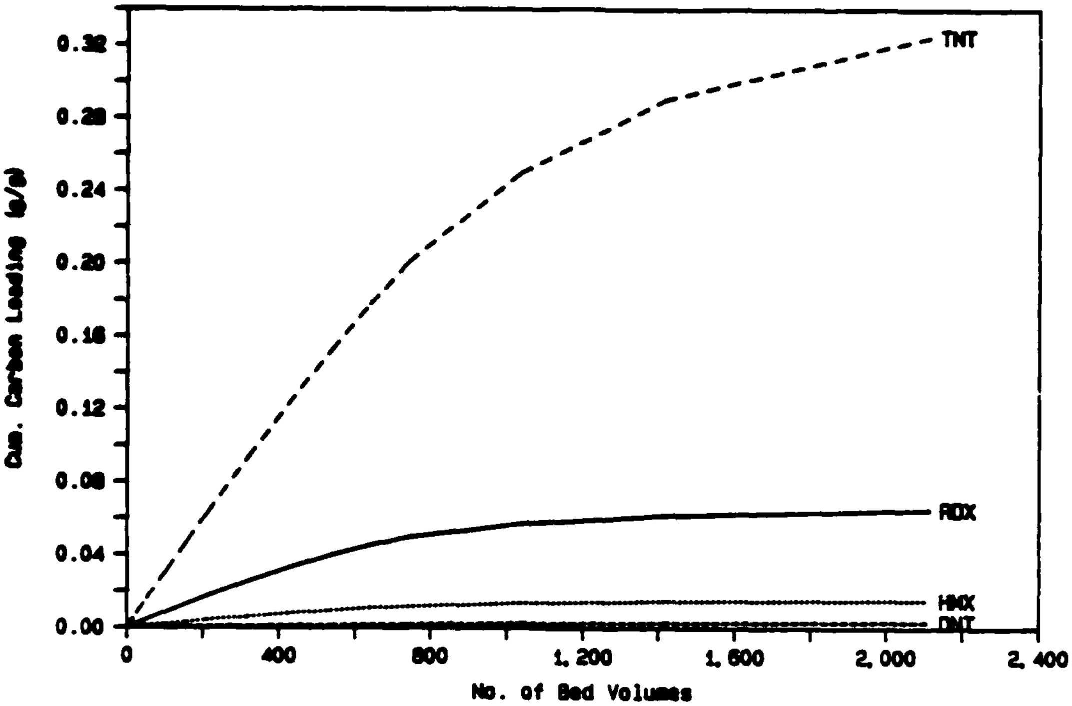

Figure 6-3. Cumulative carbon loading for preliminary column test No. 3 (column A).

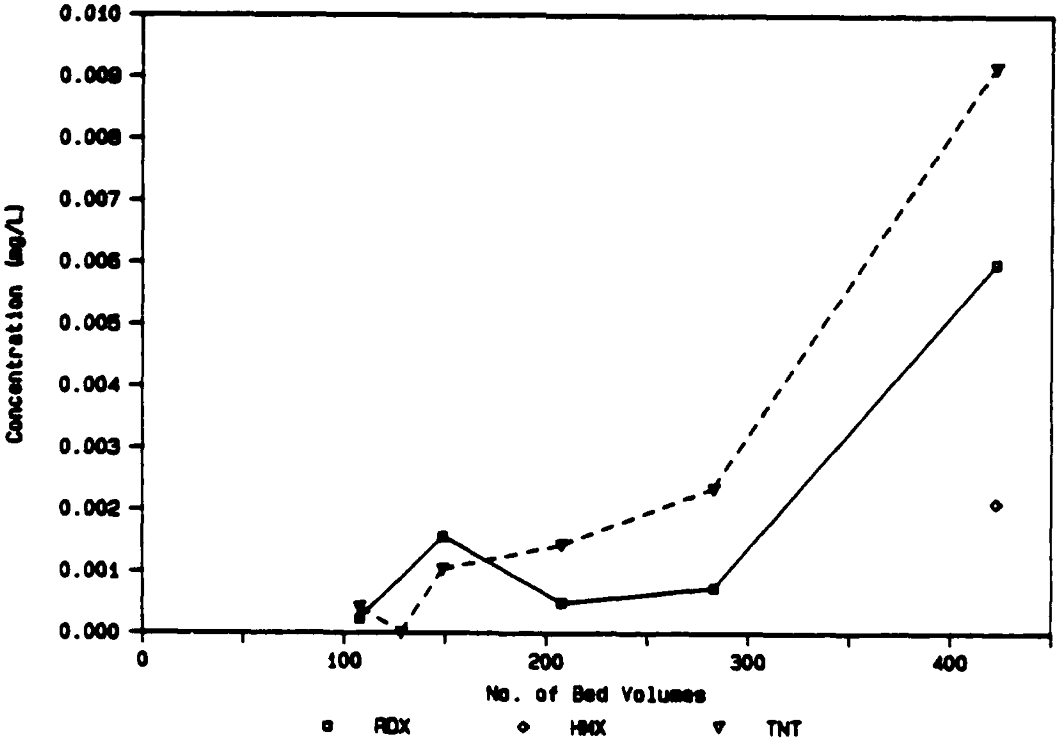

Figure 6-4. Effluent concentrations for preliminary column test No. 3 (column B).

TABLE 6-1. Preliminary Column Test Conditions.

	Test No. 1	Test No. 2	Test No. 3 Column A	 Column B	 A & B combined
GAC type	Filtrasorb 300	Filtrasorb 300	Witcarb 950		
GAC mass, g	17	140	10	40	50
Column inner diameter, cm	2.3	2.3	1.75		
Bed depth, cm	8.6	75	11	45	56
Ratio of length (depth) to diameter	3.7	33	6.3	26	32
Bed volume, cm^3	33	290	27	108	135
Liquid flow rate, mL/min	30	30	48		
Superficial velocity, cm/min	7.2	7.2	20		
Superficial contact time, min	1.2	10	0.6	2.3	2.8
Hydraulic loading, gpm/ft^2	1.9	1.9	4.8		
Total test time, hr	3.8	6.2	20		
Total liquid volume, L	68	11	57		
Total No. of bed volumes	2,100	38	2,100	530	420

TABLE 6-2. Results of Preliminary Column Test No. 1 (Using Filtrasorb 300).

Time (hr)	No. of bed volumes[a]	Effluent concentration (mg/L)				Normalized breakthrough			
		RDX	HMX	DNT	TNT	RDX	HMX	DNT	TNT
0.08	5	0.788	0.288	0.0301	1.69	0.043	0.041	0.024	0.025
0.25	14	1.05	0.392	0.0281	1.98	0.057	0.056	0.023	0.029
0.58	32	1.35	0.581	0.0548	3.53	0.074	0.083	0.045	0.052
1.62	88	1.43	0.609	0.0603	3.80	0.078	0.087	0.049	0.056
3.68	201	1.35	0.583	0.0521	3.52	0.074	0.084	0.042	0.052
7.20	393	3.97	1.42	0.105	6.76	0.217	0.204	0.085	0.100
12.7	693	5.97	2.07	0.142	9.05	0.326	0.294	0.115	0.134
23.4	1,280	9.21	3.06	0.202	12.8	0.503	0.439	0.164	0.190
37.4	2,040	14.0	4.78	0.406	25.4	0.765	0.686	0.330	0.377
Influent conc.[b]		18.3	6.97	1.23	67.4				

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[a] Bed volume = 33 cm^3.

[b] Sample taken at end of test.

TABLE 6-3. Results of Preliminary Column Test No. 2
(Using Filtrasorb 300).

Time	No. of bed	Effluent Concentration (mg/L)			
(hr)	volumes[a]	RDX	HMX	DNT	TNT
0.17	1.0	0.0790	0.0501	0.0112[c]	0.851
0.33	2.1	0.0467	0.0397	0.00537[c]	0.540
0.50	3.1	0.0221	ND	0.00430[c]	0.328
0.67	4.1	0.0162[c]	0.00561[c]	ND	0.264
0.83	5.2	0.00915[c]	ND	ND	0.0413
1.00	6.2	< MDL	< MDL	ND	0.0446
1.33	8.3	ND	ND	ND	0.0347
1.67	10.3	0.00659[c]	0.0193[c]	ND	0.100
2.00	12.4	< MDL	ND	ND	0.0595
4.22[d]	26.2	0.00422	0.000778	0.000216	0.0120
6.22	38.6	ND	ND	ND	0.0414
6.95	43.1	ND	ND	ND	ND
Influent conc.[b]		26.7	6.33	0.946	79.1

ND = Not detected

MDL = Minimum detection level (concentration at lowest level standard)

MDL = 0.0185 mg/L for RDX
MDL = 0.0208 mg/L for MMX
MDL = 0.0220 mg/L for DNT
MDL = 0.0185 mg/L for TNT

[a] Bed volume = 290 cm^3.

[b] Sample taken at end of test.

[c] Quantitated, but < MDL.

[d] Composite of samples taken at 3.22, 4.22, and 5.22 hr to allow enough sample volume for trace enrichment analysis with lower MDLs.

TABLE 6-4. Results from Two in Series Preliminary Column Test with Witcarb 950--Column A.

Test time (hr)	No. of bed volumes[a]	Effluent concentration (mg/L)				Normalized breakthrough			
		RDX	HMX	2,4-DNT	TNT	RDX	HMX	2,4-DNT	TNT
0.00	0	0.0208	0.0123[b]	ND	0.0831	0.001	0.002	0.000	0.001
0.25	26	0.0986	0.0358	ND	0.320	0.003	0.005	0.000	0.003
0.50	53	0.258	0.0882	ND	0.719	0.008	0.011	0.000	0.006
1.00	106	0.765	0.246	0.00632[b]	1.80	0.024	0.031	0.006	0.016
1.50	158	1.40	0.440	0.0106[b]	2.97	0.043	0.056	0.010	0.026
2.00	211	2.15	0.653	0.0156[b]	4.19	0.067	0.083	0.015	0.037
3.03	320	4.31	1.22	0.0336	7.81	0.134	0.154	0.031	0.069
4.02	424	6.73	1.83	0.0514	11.7	0.209	0.231	0.048	0.104
5.10	538	9.00	2.38	0.0664	15.1	0.279	0.301	0.062	0.134
6.07	640	12.5	3.09	0.105	21.5	0.388	0.390	0.098	0.190
7.03	742	15.7	3.97	0.146	28.5	0.487	0.502	0.136	0.252
9.83	1,038	23.3	5.62	0.328	51.4	0.722	0.710	0.307	0.455
13.40	1,414	27.6	6.82	0.548	73.7	0.856	0.862	0.512	0.652
20.00	2,111	30.6	7.62	0.805	94.6	0.949	0.963	0.752	0.837
Influent conc.[c]		32.3	7.92	1.07	113				

ND = Not detected

MDL = Minimum detection level (lowest concentration standard)
MDL = 0.0185 mg/L for RDX
MDL = 0.0208 mg/L for HMX
MDL = 0.0220 mg/L for DNT
MDL = 0.0185 mg/L for TNT

[a] Bed volume = 27 cm^3.

[b] Quantitated, but < MDL.

[c] Average of analyses of samples taken at beginning and end of test.

TABLE 6-5. Results from Two in Series Preliminary Column Test with Witcarb 950--Column B.

Test time (hr)	No. of bed volumes[a]	Effluent concentration (mg/L)			
		RDX	HMX	2,4-DNT	TNT
0.00	0	ND	ND	ND	ND
0.25	5	ND	ND	ND	ND
0.50	11	ND	ND	ND	ND
1.00	21	ND	ND	ND	ND
1.50	32	ND	ND	ND	ND
2.00	42	ND	ND	ND	ND
3.03	64	ND	ND	ND	ND
4.02	85	ND	ND	ND	ND
5.10	108	0.000236[b,c]	ND[b]	ND[b]	0.000402[b]
6.07	128	ND	ND	ND	ND
7.03	148	0.00156[b]	ND[b]	ND[b]	0.00103[b]
9.83	208	0.000502[b]	< MDL[b]	ND[b]	0.00143[b]
13.40	283	0.000750[b]	< MDL[b]	ND[b]	0.00234[b]
20.00	422	0.00600[b]	0.00212[b]	ND[b]	0.00916[b]
Influent conc.[d]		32.3	7.92	1.07	113

ND = Not detected

MDL = Minimum detection level (lowest concentration standard) using trace enrichment analysis

MDL = 0.000370 mg/L for RDX
MDL = 0.000416 mg/L for HMX
MDL = 0.000440 mg/L for DNT
MDL = 0.000370 mg/L for TNT

[a] Bed volume = 135 cm^3 (combined Columns A and B).

[b] Analyzed by trace enrichment method.

[c] Quantitated, but < MDL.

[d] Average of analyses of samples taken at beginning and end of test (influent to Column A).

7. FOUR IN SERIES COLUMN TESTS

7.1 INTRODUCTION

7.1.1 Background

After the isotherm tests were completed, the test plan was modified to allow the four in series column tests to be conducted in the field at an actual AAP rather than in the laboratory. The tests were conducted with actual pink water from LAP plant operations instead of with the synthetic wastewater used for the isotherm tests conducted in the laboratories.

There were several important reasons to conduct the multiple column GAC tests at an AAP. These included:

- Safety--In order to prepare enough synthetic pink water for testing, it would be necessary to handle large quantities of explosives. This safety hazard was eliminated by using pink water from Iowa Army Ammunition Plant (IAAP).

- Validity--The tests were conducted on actual, representative pink water, thus avoiding any criticisms arising from the use of synthetically made wastewater.

- Scaling--In the laboratory, size of the carbon columns is limited by the volume of synthetic pink water that can be reasonably handled. By conducting tests at IAAP, however, availability of pink water was not a limiting factor, and the operation of larger scale columns was feasible.

After considering several alternatives, the site selected was IAAP located in Middletown, Iowa. This is a government owned, contractor operated (GOCO) plant involved in both manufacturing and LAP operations. The operating contractor is Mason & Hanger - Silas Mason Co., Inc. The reasons for selecting this plant for field tests included availability of pink water for testing, willingness of the operating contractor to cooperate and assist, proximity to MRI's laboratories, and familiarity with the plant through prior contacts by MRI and USATHAMA personnel.

In addition, the technical personnel at IAAP were willing to apply the expertise they had gained from full-scale GAC column operation to assist MRI in several ways, including preparing a reservoir of pink water for the tests, providing a pre-filter, and disposing of spent GAC.

This approach was believed to be the most cost-effective method of providing useful operational data to USATHAMA relevant to the capabilities of GAC treatment to produce an effluent below the proposed low discharge levels.

7.1.2 Objectives

Isotherm test results indicated that under equilibrium conditions it was possible for GAC treatment to achieve effluent concentrations equal to or below effluent limitations of 0.04 ppm TNT, 0.03 ppm RDX, 0.03 ppm HMX, and 0.0007 ppm 2,4-DNT. Five types of GACs were screened, and the best performing GAC was selected based upon the isotherm test results for carbon loading. The carbon selected for column tests was Witco Witcarb 950, 18 x 40 mesh size. Test results indicated that temperatures in the range 40°-120°F had a negligible impact upon GAC performance. Results verified other investigators' experience that competitive adsorption occurs, interfering particularly with effective RDX removal.

The objectives for the multiple column tests were to answer these questions:

- Can GAC treatment of pink water achieve the proposed stringent effluent limits in a dynamic, multiple-column treatment system?

- For normally encountered process conditions, what will be the carbon usage rate?

- What are the economics of constructing and operating a full-scale system with the desired capabilities?

In order to answer these questions, it was necessary to start up a multiple column test system using virgin GAC, then go through several rotational cycles of the carbon columns, based upon either breakthrough in the first column or excessive discharge levels out the final column, until steady state operation was approached. This sequencing procedure is explained in detail in Section 7.4.1. Rapid turnaround on chemical analysis of effluents was required in order to decide when to rotate the columns. For this reason, a high performance liquid chromatograph (HPLC) was operated at the plant site.

7.2 SITE PREPARATION

The test site at IAAP was prepared with support by Mason & Hanger under subcontract to MRI. An ample quantity of wastewater was available to conduct multiple column GAC tests. The pink water was provided by alternating between two tanks each holding 900 gal. with provision to rapidly refill one tank while the other tank was being emptied. Ideally nitrobody concentrations would be the same as the program target values, namely 100 ppm TNT, 30 ppm RDX, 10 ppm HMX, and 1 ppm 2,4-DNT. An actual sample of pink water resulting from Cyclotol formulation was collected at KAAP on March 12, 1985, and was subsequently analyzed by MRI for the four compounds of interest. The concentrations were 49.4 ppm TNT, 22.0 ppm RDX, 4.02 ppm HMX, and 0.0663 ppm 2,4-DNT. Except for 2,4-DNT, the values were similar to those for the synthetic pink water used for isotherm testing. Nitrobody levels in the pink water used at IAAP for multiple column testing were expected to be at least as high as the above values. Desired ranges of nitrobody concentrations were defined as follows:

TNT	40 - 120 ppm
RDX	15 - 40 ppm
HMX	3 - 12 ppm
2,4-DNT	0.05 - 2.0 ppm

Wastewater characterization data from Mason & Hanger received prior to testing indicated that weekly averages of TNT, RDX, and HMX levels were generally within the above ranges. Data on 2,4-DNT were not available.

The multiple column testing apparatus was housed in Building 1-70-1 at IAAP. Mason & Hanger selected and prepared the site for housing the carbon columns. Services provided at this facility were adequate lighting, potable-grade water, and a drain for discharging the final effluent.

For efficient use of GAC columns to treat pink water, it is necessary first to remove any suspended particulate matter with a filtration system. Mason & Hanger, who are experienced in operation of diatomaceous earth filters for large GAC systems, provided a filter unit for this testing program. They also provided a pump capable of transferring the pink water from the storage tanks to the test apparatus, with sufficient head to allow for pressure drops across the prefilter and carbon columns. Site modifications are shown in Figure 7-1.

Another important aspect of site preparation involved the HPLC analysis. Mason & Hanger provided laboratory space with the required services including a laboratory fume hood, compressed nitrogen for powering an autosampler, electric power, and water.

Mason & Hanger assisted MRI staff in installing the test columns and setting up analytical equipment, disposing of the spent GAC, and arranging clearances for bringing in test equipment, allowing MRI staff to work on site, and releasing samples.

7.3 FOUR IN SERIES COLUMN TEST ASSEMBLY

7.3.1 Design Considerations and Materials Selection

Due to the special research needs of this project as well as the hazardous characteristics of the wastewater to be treated, the test assembly had to meet several demanding criteria:

- Safety--All components had to be approved for operation with munitions wastewater. Valves or fittings that impact a shearing force could not be used. The final assembly was inspected by IAAP's safety manager.

- Functionality--The equipment had to be capable of providing the flow configuration desired for multiple column operation and provide for sampling at the inlet and outlet of all columns.

- Ease of use--Since the tests were to be performed at a field site for round-the-clock operation and by a limited crew, the job of installing and removing columns, changing GAC, sampling, and changing the flow pattern all had to be simple and straightforward.

- Transportability--The equipment had to be capable of being disassembled, transported in a van, and reassembled on site.

- Compatible materials construction--The materials and components of choice had to be compatible with the hazardous constituents as well as being free from contaminants that would interfere with chemical analysis.

The test column outer shells were fabricated from sections of clear acrylic plastic tubing 3-in. ID, 1/4-in. wall thickness, and 24 in. long. End caps were fabricated from brass, attached by a screw-on connection, and sealed with Viton O-rings. Diffusers were designed to fit at the entrance and exit of each column to prevent channeling.

The diffuser units were fabricated of acrylic tubing 3-in. OD, 1/8-in. wall thickness, and 2 in. long. The diffusers were filled with 4-mm diameter glass beads and were capped with screens made of 80-mesh brass wire cloth. To adjust the GAC bed depth, spacers were fabricated of 3-in. OD polyethylene (PE) rod stock drilled out in the center to 1/2-in. diameter. Spacers were made in 2-, 4-, and 6-in. lengths. Due to attrition of the carbon or from other sources, enough particulate material passed through the columns to create plugging problems. In order to alleviate these problems, filters were fabricated on site. These filters were made of 3-in. OD acrylic tubing, 1/8-in. wall thickness, 2 in. in length, and filled with pyrex wool that was changed as needed.

The test columns and associated equipment were housed in a frame fabricated from Dex angle. The frame dimensions were approximately 3 x 6 x 8 ft. The columns were initially interconnected by a network of copper tubing and brass ball valves, but the valve design did not satisfy safety requirements at IAAP. Diaphragm valves with a PVC body, an EPDM diaphragm, and iron bonnets were substituted for safety considerations. In the final design, the valves and the test columns were connected with PVC pipe (1/2-in. Schedule 40). For ease of disassembly, transportation to the site, and reassembly, PVC pipe unions were used judiciously throughout the pipe network.

A drain trough was fabricated of stainless steel sheet metal.

A diagram and further description of the test assembly and other components [illegible] purchased "off the shelf" are provided in the following section

The carbon bed diameter in the test columns was 3 in. The [illegible] was designed so that the bed depth could be varied from [illegible] ing the PE spacers. The design flow rate range was [illegible] corresponded to a hydraulic loading rate of about [illegible]

The columns were sized large enough to allow meaningful scale-up of test results and to eliminate channeling problems, but small enough so that, for testing purposes, breakthrough would occur within a reasonable time. The size was a 3-in. ID column, 2 ft in length. The bed depth initially was 1 ft. For a 1-ft bed depth, the length-to-diameter ratio was 4-to-1.

Typically the range of hydraulic loading rate used in GAC systems is 2 to 10 gpm/ft^2. The planned rate for these tests was 8 gpm/ft^2, which represented a fairly conservative value (that is, if actual practice uses a lower hydraulic loading, the pollutant removal and carbon utilization should be better).

At a hydraulic loading rate of 8 gpm/ft^2, the superficial velocity is 1.07 ft/min. For a 1-ft bed depth, the superficial contact time is 0.94 min. Results from a preliminary laboratory column test indicated that effluent breakthrough to 90% of the influent levels of RDX and HMX required 16 hr at a contact time of 0.6 min. (This test was run at a lower hydraulic loading (5 gpm/ft^2) than planned for field testing.) Based strictly upon contact time, the tests were expected to require 25 hr to reach a 90% breakthrough level in the first column effluent. This assumed a startup with virgin GAC, as would be the case for the first cycle of column operation. However, use of a higher hydraulic loading rate was expected to reduce the breakthrough time somewhat. For planning purposes, a cycle time (the time to reach 90% breakthrough in the first column effluent) of 24 hr was used. This cycle time was expected to decrease as the columns were rotated, and the last column in series became progressively more exhausted, until it had a maximum prior use of three cycles before arriving at the first position. This sequencing is explained further in Section 7.4.1.

Based upon manufacturer's data, the expected pressure drop for Witcarb 950 GAC in 18 x 40 mesh is 9.3 in. water/ft bed depth at 8.0 gpm/ft^2 and 68°F. With a total bed depth of 4 ft, the minimum pressure drop across the four carbon columns was predicted to be 3.1 ft water (or 1.3 psi).

The actual consumption of GAC for these tests was expected to be relatively low. Based upon laboratory experience, the bulk density of Witcarb 950, 18 x 40 mesh, was about 25 lb/ft^3. For a 1-ft bed depth, each carbon column had a bed volume of 0.049 ft^3, so the amount of GAC to be loaded into each column was about 1.2 lb. To start the system with virgin GAC in each column and then run through eight complete cycles required about 13 lb of carbon.

A storage reservoir for pink water was required. Ideally, a tank with a minimum volume of 5,000 gal. would be used, based upon 8 days of continuous operation at 8 gpm/ft^2. The actual flow rate for a 3 in. ID column (0.049 ft^2 cross sectional area) is 0.39 gpm, or 570 gpd. Use of a single source of wastewater would eliminate some variables for the GAC column operation. In normal LAP plant operation, the nitrobody concentrations in pink water are highly variable, but it is believed that more useful operating data can be generated by keeping the concentrations fixed. In actual practice, however, it was necessary to use two smaller sized tanks and to refill one while the other was being emptied.

Effluent samples from the first and last column were analyzed in the field to determine when the columns should be rotated. After the fifth cycle was reached, the operating history of each column in the series was the same from one cycle to another.

7.3.2 Description

A detailed view of a carbon test column is provided in Figure 7-2, illustrating how the column is fastened to the associated piping network. The compression nut fittings silver-soldered into the brass end caps were originally selected to connect to 1/2-in. copper tubing (5/8-in. OD actual). For safety considerations Teflon and nylon ferrules were substituted for the standard brass ferrules in the compression fittings. A short length of chlorinated PVC tubing (5/8-in. OD) was connected to the compression fittings, and it in turn was adapted to the PVC pipe (a larger OD) with commercially available fittings.

The Teflon ferrules could be finger tightened, thus avoiding the need for wrenches to attach the columns. Each column was held in place with a large U-bolt attached to the Dex angle framework. The overall design allowed ease of removal and installation of test columns.

Figure 7-3 provides an overall view of the test assembly. Pink water was first filtered through a large diatomaceous earth filter. A final filter was installed on the test assembly as an additional precaution in case pink water constituents precipitated out in the plumbing between the diatomaceous earth filter and the first column. The filter used was a commercially available cartridge-type capable of removing 25-μm particles. The temperature was measured at the outlet of this filter; then the pink water was routed to an inlet manifold. Valves near the inlet manifold were positioned so that pink water could pass from the inlet manifold to any desired column. Other valves were adjusted for the desired flow pattern. The final column in the series emptied into the outlet manifold. From the outlet manifold, the pink water passed through a flow meter and a water meter. The final discharge point was into an existing line for treated pink water. The column not used during testing was the "standby" column. After filling the "standby" filter with GAC, it was washed (upflow) with potable-grade water while the other columns were in operation. The backwashing operation occurred with the top diffuser and screen absent from the column, in order to allow the GAC to expand. A flowmeter was used to monitor the backwashing operation.

7.4 TEST PLAN

7.4.1 Operation of Columns

A GAC unit employing multiple columns in series operates until the first column is at or near breakthrough. A fresh column is then brought on-line as the last column, and the original first column is removed from service. The original second column now becomes the first column in the series. In this way, the maximum adsorption capability of the GAC in each column is utilized without exceeding effluent discharge guidelines or regulations.

This is possible because even though the column in the first position is near breakthrough, the columns in the second, third, and fourth positions are far enough away from full saturation to provide low effluent concentrations.

The overall purpose of these tests was to test a pilot-scale four-column GAC unit to simulate actual units used at AAP wastewater treatment facilities. Tests were conducted using Witco Witcarb 950, 18 x 40 mesh GAC, and a column bed depth of nominally 1 ft. Tests were to be run at ambient temperature, a nominal hydraulic loading of 8 gpm/ft^2, and using one multiple compound solution of pink water. These operating parameters were selected in order to:

- Operate a four column in series GAC adsorption unit at the most favorable conditions to demonstrate the capability of such a unit.

- Operate a four column in series GAC adsorption unit at conditions similar to actual AAP conditions to simulate performance of existing units.

To simulate long-term plant operating conditions, the unit was to be operated long enough that each column would be in all four positions twice. When the unit is first operated, all columns contain fresh carbon. As the test progresses the percent saturation of the other columns will be different each time the column in the first position is changed, until a steady state situation is reached. By the time the test has proceeded to the point where each column has been in the first position twice, steady state should have been reached and the saturation of columns in the second, third, and fourth position will be the same each time the first column is changed.

The first column should not be changed until it is near or at breakthrough unless the last column effluent exceeds the discharge levels. Based on preliminary laboratory column tests, this time was estimated to be about 24 hr.

The four column test set-up is shown in Figure 7-3. Eight column sequences are required in order for each column to rotate through all four positions. As shown below, positions are numbered I through IV and columns are labeled A, B, C, D, and E. The one extra column is the "standby." At the start of each sequence, Position IV is always virgin GAC, and the sequence is run until the column in Position I is at or near breakthrough.

	Position of each column			
Sequence	I	II	III	IV
1	A	B	C	D
2	B	C	D	E
3	C	D	E	A
4	D	E	A	B
5	E	A	B	C
6	A	B	C	D
7	B	C	D	E
8	C	D	E	A

At the start of a test, all four columns are refilled with virgin GAC. The columns are then prepared for starting the above eight sequences. Filling a column with GAC involves weighing the carbon (for consistency of results), filling the column, washing with potable-grade water to remove any fine particles, and allowing to stand long enough for the pores to become saturated with water.

7.4.2 Sampling Plan

Samples were taken at a regular time interval at the outlet of columns in all four positions as well as the influent pink water. The Position IV samples are used to show final effluent concentration (C_f) versus time. The Position I samples are used to determine breakthrough on the first column. While the breakthrough time for a column filled with virgin GAC is known from the first preliminary test, after the first sequence the column which is now in the first position is no longer virgin GAC. Therefore, it is necessary to take samples at the outlet of Position I to determine breakthrough during each test cycle.

Rapid turnaround of HPLC analytical results is required in order to know the appropriate time to rotate the columns. The limiting factor for rotating the columns was expected to be when 80% of the influent level of RDX or HMX was found in the effluent from Column I. The final effluent also had to be checked, however; and if the proposed effluent standard was reached for any of the nitrobodies, the columns would need to be rotated.

Based upon preliminary column tests, the 2,4-DNT concentration in the final effluent was not expected to approach the 0.0007 ppm level. Therefore, the very low detection limits developed previously were not necessary for field analysis. Criteria for field testing were as follows; reaching any one of these possible conditions would require rotating columns.

1. RDX concentration in Column I effluent = 80 to 90% of influent concentration.

2. HMX concentration in Column I effluent = 80 to 90% of influent concentration.

3. RDX concentration in final (Column IV) effluent = 0.03 ppm.

4. HMX concentration in final (Column IV) effluent = 0.03 ppm.

5. TNT concentration in final (Column IV) effluent = 0.04 ppm.

It was expected that Criterion 1 or 2 would always be limiting, but Criteria 3 to 5 were monitored as well.

Samples were taken and analyzed from Columns II and III to help understand how the adsorptive capacity of a column changes throughout its history of operation, and also to help predict breakthrough times from one cycle to another.

7.4.3 Final Analysis of Selected Samples

Samples were taken from each of the four carbon columns just prior to switching columns, and were analyzed in MRI laboratories in order to verify field results and provide lower detection limits for the low level samples.

7.5 TEST CONDITIONS AND RESULTS

7.5.1 Description of Test Conditions

At the beginning of this project, a variety of different column tests at different hydraulic loading rates and other conditions were planned in order to do optimization studies under dynamic conditions. However, as hands-on experience was gained through the isotherm tests and preliminary column tests, it became apparent that it would be necessary to limit the operating parameters to those believed to provide the best information for scaleup, while still being manageable for field testing. At the time that the pilot-scale GAC assembly was set up at IAAP, the plan was to conduct one or two preliminary tests, called A and B, and one extensive test, to be called C. Tests A and B were to involve no more than two cycles each, while Test C was to include as many cycles as feasible, up to a maximum of eight.

The plan at the start of field testing was to use only one type of GAC and to use a hydraulic loading rate of 7 to 8 gpm/ft^2, which was believed to represent typical values used in full-scale systems.

When Test A was started, a higher hydraulic loading rate was used (nominally 10 gpm/ft^2) in order to accelerate breakthrough and to more rapidly examine system performance. Results from Test A were encouraging in that effluent criteria were met for TNT, RDX, and HMX; and DNT was below the detection limit of 0.02 mg/L. It was decided to proceed with Test B at a lower hydraulic loading rate and to run two cycles in order to see how much the breakthrough time would change from Cycle 1 to Cycle 2. Results from Test B showed much slower breakthrough, as expected, but were disappointing in terms of TNT effluent levels. In an effort to improve overall effluent quality, an additional preliminary test was planned. The contact time was lengthened by increasing the bed depth from 12 to 16 in. Since a great number of sample labels had been prepared in advance for Test C, this preliminary test was called Test D. About half-way through Test D, the flow rate was reduced further because TNT levels still exceeded criterion levels. This action did not seem to improve the effluent quality significantly.

It was decided to try another test using the longer bed depth and a fairly low hydraulic loading rate from the start (nominally 4 gpm/ft^2), which would result in a total bed contact time of about 10 min. Based upon discussions with a representative of Radford AAP, this was believed to be the minimum contact time that would be representative of full-scale GAC columns for AAPs. This test was started under the name Test E. Toward the end of Cycle 1, it was decided to continue running additional cycles and to convert the name to Test C, in order to take advantage of preprinted labels. Even though the effluent quality was still inadequate, the tests were continued because it was believed that the conditions were the best achievable.

Since a much longer contact time was used for Test C than had been anticipated, fewer test cycles were possible within the constraints of time and the budgeted cost for field testing. For these reasons, and because the data suggested that the system was approaching "steady state," only four cycles were conducted. Subsequent data analysis has indicated that four cycles were sufficient.

Because the effluent quality results were disappointing for Witco 950, it was decided to conduct an additional brief test using another carbon, in this case Calgon Filtrasorb 300, the standard GAC used at AAPs. Filtrasorb 300 is used at IAAP, and sufficient quantities were provided by Mason & Hanger to conduct a test. In order to expedite this comparative test, the hydraulic loading rate was chosen to match Test B (nominally 6 gpm/ft^2 and 12-in. bed depth) instead of using conditions similar to Test C. This test was called Test F.

A summary of the overall test conditions and results from the column studies is provided in Table 7-1. Several points need to be made regarding this table. The final breakthrough in Column I is a measure of how close the leading column came to reaching its capacity to remove a pollutant. The target value was 80% for any one compound. Either RDX or HMX were the first compounds to approach breakthrough in all cases, and generally these two compounds "tracked" each other fairly consistently. The first column never approached saturation with respect to either TNT or 2,4-DNT.

Pressures were also measured at the inlet and outlet of each column. The total pressure drop of the entire four column system generally ranged from 5 to 10 psi. Because many valves, fittings, screens, and glass wool filters were in the flow stream, pressure drops were judged to be abnormally high for the pilot-scale system and not representative of a full-scale system.

7.5.2 Concentration Results

Results from the chemical analysis of samples taken during Tests A, B, C, and F are provided in Tables 7-2 through 7-9. Concentrations are given for the four compounds of interest referenced to test time and wastewater volume. Test time is simply the elapsed time since the test began. Wastewater volume is based upon readings taken on the water meter and is not corrected for any meter calibration factors. Also provided is the cumulative number of bed volumes that the column being sampled has experienced throughout the test.

An explanation of the sample numbering system follows as an aid in interpretation of these data. The initial letter/number combination which appears in the column heading is the test name and column number.

The first number in the row headings is the relative column position, according to the flow pattern of the pink water. (Position 0 is the influent to the columns, i.e., the effluent from the prefilter.) The letter/number combination in parentheses is the absolute column number (or tank number for Position 0), assigned when the column is filled with virgin GAC and which is retained as long as it is used in that test. The final number is a sequential sample number, where "1" is taken at the beginning of the test cycle. The final sample number in each table has a "TE" suffix, which stands for trace enrichment analysis. This analysis was conducted later in the MRI laboratories and was performed only for 2,4-DNT. This compound was not detected in any of the trace enrichment analyses, but the results are questionable due to the possibility of problems involving sample integrity (see Appendix A).

Two examples of sample numbers should help to illustrate the numbering system. "B1 - 0 (T2) - 11" is the 11th sample taken of the influent for Test B, Cycle 1. "T2" means Tank No. 2. The pink water tanks were numbered as an aid in keeping track of which tank was being drawn from and which tank was being refilled. Another example is "B2 - 3 (D1) - 1," which is the first sample taken at the effluent from the third column during the second cycle of Test B. The column number is "D1," which was at the fourth position during the first cycle.

Influent pink water concentrations were generally similar to the synthetic pink water used for the isotherm tests, although TNT, RDX, and HMX levels were sometimes higher and 2,4-DNT levels were lower. Pink water concentrations encountered in this project are summarized below.

	Pink water concentrations (mg/L)			
Source	TNT	RDX	HMX	2,4-DNT
Synthetic	59-73	23-28	4.5-5.8	0.76-0.94
Kansas AAP	49	22	4.0	0.066
Iowa AAP	55-120	34-91	4.6-13	0.035-0.21

7.5.3 Carbon Loading Results

Carbon loading rates show how efficiently GAC adsorbs each pollutant. Final loading rates were calculated for each column and each test cycle on a compound-by-compound basis and are summarized in Table 7-10. The column number is the absolute column number used throughout a test for a particular "batch" of carbon. When more than one cycle was completed for a test, the loading contribution from each cycle is shown as well as the total amount loaded during the test. The positional sequencing of the carbon columns was the same as appears from left to right in this table.

In order to perform these calculations, the average flow rate for each sampling interval was calculated. The equation used to calculate the loading rate is:

$$\text{Cumulative carbon loading} = \sum_{i=1}^{n} [(C_i - C_{i-1}) \times (V_i - V_{i-1})] \times K$$

C_i = Concentration at the i^{th} sampling time

V_i = Volume at the i^{th} sampling time

K = Constant for units conversion

In several cases a negative value was obtained, meaning there was a slight net loss of that particular pollutant over the cycle period.

Because analyses were not performed on all samples taken at all sampling points, and complications in the analyses sometimes prevented quantitation, the sampling period was adjusted to compensate for the missing data. In a few cases (e.g., the beginning or end of a test), the "best expected value" was used. Estimates contributed only slightly, however, to the total calculated loadings.

These carbon loading rates correspond to the q_e values obtained for the isotherm tests, representing the best carbon utilization obtained under either dynamic conditions or static conditions. For ease of displaying the data, the values shown for the column studies are in units of pounds of pollutant per 100 lb of GAC, or on a percentage basis.

7.6 DATA ANALYSIS AND DISCUSSION

7.6.1 Effluent Quality

One of the project objectives was to determine if the proposed effluent criteria are achievable under representative AAP conditions. The effluent limits seem feasible based strictly upon isotherm test results, but isotherm tests represent nearly ideal equilibrium conditions. It was expected that the limits would be achievable in a multiple column GAC system, providing that sufficient contact time was allowed. It was also expected that the nitrobody concentrations would be successively lowered through each column in the series. As will be explained in this section, however, the test system did not always behave as expected during the tests at IAAP.

The analytical results describing the final effluent quality have been given previously in Section 7.5.2. The results of interest are those listed under Column 4, or sample numbers in the form XX - 4 - (XX) - X, where "X" is a variable. The tests passed or failed the effluent limits as shown below.

	Test cycle							
Compound	A1	B1	B2	C1	C2	C3	C4	F1
TNT	+	-	-	-	-	-	-	-
RDX	+	+	-	+	-	+	-	-
HMX	+	+	-	+	+	+	+	-
2,4-DNT	+	?	+	+	+	+	+	+

Passing the effluent limit is shown by a "+," while failure is shown by a "-." For this purpose, a single exceedance of the limit is considered a failure.

Trace enrichment analysis was performed on the final samples from each cycle to achieve low enough detection limits for the 2,4-DNT limit. The sample for cycle B1 was lost during preparation. As noted before, the results are questionable for 2,4-DNT. The reader is referred to Appendix A for further discussion of problems encountered in analysis.

The most problematic compound was TNT. Only in the first preliminary test (Test A) was the limit passed, with the maximum concentration just below the limit. Test conditions were changed following Test A, partly in an attempt to improve final TNT quality, but these attempts were not successful; instead, TNT levels were well above the desired limit. The main test series (Test C) was still conducted in spite of the TNT problem, using conditions believed to be optimum in terms of providing the best scaleup data.

The effluent limit of 0.03 mg/L was generally met for both RDX and HMX, although occasional exceedances resulted in several test failures, as shown above. It is expected that this limit can be achieved in a properly designed and monitored full-scale GAC system, although there may not be a sufficient "safety" margin to cover certain cases.

Generally the nitrobody concentration was reduced with each successive column, but this was not always the case with TNT levels following the first column. The analytical data for each compound and each column have been plotted for Tests A, B, C, and F. These graphical results are given in Figures 7-4 through 7-19. A key to interpreting these figures is the table given in Section 7.4.1 that describes the rotational sequence of the columns. The legends in the graphs refer to Columns A, B, C, D, and E, and the influent pink water. For Test C, there are two sets of data for Columns A and B, referred to as A2 and B2 in Tables 7-7 and 7-8. GAC in Column A1 was used only in the first cycle, while GAC in Columns B1, A2, and B2 was used in more than one cycle as the columns were rotated.

It is important to remember that the order of column positions according to the pink water flow pattern is A, B, C, D, and E, where any letter can represent the first column.

Dotted lines are used to join data points when a sample was not analyzed, the results are not available, or the analytical results were "not detected" or "less than MDL."

The concentration data are plotted on a logarithmic axis (y-scale) in order to clearly show all the results, which ranged over several orders of magnitude. Since the y-scales all span six orders of magnitude, the data are easily compared from one compound to another. This represents a method for normalizing the data. The exact range of concentration on the y-scale is the same for TNT, RDX, and HMX (0.001 to 1,000 mg/L). The range used for 2,4-DNT is 0.00001 to 10 mg/L.

The horizontal line on each graph at 1 mg/L is an artifact of the computer graphing function. The lower horizontal line in each graph is intentional, however, representing the proposed effluent limit for each compound. When data points for the fourth column in each test series are below this line, the limit is passed.

The graphical method of data analysis allows the breakthrough curves for each column to be seen readily. Changes in the breakthrough curves from one cycle to the next may also be seen. All the concentration data are plotted in terms of number of bed volumes, which normalizes the data for variation in bed depth. The x-scale is the same for each graph. It has been chosen to cover all four cycles of Test C. Thus, variation in the breakthrough volume from one test (or cycle) to another may be readily seen.

It is interesting to note that the curve shapes for RDX and HMX are usually nearly identical in the same test cycle, even though the initial concentrations are quite different. This indicates that the percent removal efficiency for these two compounds remained about the same in each column. Breakthrough curves are steeper for RDX and HMX than for TNT, meaning the first column becomes saturated with these compounds first. (More discussion of this topic is found in Section 7.6.2.) Only limited data are available for 2,4-DNT, but breakthrough curves for this compound generally seem to emulate those for TNT. This similarity in curve shape between RDX and HMX and between TNT and 2,4-DNT is analogous to the isotherm test results.

High TNT levels plagued all of the tests except for Test A, which was run at a very high hydraulic loading rate. At first, this problem with TNT was thought to be a result of channeling or improper carbon conditioning, so improvements in technique for conditioning and loading the GAC were attempted from one test to another, as described in Appendix B. As Figures 7-6, 7-10, 7-14, and 7-18 clearly show, there was very little change in TNT concentration beyond the first column in series, which means that there was little or no further removal of TNT from solution. Since this behavior was generally not evident in the other compounds, and since changes in GAC conditioning and loading procedures did not affect the TNT behavior, it was determined that this was not an artifact, but was an actual physicochemical phenomenon. Extensive data review have indicated that the TNT effluent limit cannot be met for the conditions used in Tests B, C, D, and F. It should be noted that use of the conventional GAC type used at AAPs during Test F did not improve the TNT effluent quality.

7.6.2 Carbon Utilization

Carbon loading rates for each nitrobody were previously given in Table 7-9. These data were analyzed graphically in various ways. The relative contribution from each compound to the total loading rate of each column is shown in Figures 7-20 through 7-23. Results for Tests A, B, C, and F are provided in these figures, which may be readily compared since the y-scale is identical in each figure. Not all of the column numbers appearing on the x-scale were used for each test. Only for Test C are all column numbers used. Tests A and F did not use Columns E1, A2, and B2, and Test B did not use Columns A2 and B2. The "N/A" shown for Columns B1, C1, and D1 in Figure 7-23 indicates that the data are not available. Insufficient samples from Test F were analyzed to perform these calculations.

All data for Column A1 involve only one test cycle, as that column was removed in any subsequent cycles. Also, since only one cycle was conducted for Tests A and F, the other columns involved only a single cycle. For Tests B and F, however, columns other than A1 may involve more than one test cycle; that is, the results are cumulative for all test cycles. The number of cycles for each column number is shown below.

	Column No.						
Test	A1	B1	C1	D1	E1	A2	B2
A	1	2	2	2	-	-	-
B	1	2	2	2	1	-	-
C	1	2	3	4	3	2	1
F	1	1	1	1	-	-	-

The highest total loading rate for a column used in only one cycle was for Column A1 in Test C, in which 0.25 lb nitrobodies were adsorbed per pound of GAC. The lowest total loading rate for Column A1 was 0.19 lb/lb in Test F. The maximum total loading rate experienced by any column was 0.32 lb/lb for Column B1 in Test C.

The carbon loading rates from the column tests are analogous to the q_e values from the isotherm tests. Ordinarily, lower carbon loading is expected from column (dynamic) tests than from isotherm (equilibrium) tests. Test results are compared below. The isotherm q_e values are from testing Witcarb 950 at ambient temperatures using four-component pink water. The q_e values are those from the minimum carbon dosage, which approximates extrapolation to C_o. The column test results are the cumulative carbon loading in the leading column at the end of Cycle C4.

	Carbon loading rate or q_e, lb/100 lb				
	TNT	RDX	HMX	DNT	Total
Isotherm tests	55.9	6.62	2.35	1.16	66.0
Column tests	16.2	11.6	1.50	0.026	29.3

Overall, the loading rate of all nitrobodies in the isotherm tests was over double that in the column tests. Most of this difference is accounted for by TNT, which was removed much better in the static isotherm tests. On the other hand, the RDX loading rate was much higher in the column tests than in the isotherm tests.

In the column tests, the order of carbon loading rate for each compound in Column A1 is the same as the order of influent concentration. The relative contribution from each compound is apparently about the same as the relative loading in the influent pink water.

Upon examining Figure 7-22 in more detail, it appears that little additional loading is experienced when the columns are involved in more than two cycles. To further explore this trend, the data were analyzed differently, with the results shown in Figures 7-24 through 7-28. These data all involve Test C, during which four cycles were conducted. Looking at each compound individually, the amount of pollutant loaded on each column is shown, with the contribution from each position provided. In the case of TNT, little improvement was made beyond the loading for a virgin column used for one cycle in the leading position (i.e., Column A1). For RDX and HMX, however, significant improvement is achieved by using columns first in the second position, then in the first position. Little additional loading results from the columns starting in the third or fourth position, however. Data for 2,4-DNT were not as reliable as for the other compounds, but it does appear that little improvement in loading occurs by starting columns in the second or further position.

The ramifications from this data analysis are quite important in terms of design of full-scale systems. Data from these pilot-scale tests indicate that carbon utilization is enhanced by using two columns in series as opposed to a single column, but little is gained by using more than two columns in series. Of course, more tests need to be conducted to verify these findings, and it would be best to conduct more than four cycles of column rotation. It does appear, however, that the system in these tests was approaching steady-state operation, both in terms of carbon loading and breakthrough volume.

7.6.3 Effect of Hydraulic Loading Rate

The hydraulic loading rate is the flow rate per unit cross-sectional area of the carbon column, expressed in units of gpm/ft^2 or equivalent. It is actually a measure of linear velocity, or the superficial velocity through the carbon bed. Many studies have shown that for the same contact time variations in velocity have no effect on the performance of a carbon system.[18] Of course, if the velocity is increased without increasing the bed depth accordingly, the contact time is decreased; thus, breakthrough is hastened.

Some studies have shown that certain systems may actually perform better at higher velocity, taking into account the contact time. The rationale for this behavior is that higher velocities increase the diffusion rate across the surface film around the particle. Results from a laboratory study involving phenol are shown in Figure 7-29. The superficial contact remained constant at 20 min. In this study, by increasing the linear velocity (LV) more volume of liquid is treated with the same volume of carbon and the mass transfer zone (MTZ) is shortened. The MTZ is the length of adsorbent bed in which the adsorbate concentration varies from the influent concentration to zero or the target concentration. Similar tests conducted on a refinery wastewater indicated that, for the same contact time, a higher LV lengthens the breakthrough time (Figure 7-30).[18]

In another case involving sugar plant wastewater, a change in configuration of the carbon columns was made from three parallel trains of two beds in series to two parallel trains of three beds in series, thus keeping the contact time the same but increasing the LV. This resulted in an improvement in effluent quality and a decrease in carbon dosage.[19]

Data from the tests conducted at IAAP were analyzed to determine what effects, if any, variations in LV had on the performance of the GAC system. Three different linear velocities, or hydraulic loading rates, were used in Tests A, B, and C. Results from the first cycle of each test were used for this comparison, so that the GAC had no prior usage in all cases. By taking samples from each column in series, a variety of cumulative contact times were obtained, as shown below.

	Cumulative superficial contact time, min		
Sampling Point	Cycle A1 (9.4 gpm/ft^2)	Cycle B1 (6.5 gpm/ft^2)	Cycle C1 (4.1 gpm/ft^2)
Column 1	0.78	1.13	2.41
Column 2	1.56	2.26	4.82
Column 3	2.34	3.39	7.23
Column 4	3.12	4.52	9.64

By selecting appropriate combinations of tests and sampling points, the following three sets of conditions were obtained.

Range 1 = 2.3-2.4 min contact time
Cycle A1/Column 3, 9.4 gpm/ft^2, 2.34 min
Cycle B1/Column 2, 6.5 gpm/ft^2, 2.26 min
Cycle C1/Column 1, 4.1 gpm/ft^2, 2.41 min

Range 2 = 3.1-3.4 min contact time
Cycle A1/Column 4, 9.4 gpm/ft^2, 3.12 min
Cycle B1/Column 3, 6.5 gpm/ft^2, 3.39 min

Range 3 = 4.5-4.8 min contact time
Cycle B1/Column 4, 6.5 gpm/ft^2, 4.52 min
Cycle C1/Column 2, 4.1 gpm/ft^2, 4.82 min

In the first range of contact times (2.3-2.4 min), sufficient data were available to compare breakthrough curves for RDX, HMX, and TNT, shown in Figures 7-31, 7-32, and 7-33, respectively. Three different hydraulic loading rates or velocities were used at about the same contact time. As the velocity increases, more volume of pink water can be treated prior to breakthrough above a particular concentration. Conversely, when a given volume of pink water has been treated, the system operating at the higher velocity will produce the better quality effluent.

In the second range (3.1-3.4 min), only enough data for TNT were available to look at velocity effects (Figure 7-34). It should be noted that the effluent concentrations are lower at the longer contact time; therefore, the y-scale has been changed from 0-2 mg/L to 0-0.5 mg/L. It can be seen that a steep breakthrough curve developed at a hydraulic loading rate of 6.5 gpm/ft^2, whereas a level curve developed at a hydraulic loading rate of 9.4 gpm/ft^2, in agreement with the previous results.

At the highest range of contact time (4.5-4.8 min), data for both RDX and TNT were compared, as shown in Figures 7-35 and 7-36. At this contact time, there was little difference between the two velocities.

Overall, the results from conducting multiple column tests at IAAP indicate that better effluent quality may be achievable by operating at higher superficial velocities. One way to achieve this, without increasing the total volume of carbon bed, would be to increase the length-to-width ratio of the carbon beds, thus increasing the hydraulic loading rate. Of course, attendant increases in pressure drop may create a practical limit on hydraulic loading rate.

7.6.4 Comparison of GAC Types

Following completion of the four-cycle test involving Witco Witcarb 950, an additional test was conducted using the type of GAC conventionally used at AAPs, Calgon Filtrasorb 300. There was concern over the poor results encountered for TNT using the Witcarb product, which had been selected for column testing based strictly upon isotherm results. The comparative tests were therefore designed to indicate whether the Witcarb had been a suitable choice for column testing of pink water.

Due to schedule limitations, the total test time for the comparative test could not be extensive. Thus, operating conditions were selected to encourage rapid breakthrough, and only a single cycle was run. The test cycle was called F1, and the conditions were matched to those for Cycle B1; that is, a bed depth of 11.75 in. and a nominal hydraulic loading rate of 6 gpm/ft^2. Although the volume of the GAC in each column was the same between tests, the bed weight for Test F was higher because the Calgon Filtrasorb 300 had a bulk density of 34 lb/ft^3, whereas the bulk density of the Witco Witcarb 950 was only 25 lb/ft^3.

Test Cycle F1 was run to about the same relative breakthrough as was Test B1 (approximately 80% for RDX and HMX and 50% for TNT). The actual volume treated prior to breakthrough for Cycle F1 was considerably less than for Cycle B1, however. The breakthrough volume was 366 gal. or 1,018 bed volumes for Cycle F1 compared to 510 gal. or 1,417 bed volumes for Cycle B1. The pink water was more concentrated with respect to each nitrobody for Cycle F1 than for Cycle B1, which may account for the earlier breakthrough experienced by Filtrasorb 300.

The maximum effluent concentration of each nitrobody was higher in Test F than in Cycle B1, as previously indicated in Table 7-1. This may also be due to the higher influent concentrations, but considering that there were four columns in series, that factor may not account for all of the difference.

The data for the carbon loading rates for each pollutant were examined in more detail in order to compare the carbon usage rate of the first column in series for the two GAC types tested. The loading rates for TNT, RDX, and HMX on the leading column for Cycles B1 and F1 are shown in Figure 7-37. The loading rate of 2,4-DNT was insignificant by comparison, and is not shown. As can be seen, the loading rates for total nitrobodies, TNT, and RDX are considerably higher for the Witcarb 950 than for the Filtrasorb 300. Since more weight was present in the same bed volume for the Filtrasorb 300, this trend is not surprising. However, since GAC is normally purchased on a weight basis, this seems to be a valid comparison. The total loading rate for the Witcarb 950 was 0.266 lb/lb, and the total loading rate for the Filtrasorb 300 was 0.185 lb/lb.

The actual weight of pollutant adsorbed on the first column was about the same for these two test cycles, as shown below.

	Weight adsorbed on first column (g)	
	Cycle B1	Cycle F1
TNT	93	82
RDX	44	47
HMX	5.5	7.2
2,4-DNT	0.11	0.12
Total	142	136

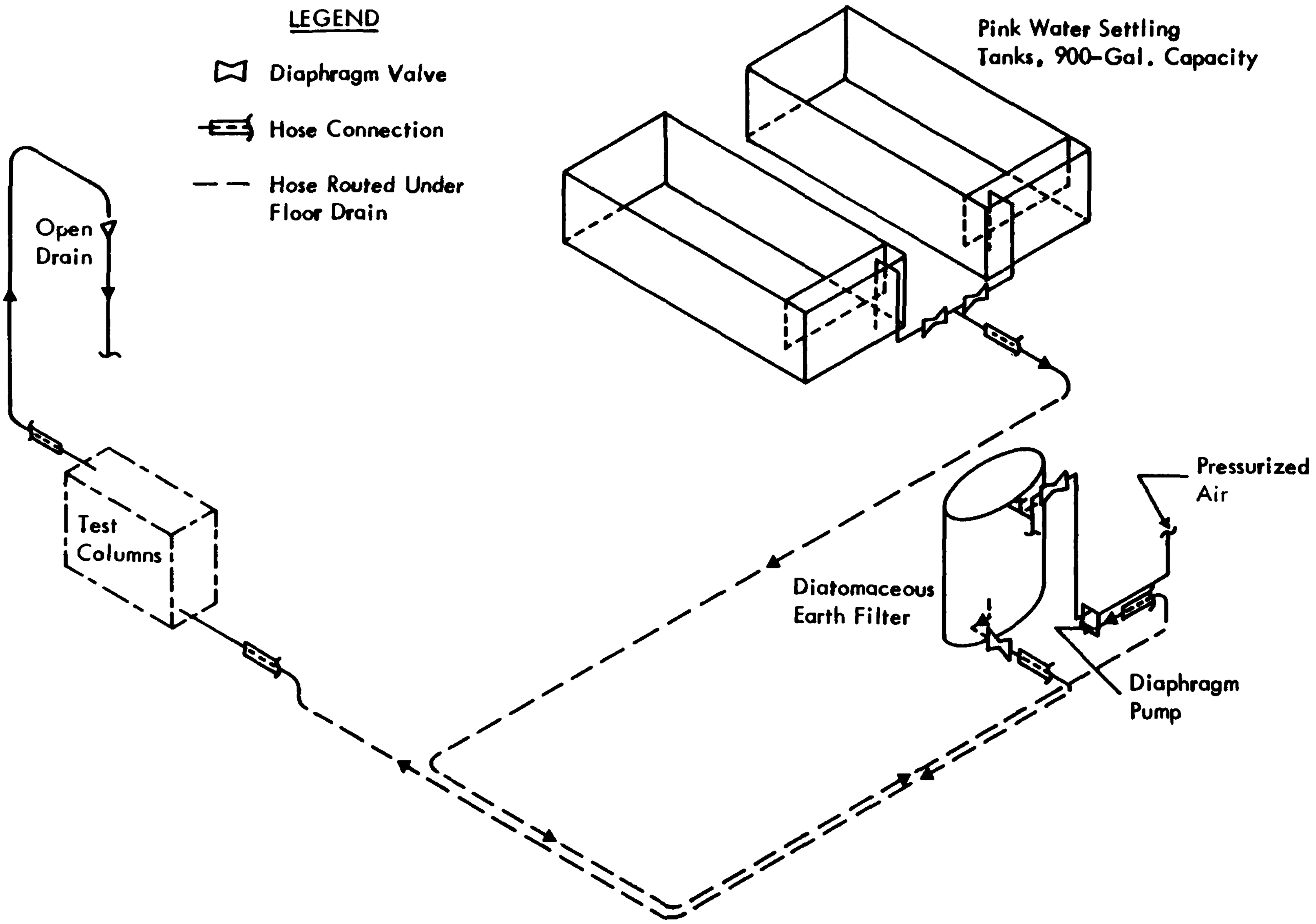

Figure 7-1. Site modifications for test columns.

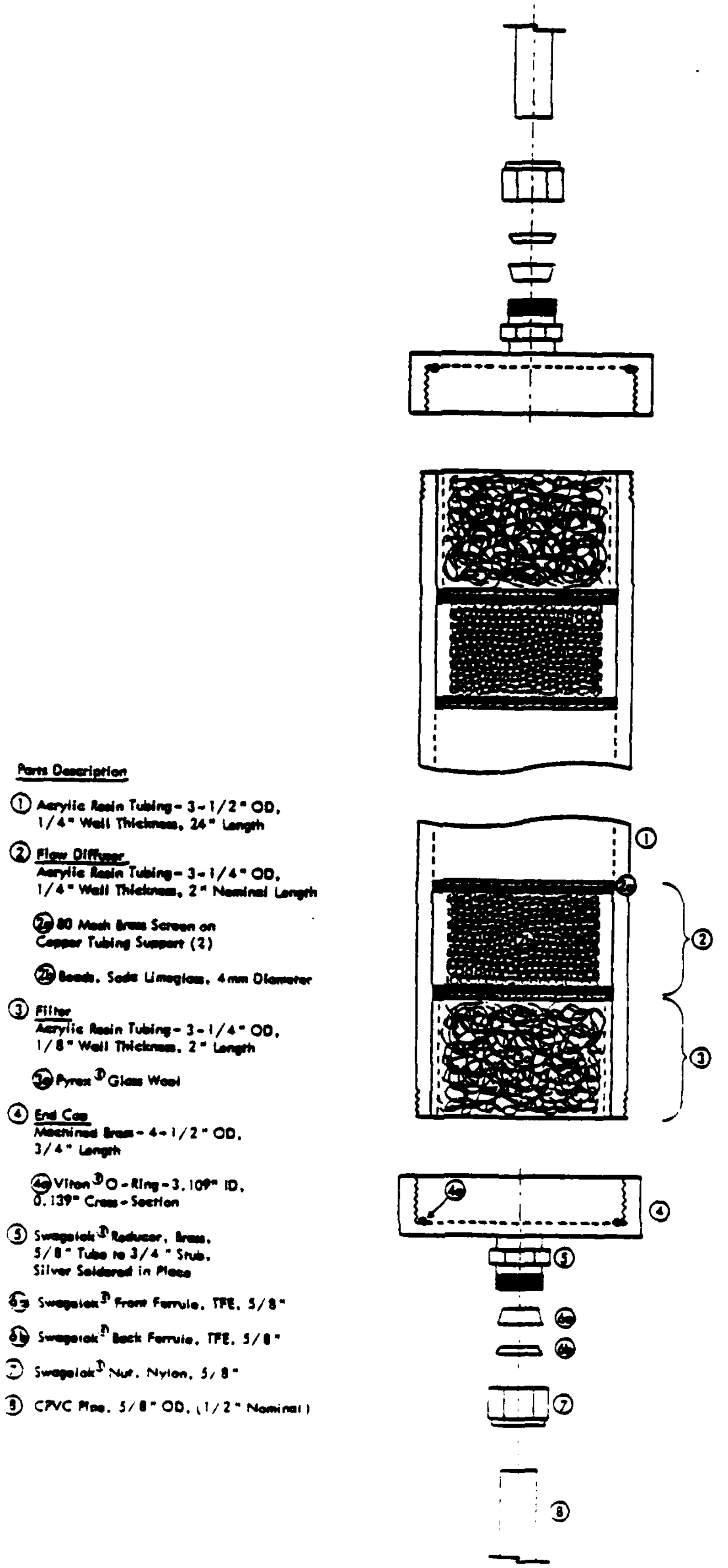

Figure 7-2. Detail of test column.

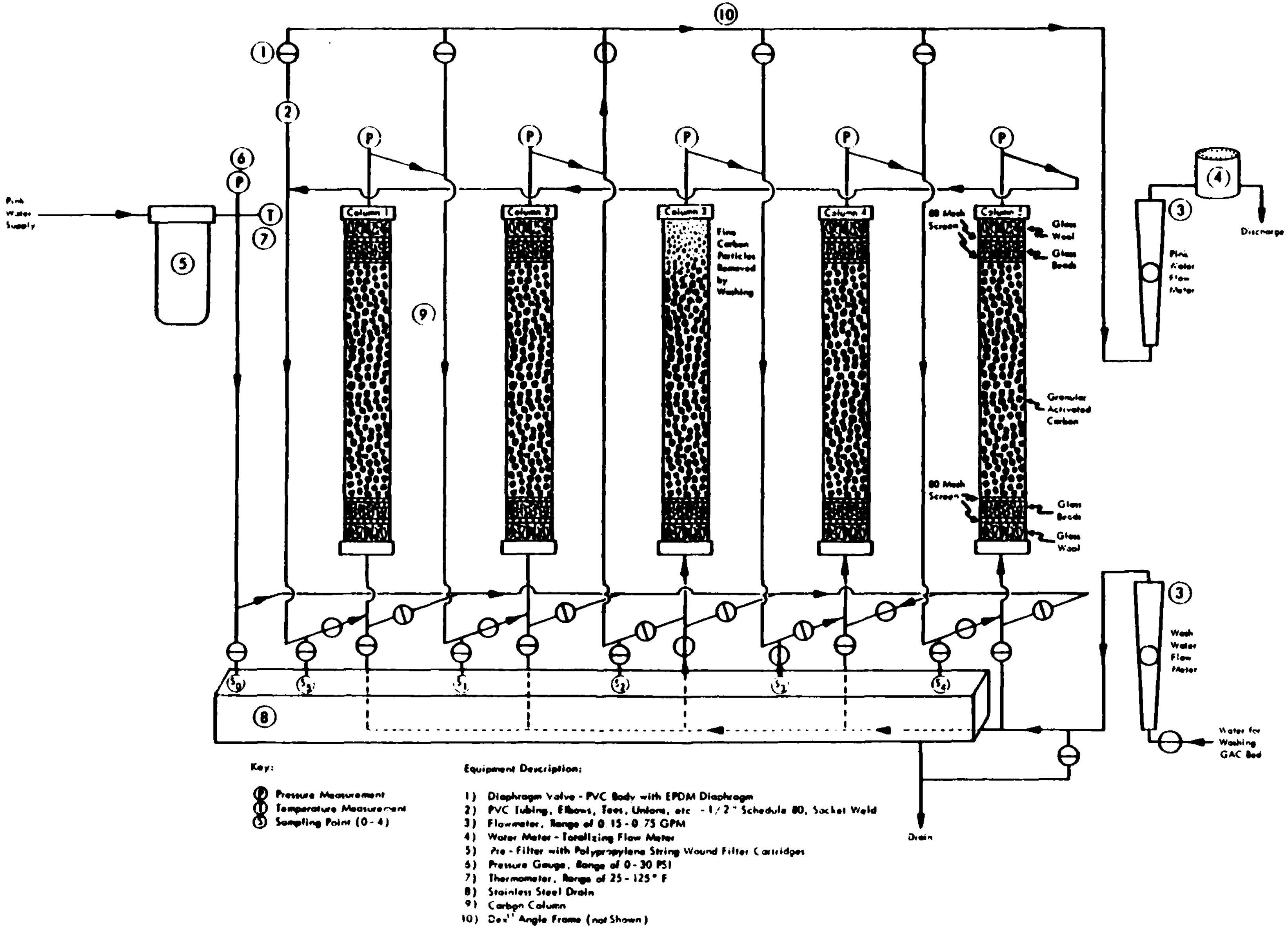

Figure 7-3. Four in series column test assembly.

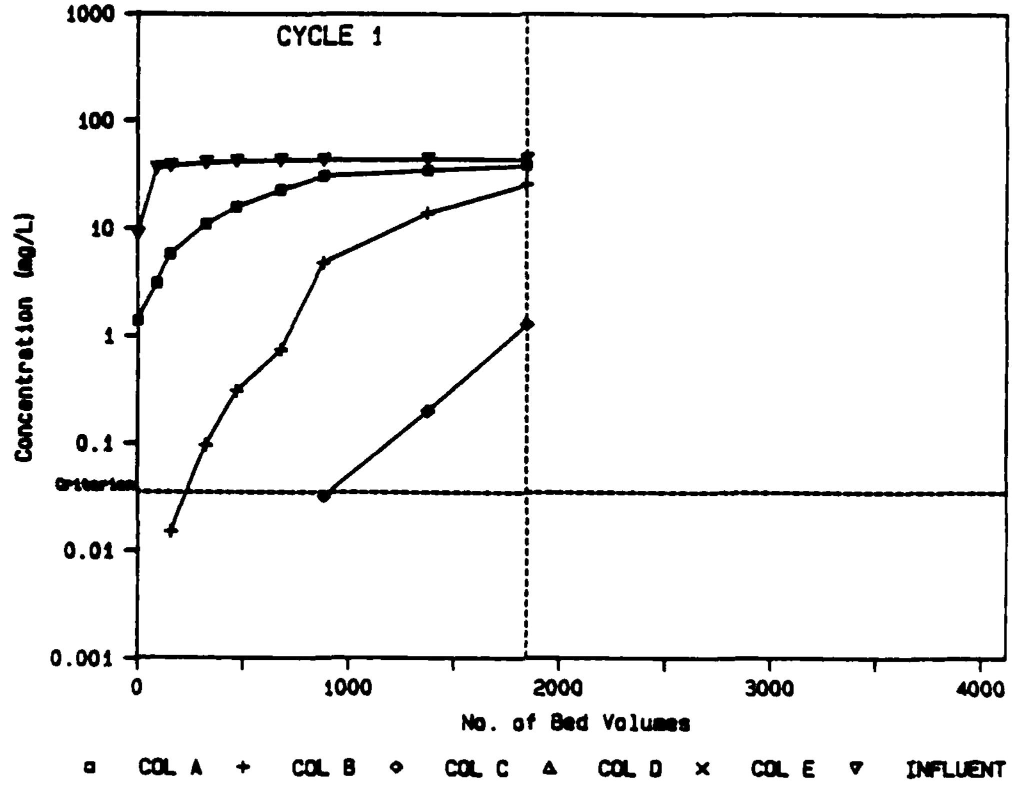

Figure 7-4. RDX breakthrough curves for test A.

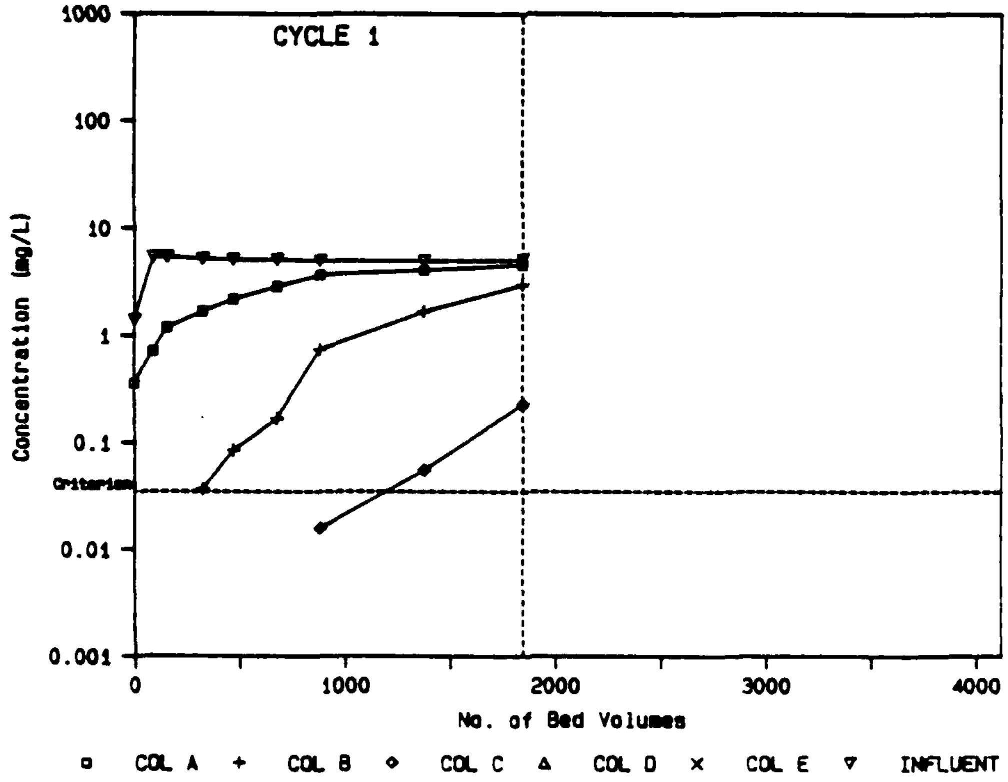

Figure 7-5. HMX breakthrough curves for test A.

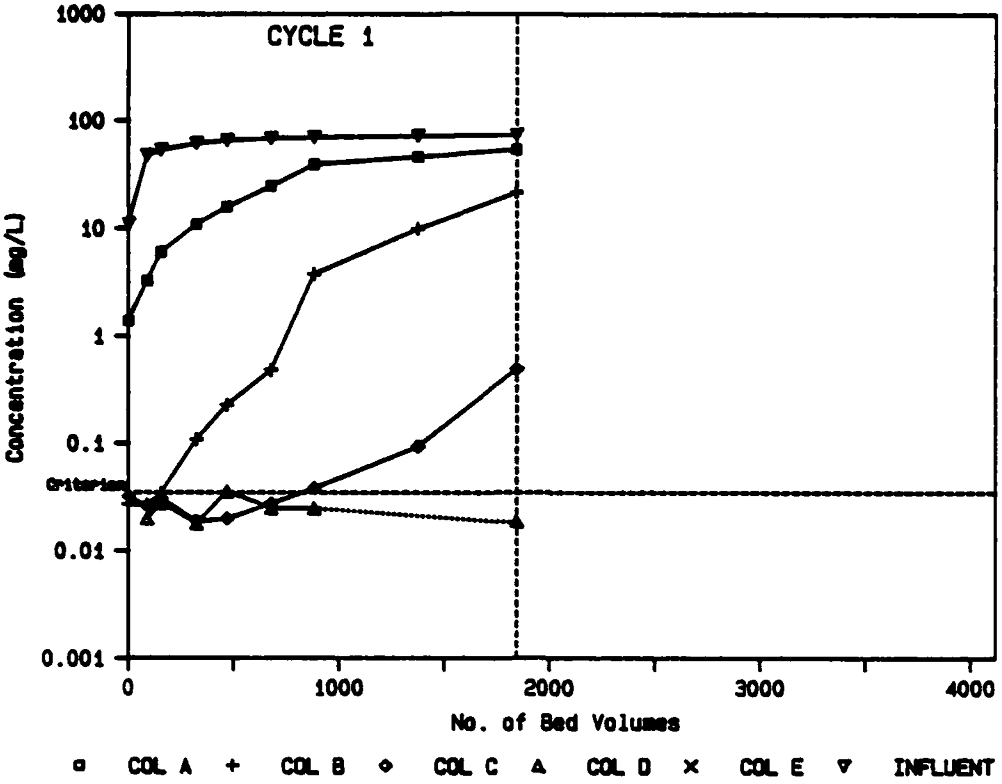

Figure 7-6. TNT breakthrough curves for test A.

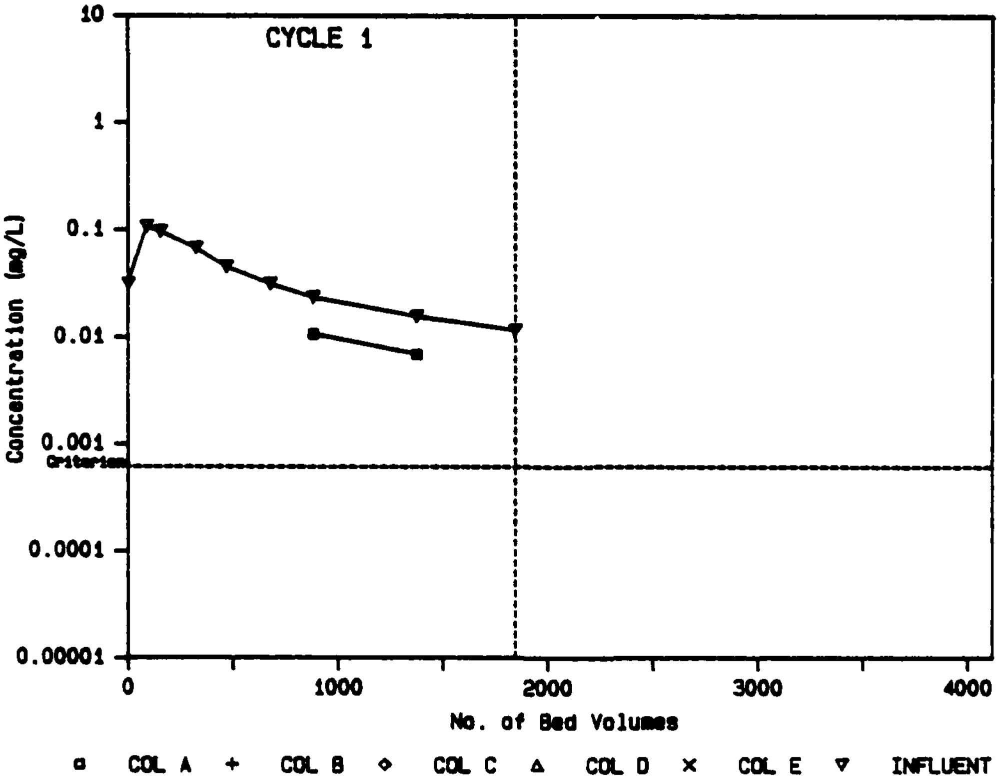

Figure 7-7. DNT breakthrough curves for test A.

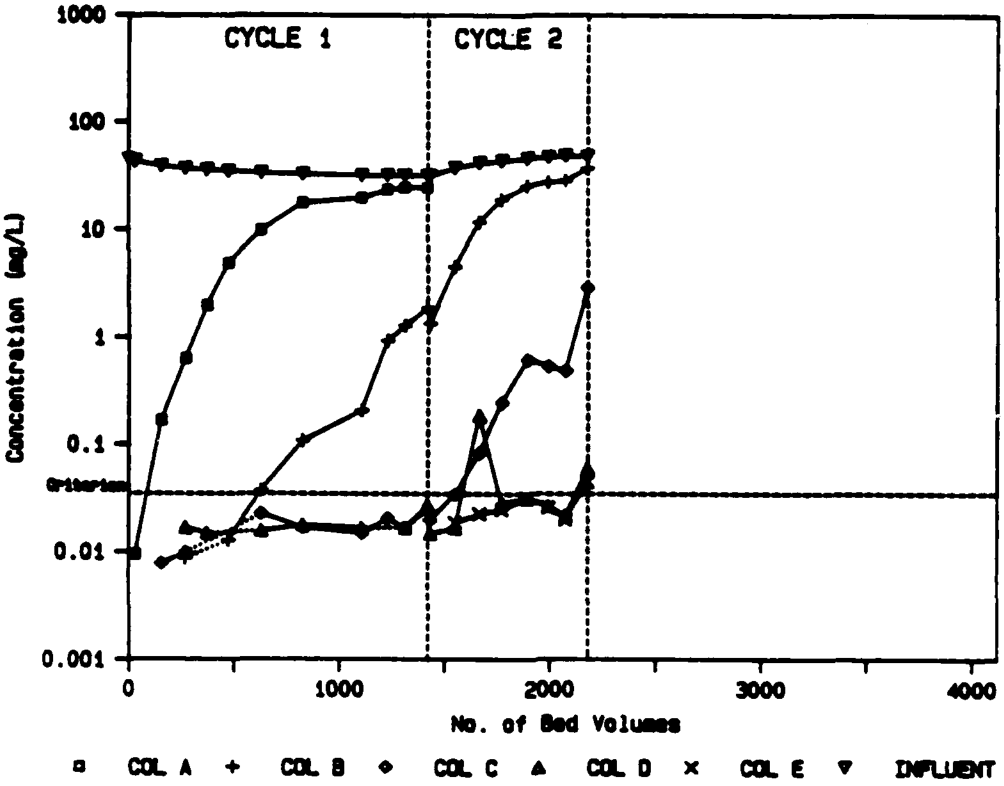

Figure 7-8. RDX breakthrough curves for test B.

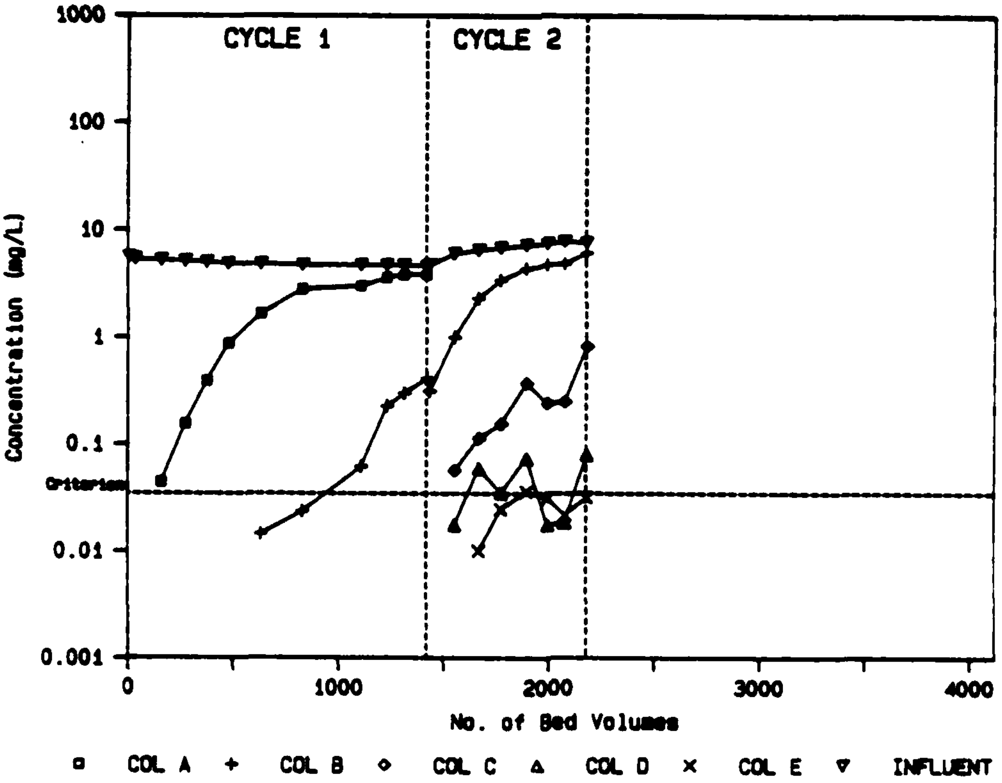

Figure 7-9. HMX breakthrough curves for test B.

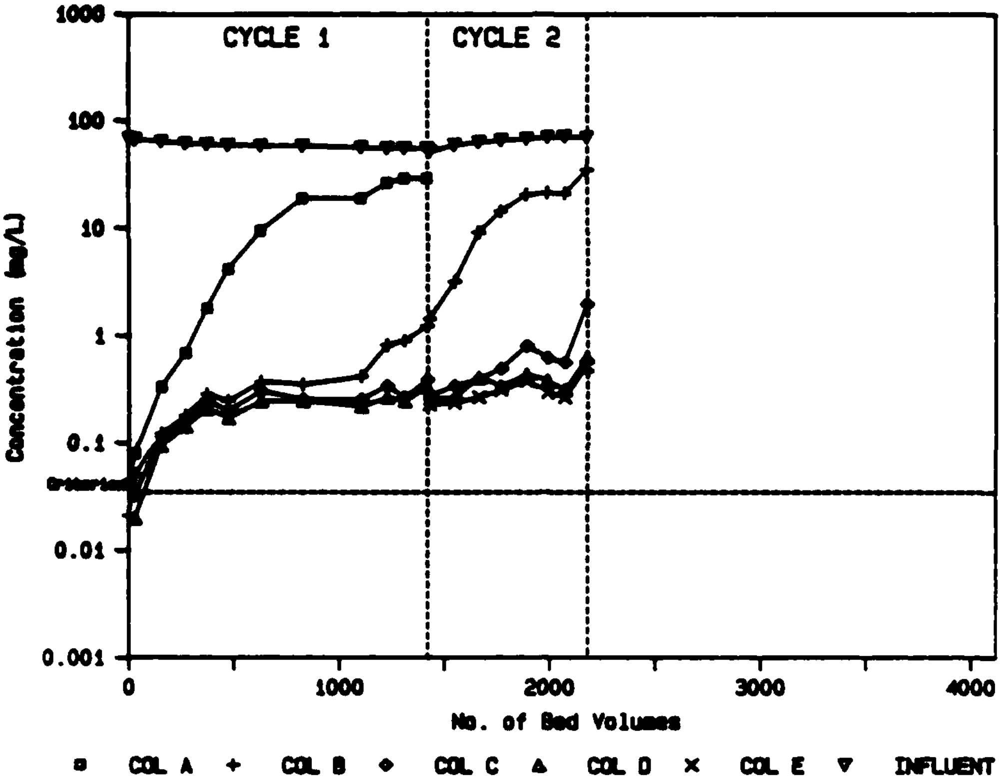

Figure 7-10. TNT breakthrough curves for test B.

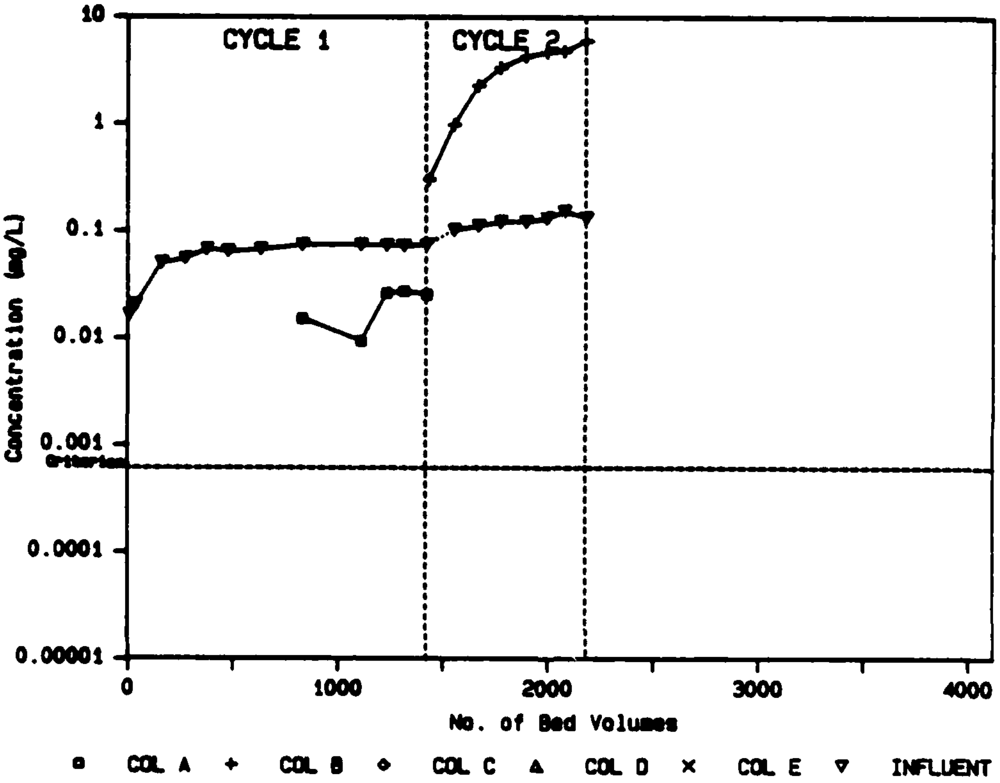

Figure 7-11. DNT breakthrough curves for test B.

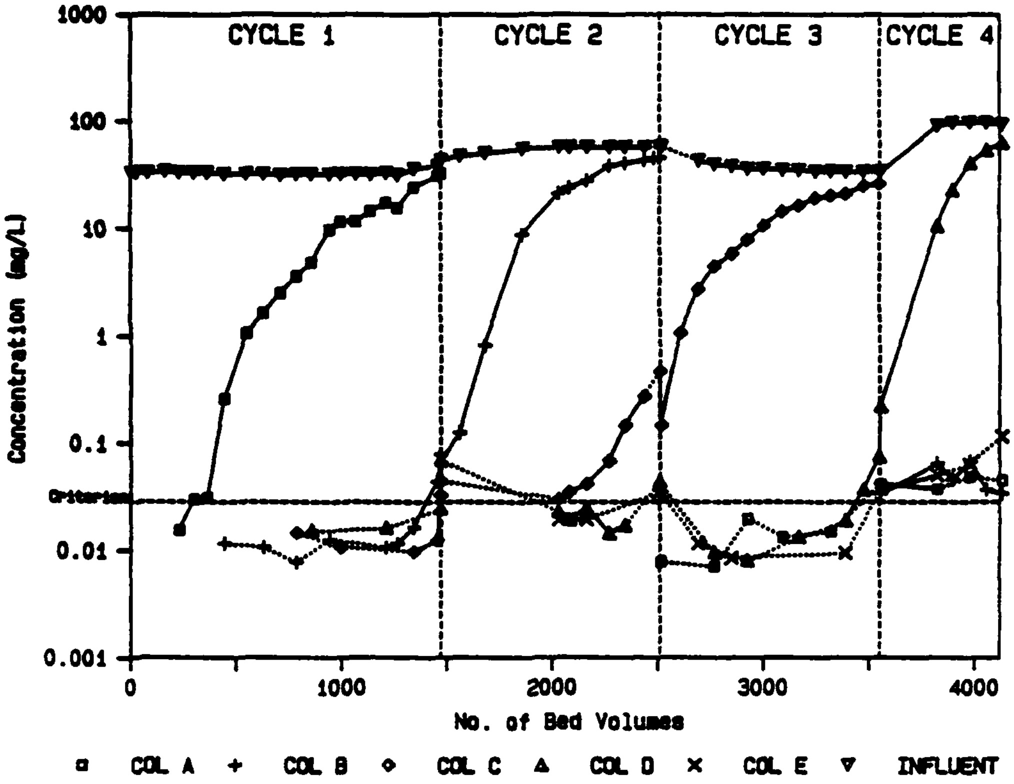

Figure 7-12. RDX breakthrough curves for test C.

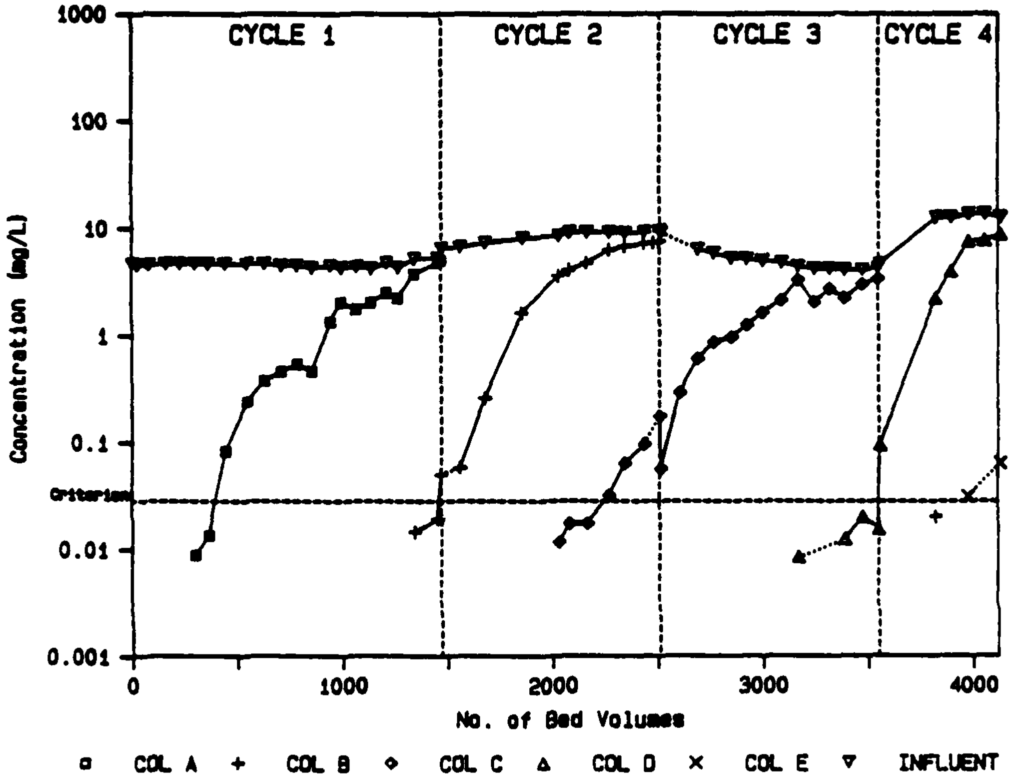

Figure 7-13. HMX breakthrough curves for test C.

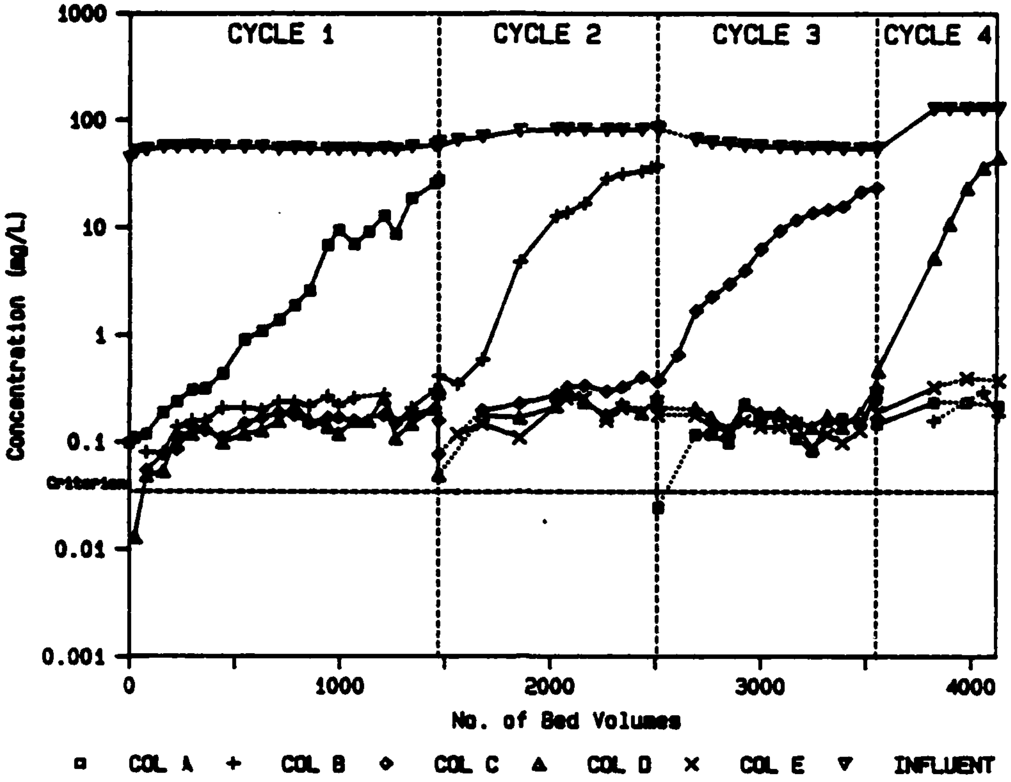

Figure 7-14. TNT breakthrough curves for test C.

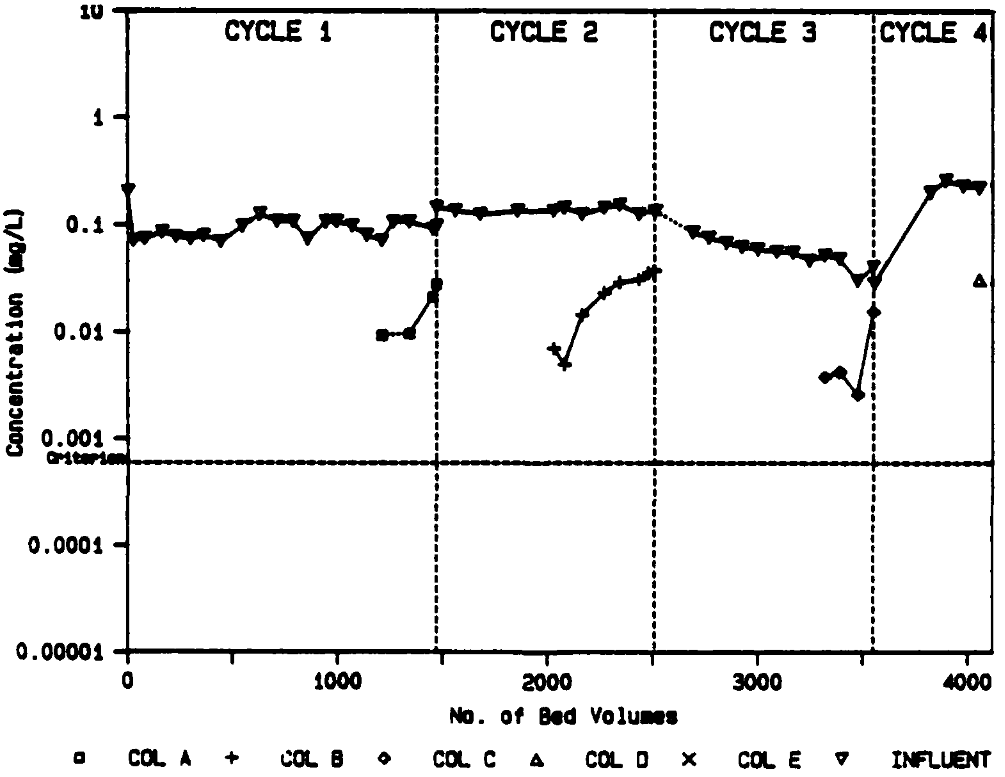

Figure 7-15. DNT breakthrough curves for test C.

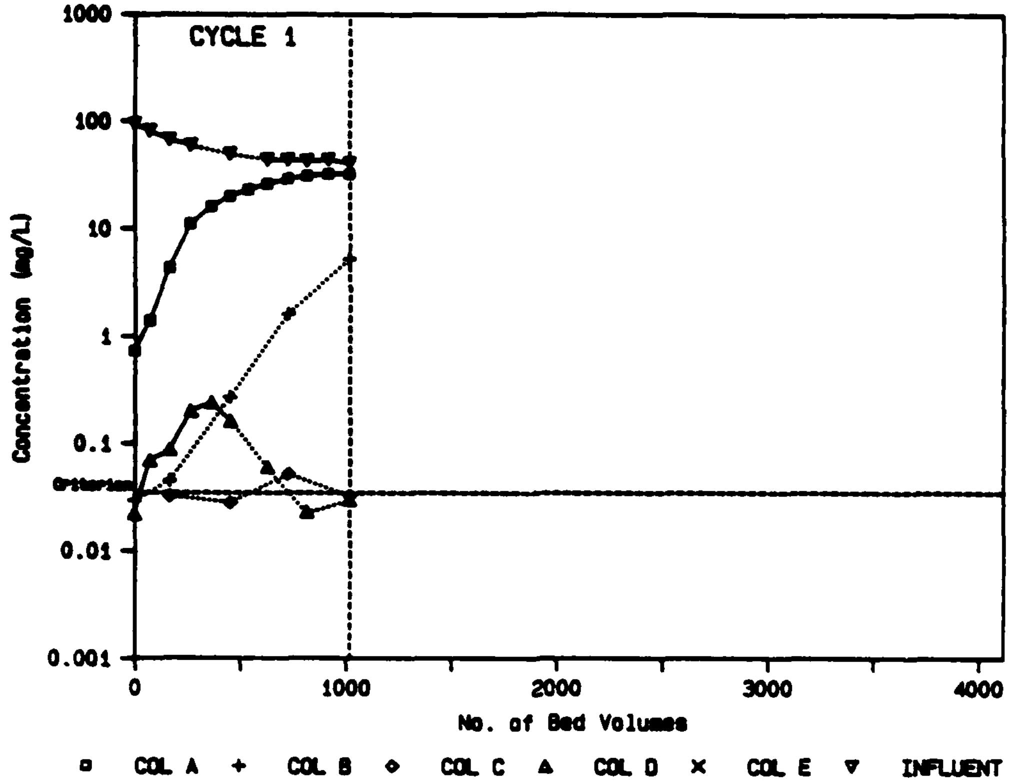

Figure 7-16. RDX breakthrough curves for test F.

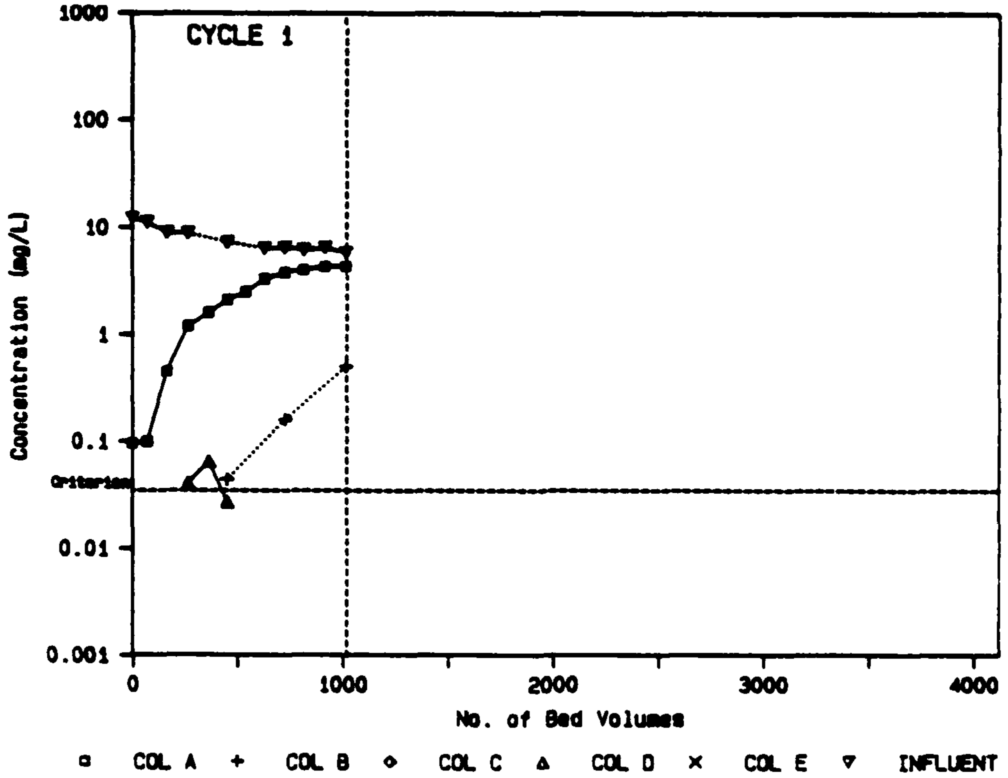

Figure 7-17. HMX breakthrough curves for test F.

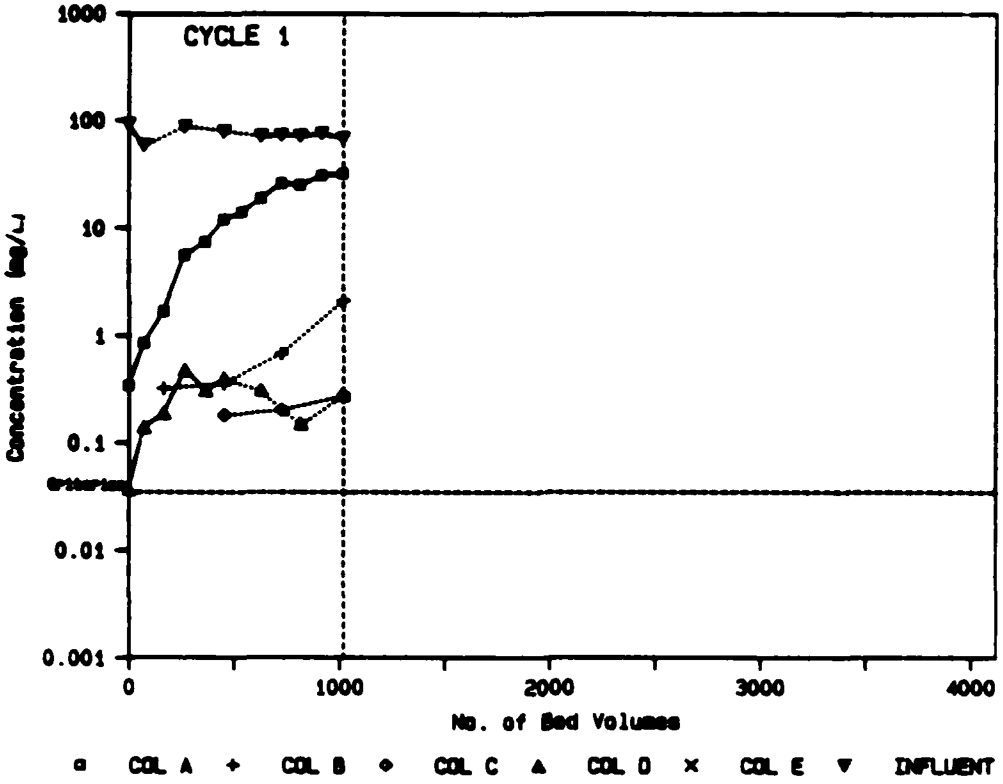

Figure 7-18. TNT breakthrough curves for test F.

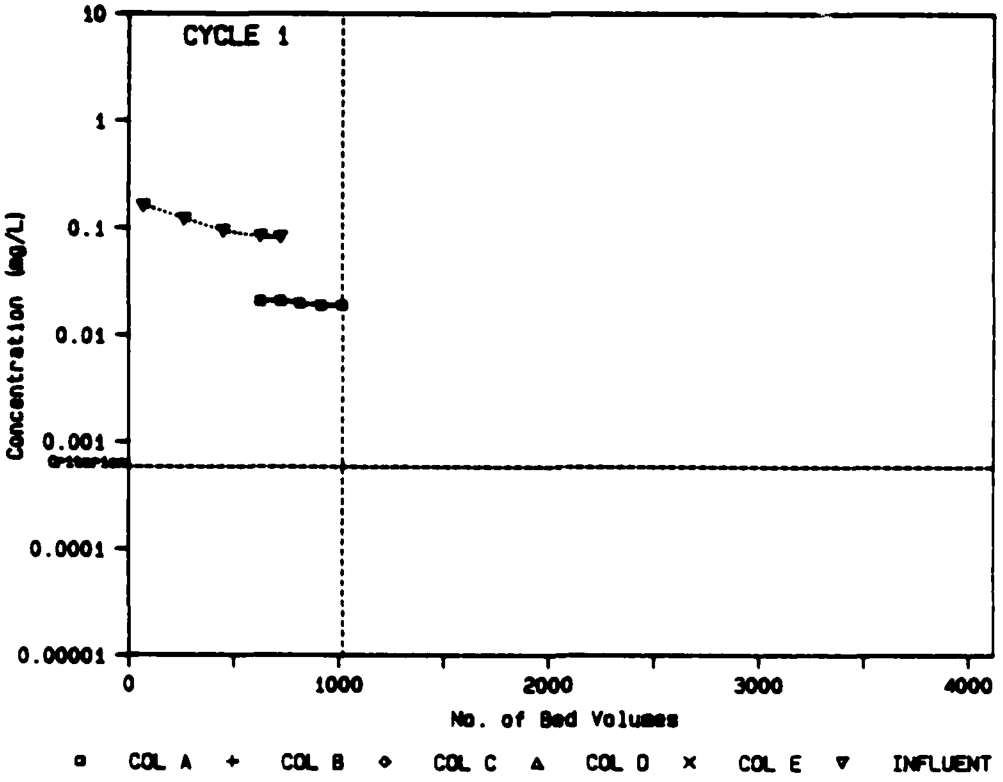

Figure 7-19. DNT breakthrough curves for test F.

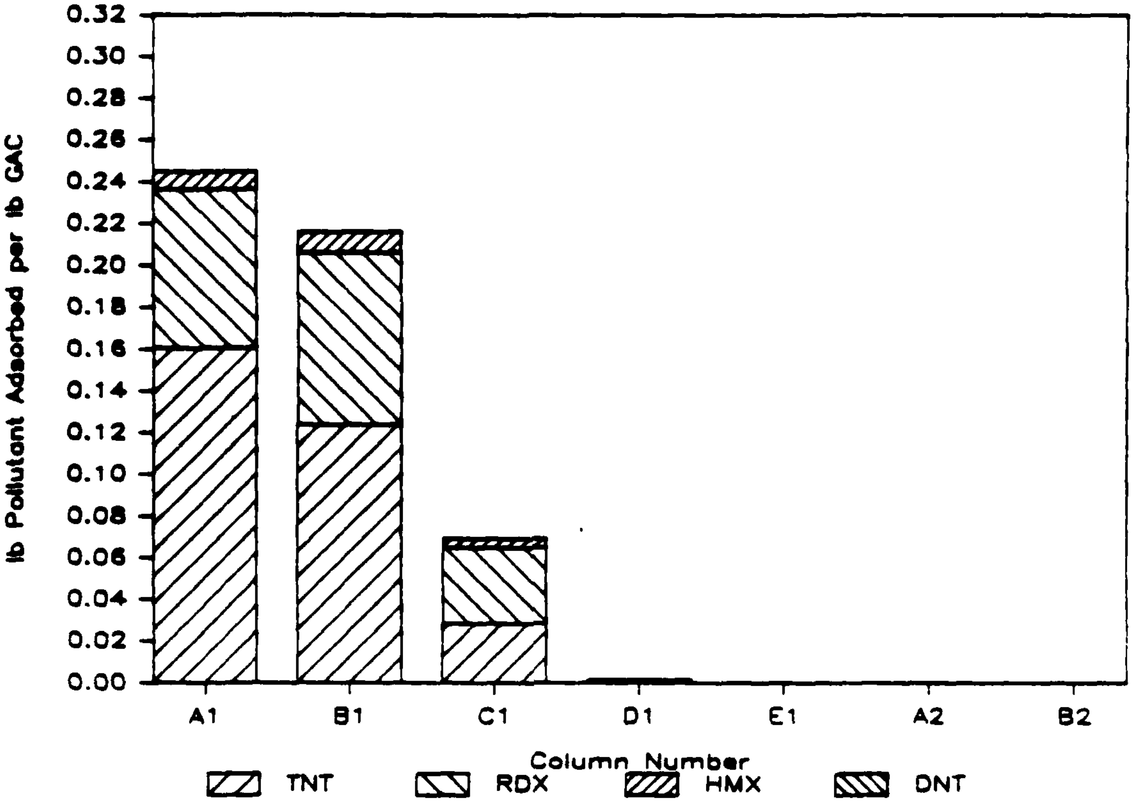

Figure 7-20. GAC loading for test A (1 cycle).

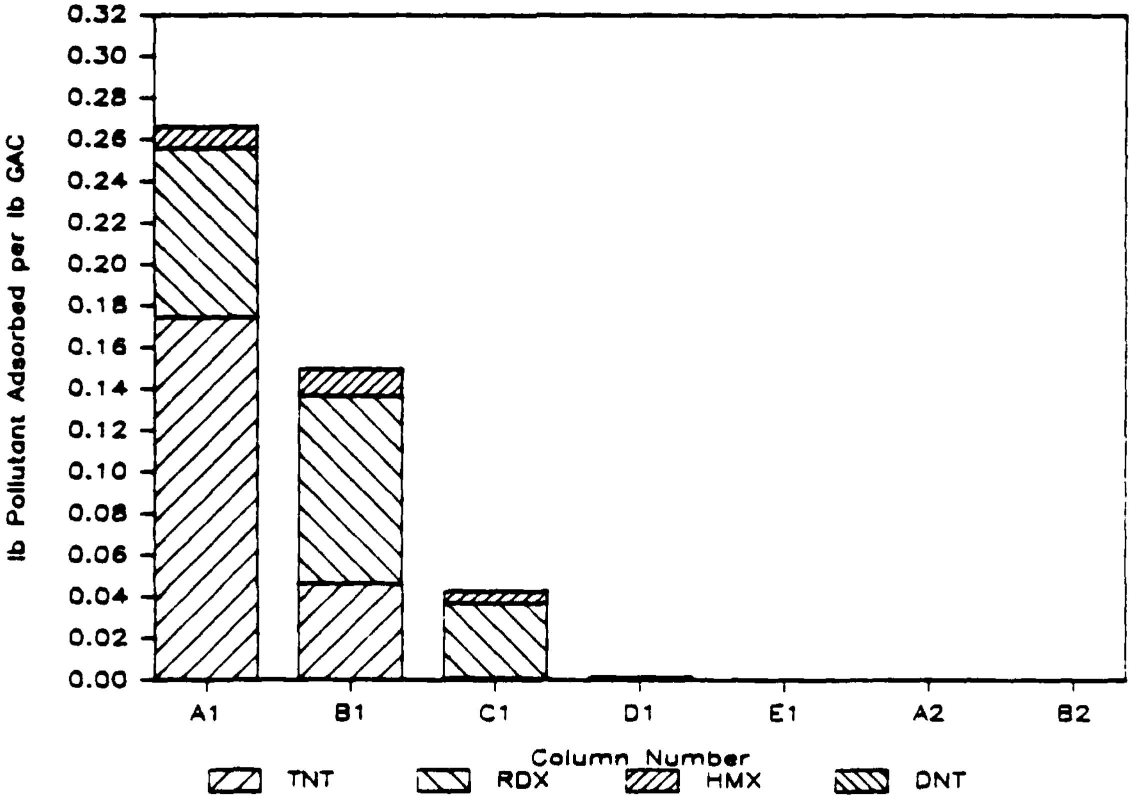

Figure 7-21. GAC loading for test B (2 cycle).

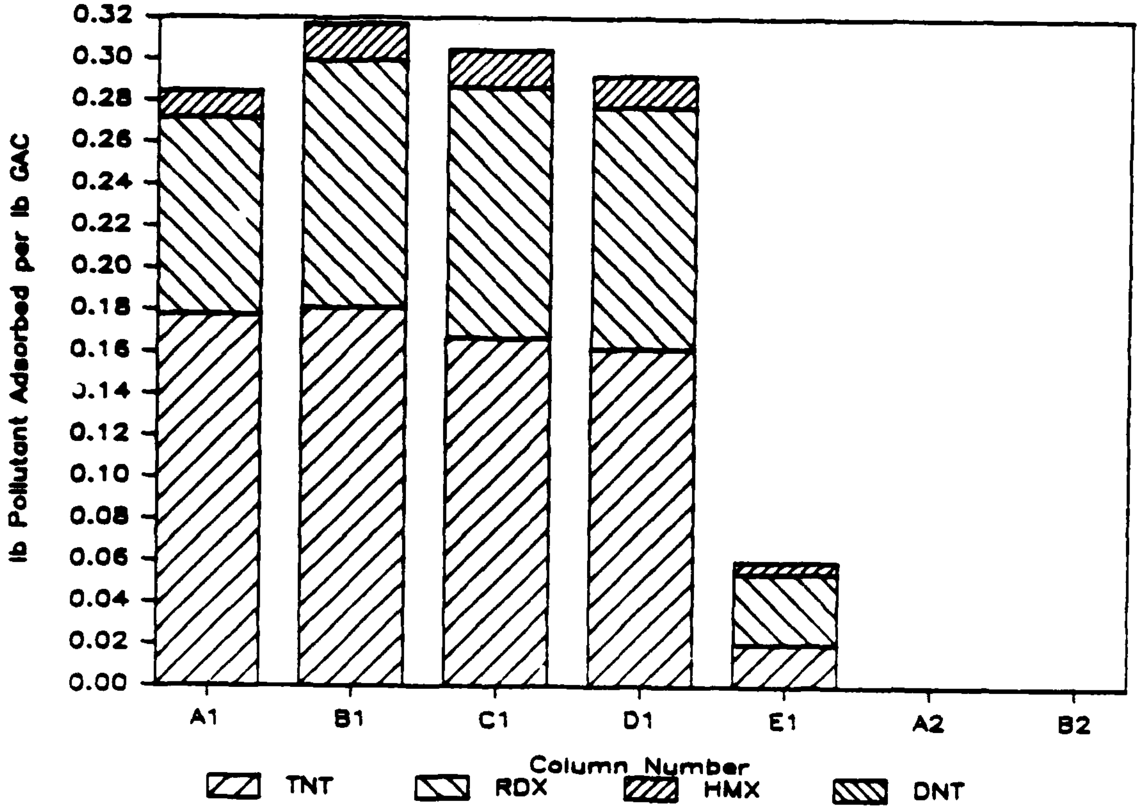

Figure 7-22. GAC loading for test C (4 cycle).

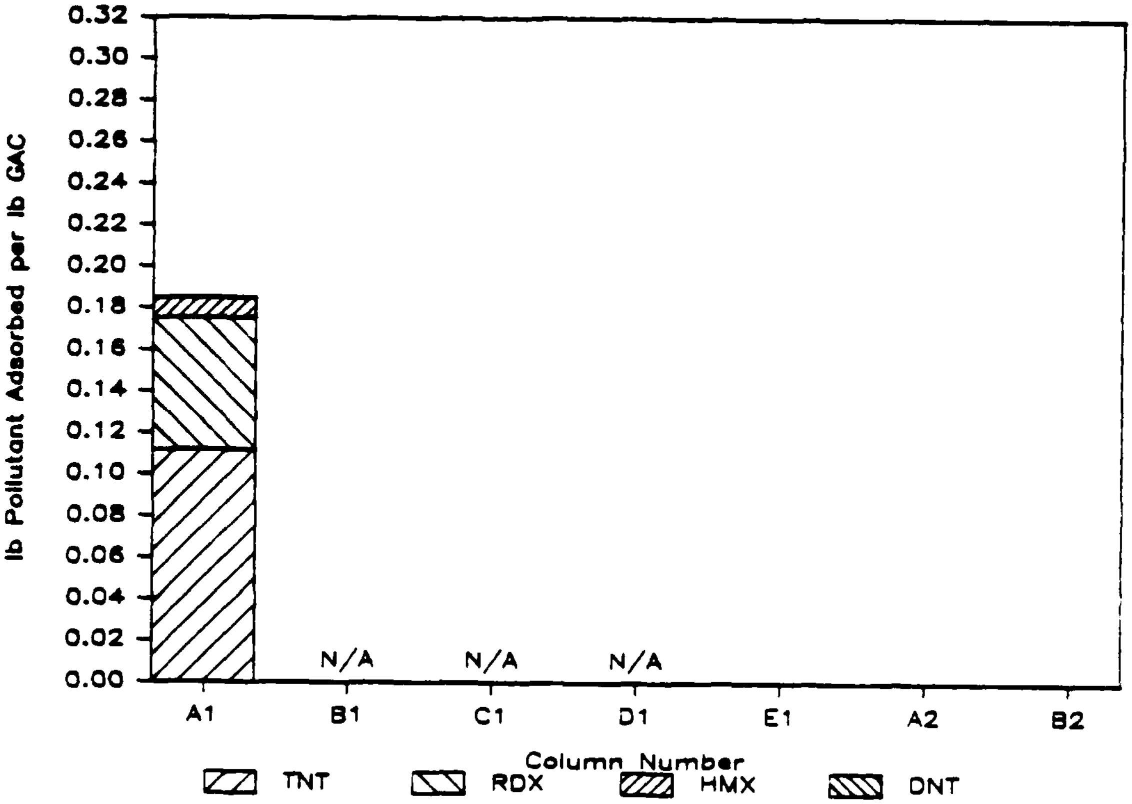

Figure 7-23. GAC loading for test F (1 cycle).

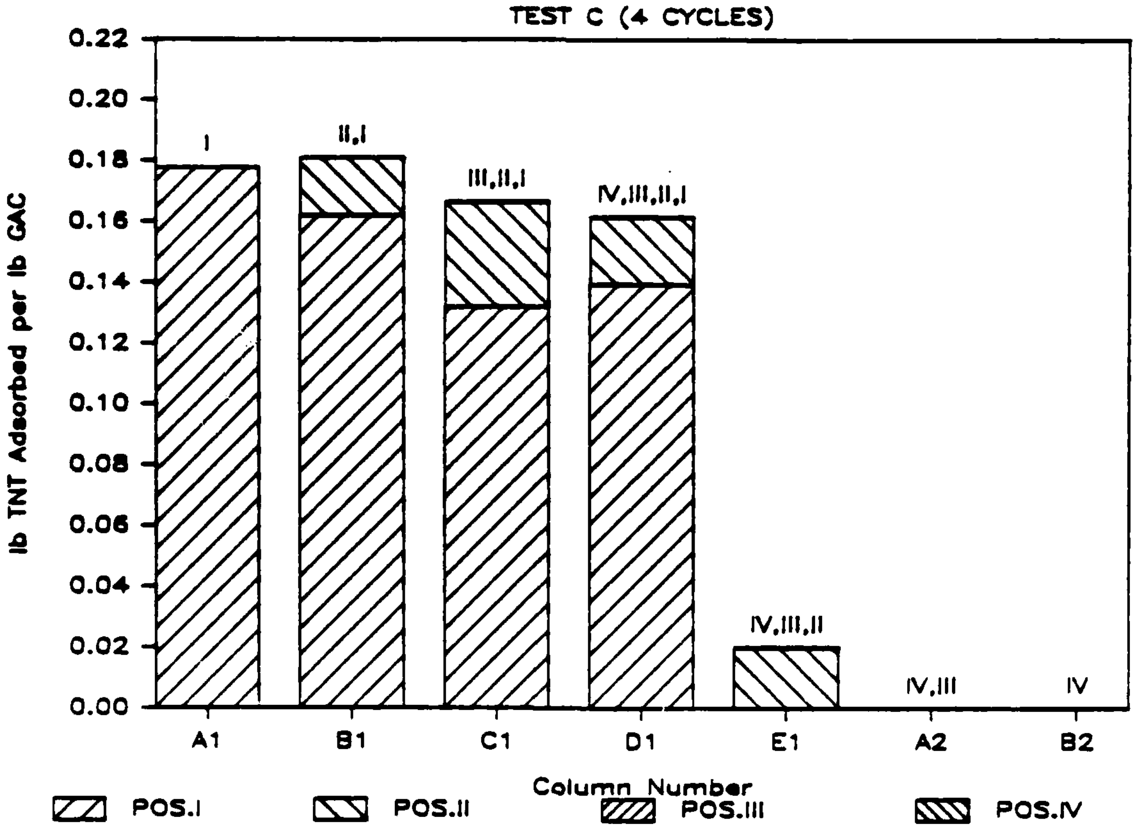

Figure 7-24. <u>TNT loading by column position for test C</u>.

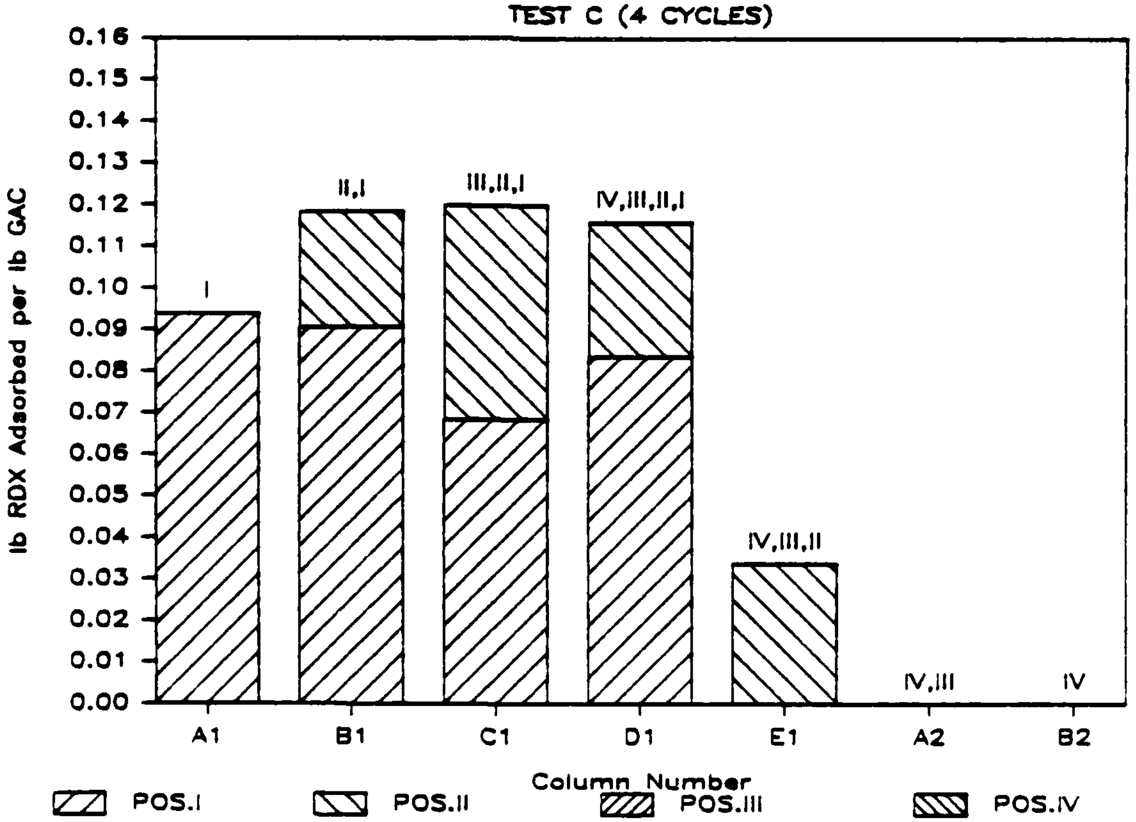

Figure 7-25. <u>RDX loading by column position for test C</u>.

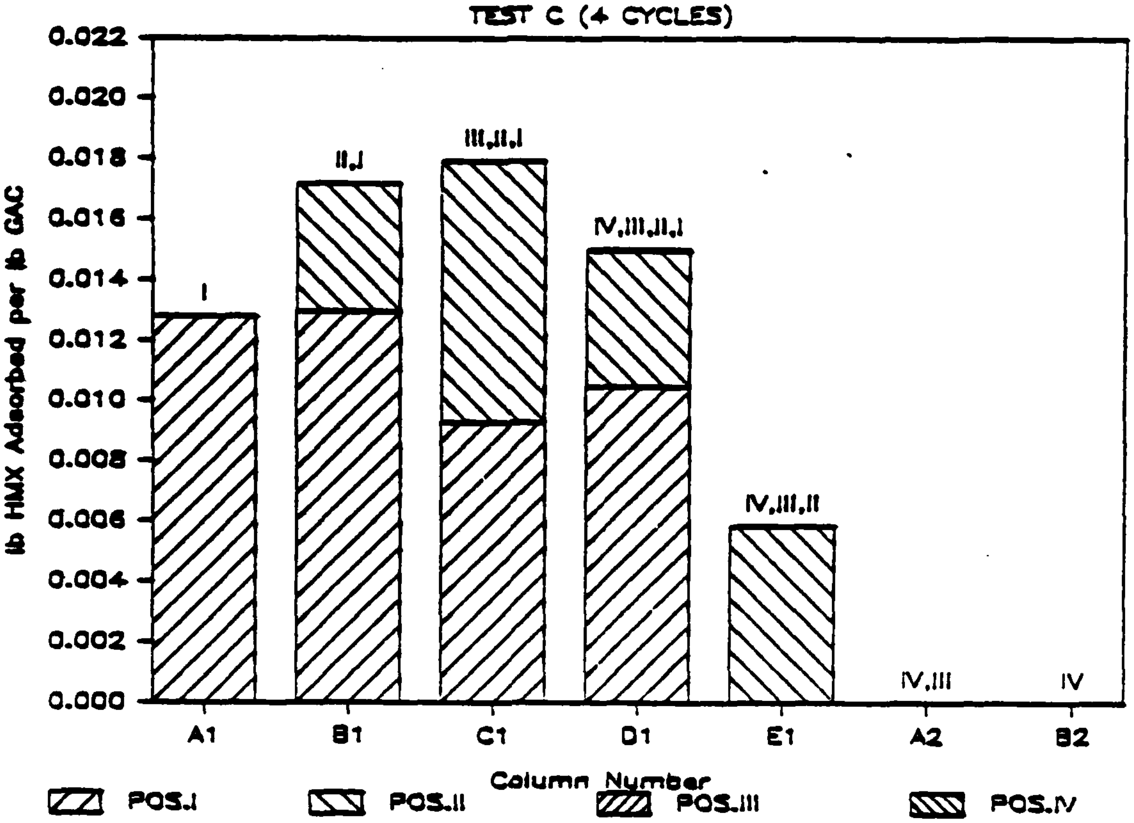

Figure 7-26. HMX loading by column position for test C.

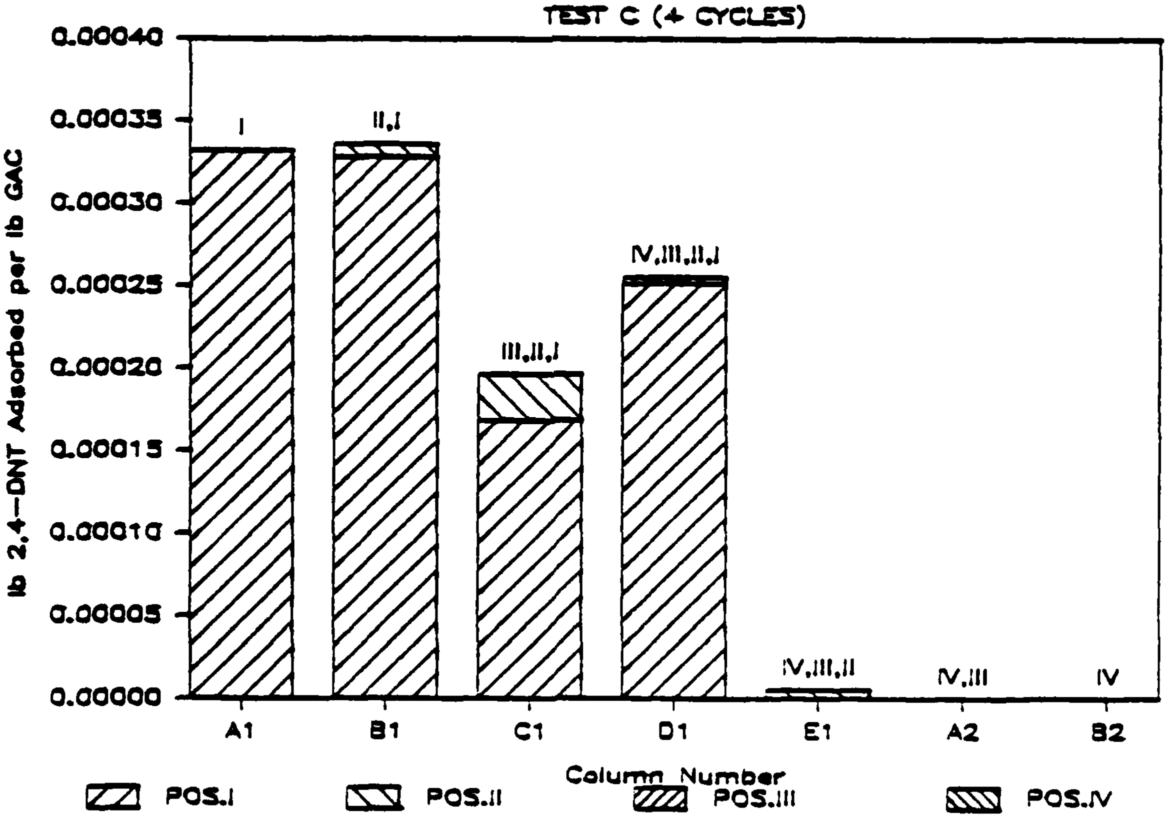

Figure 7-27. DNT loading by column position for test C.

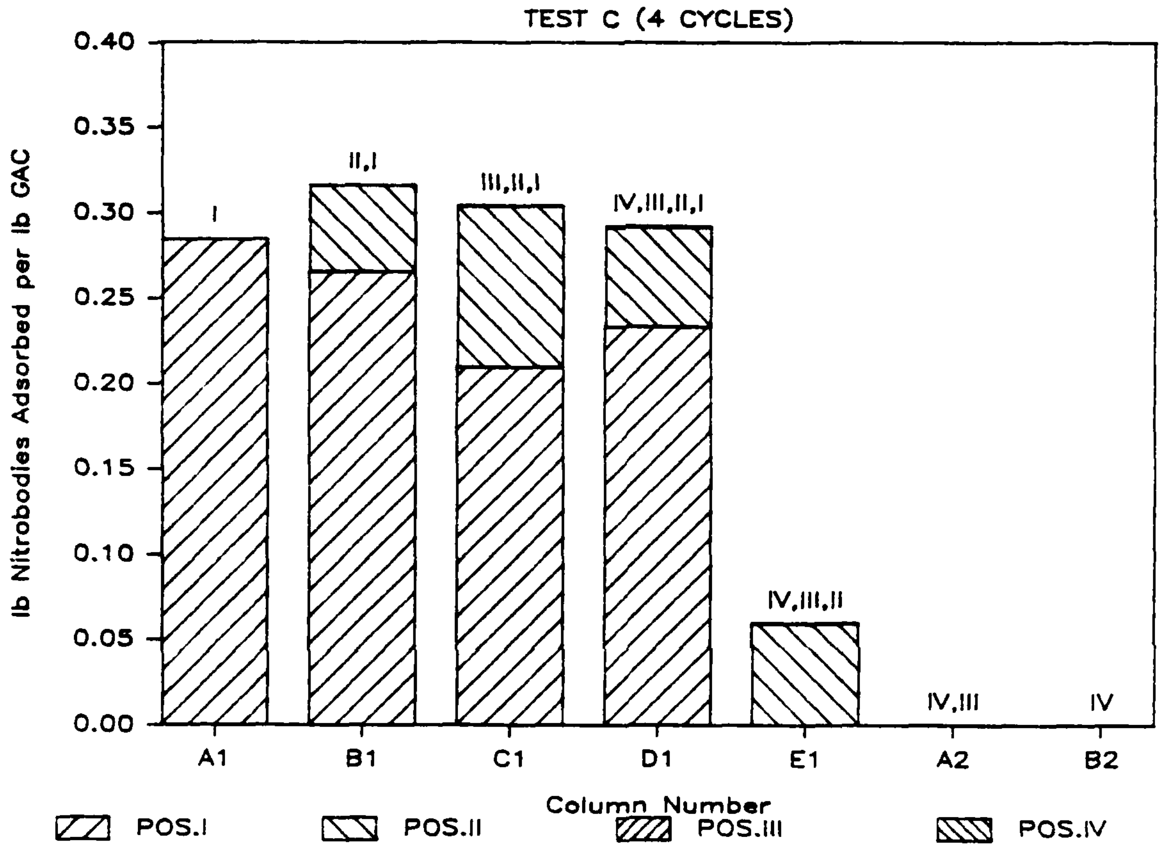

Figure 7-28. Total loading by column position for test C.

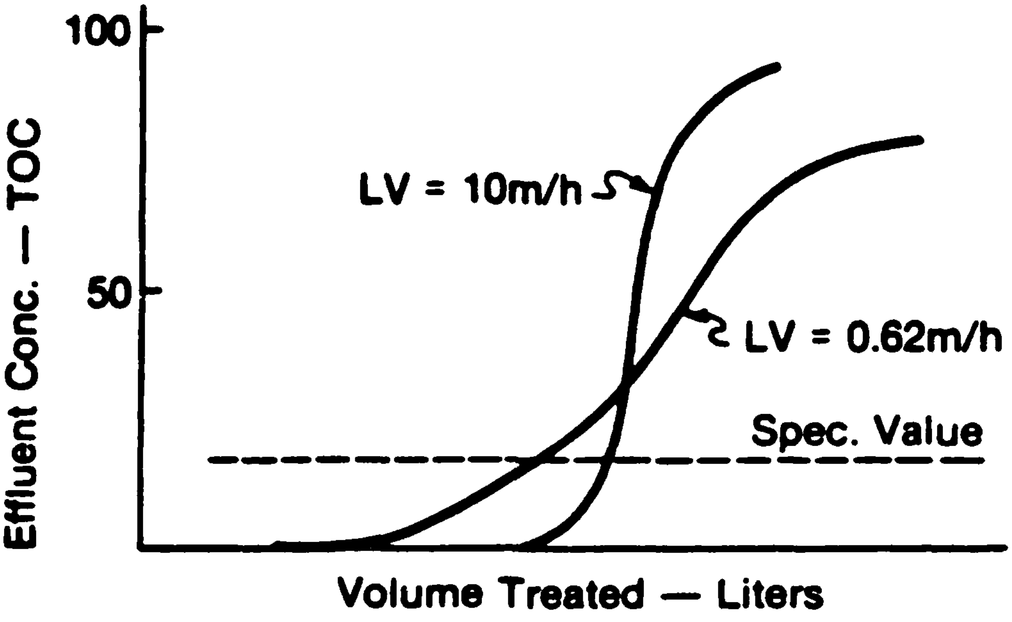

Figure 7-29. Effect of linear velocity on mass transfer zone.

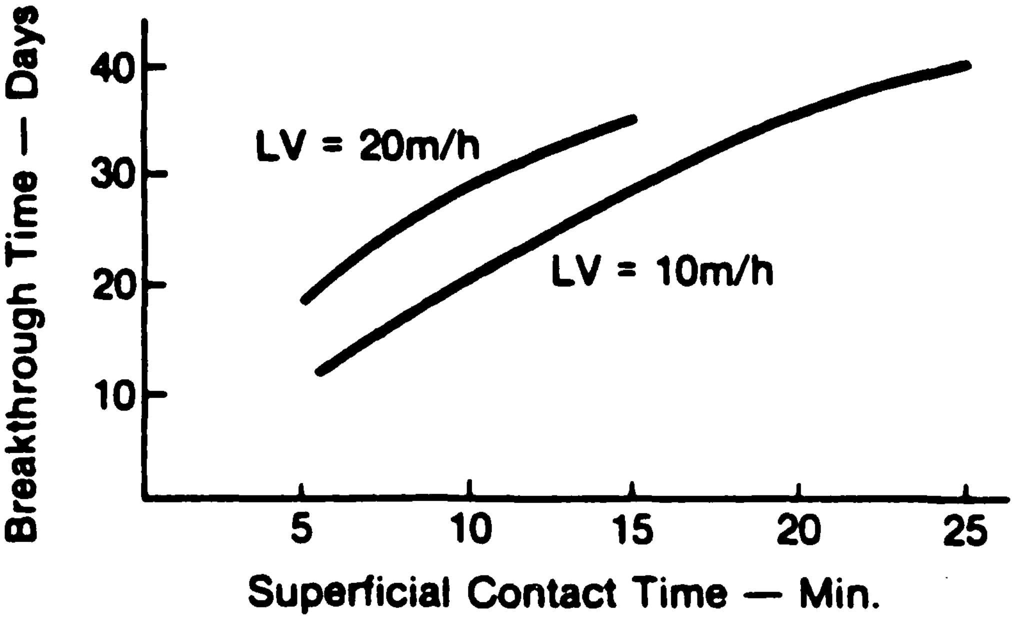

Figure 7-30. Effect of linear velocity on breakthrough time.

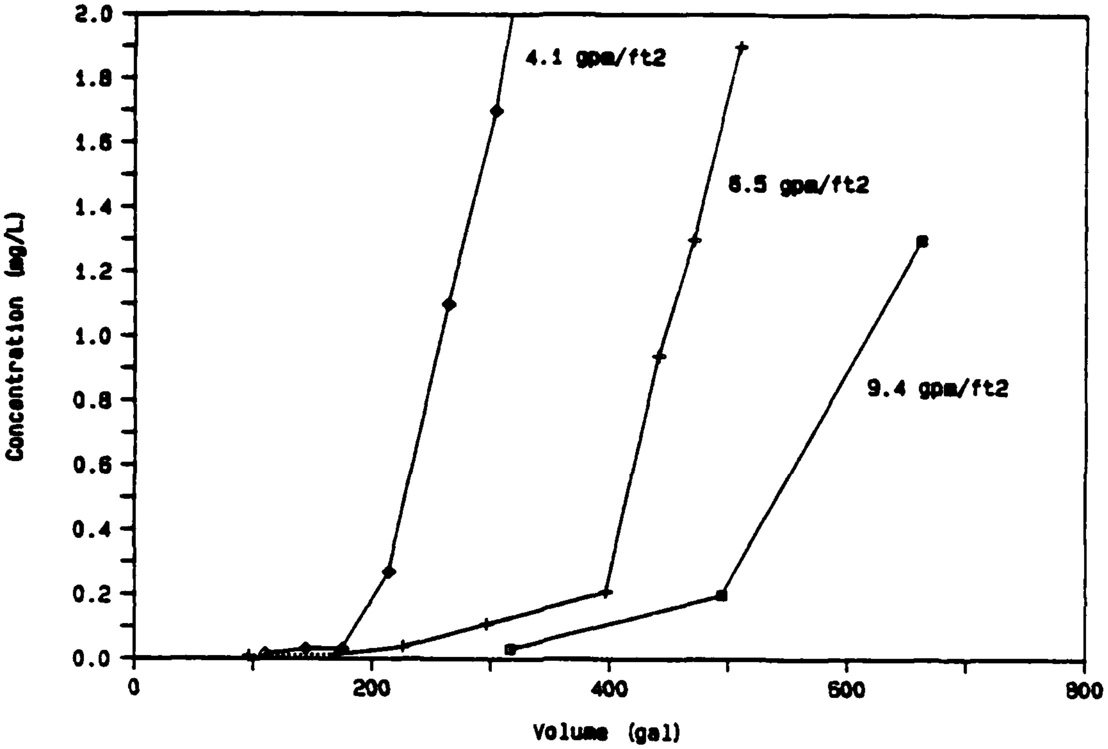

Figure 7-31. Effect of hydraulic loading rate on RDX concentration (2.3-2.4 min contact time).

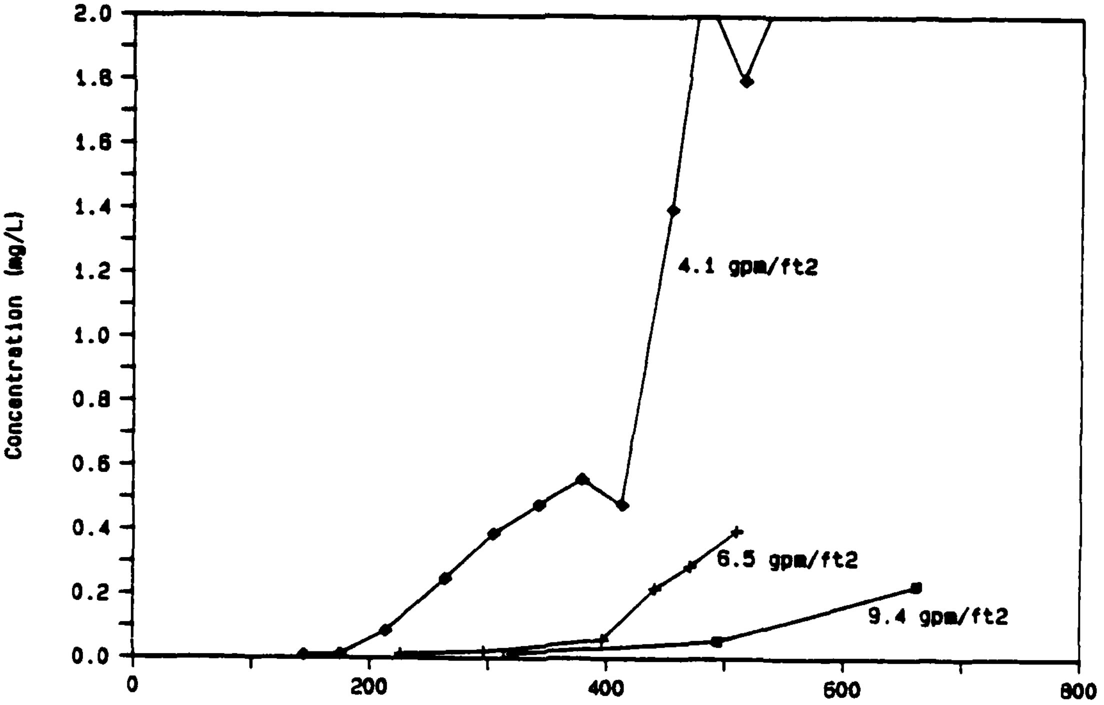

Figure 7-32. Effect of hydraulic loading rate on HMX concentration (2.3-2.4 min contact time).

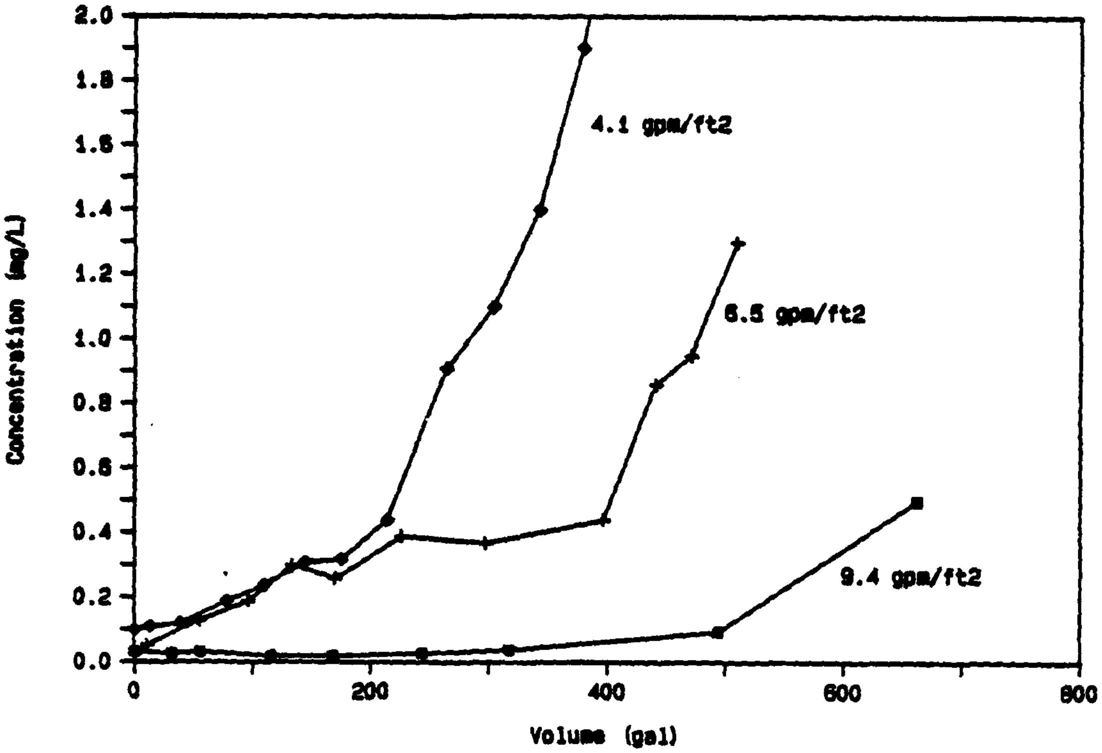

Figure 7-33. Effect of hydraulic loading rate on TNT concentration (2.3-2.4 min contact time).

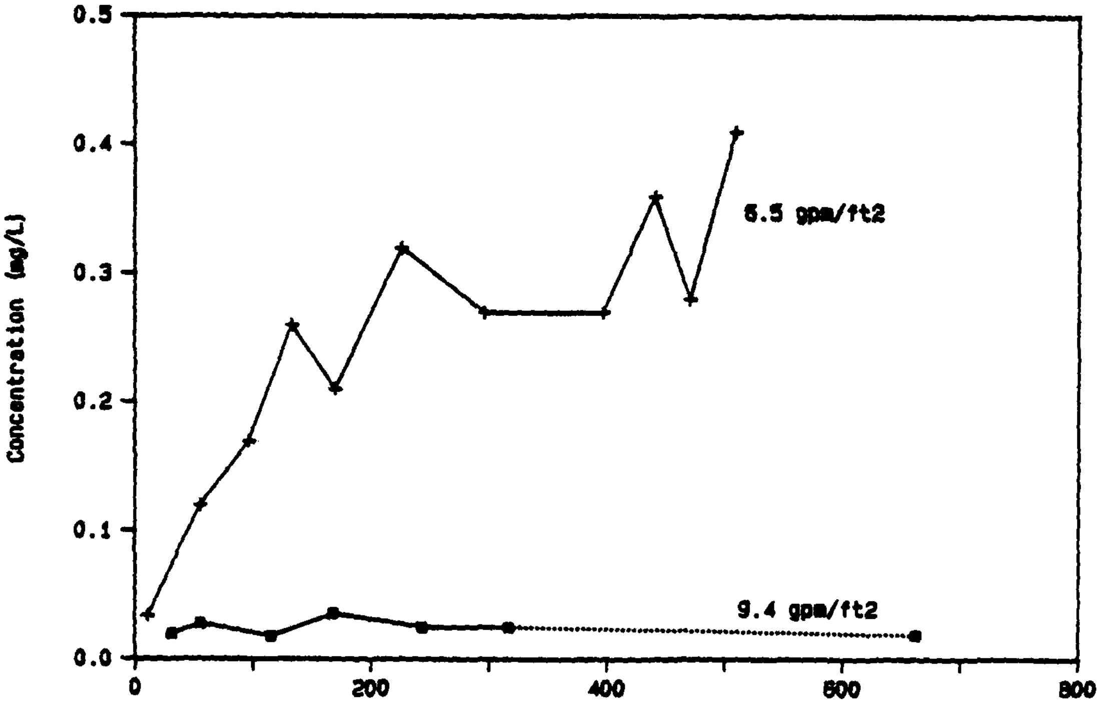

Figure 7-34. Effect of hydraulic loading rate on TNT concentration (3.1-3.4 min contact time).

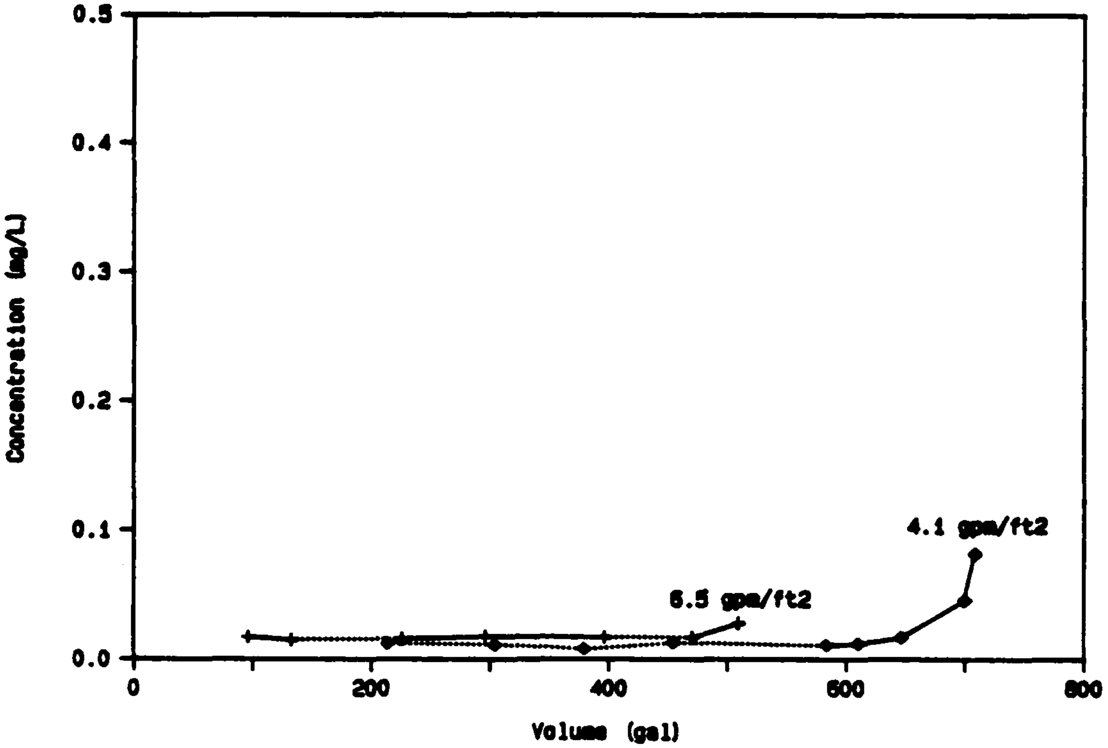

Figure 7-35. Effect of hydraulic loading rate on RDX concentration (4.5-4.8 min contact time).

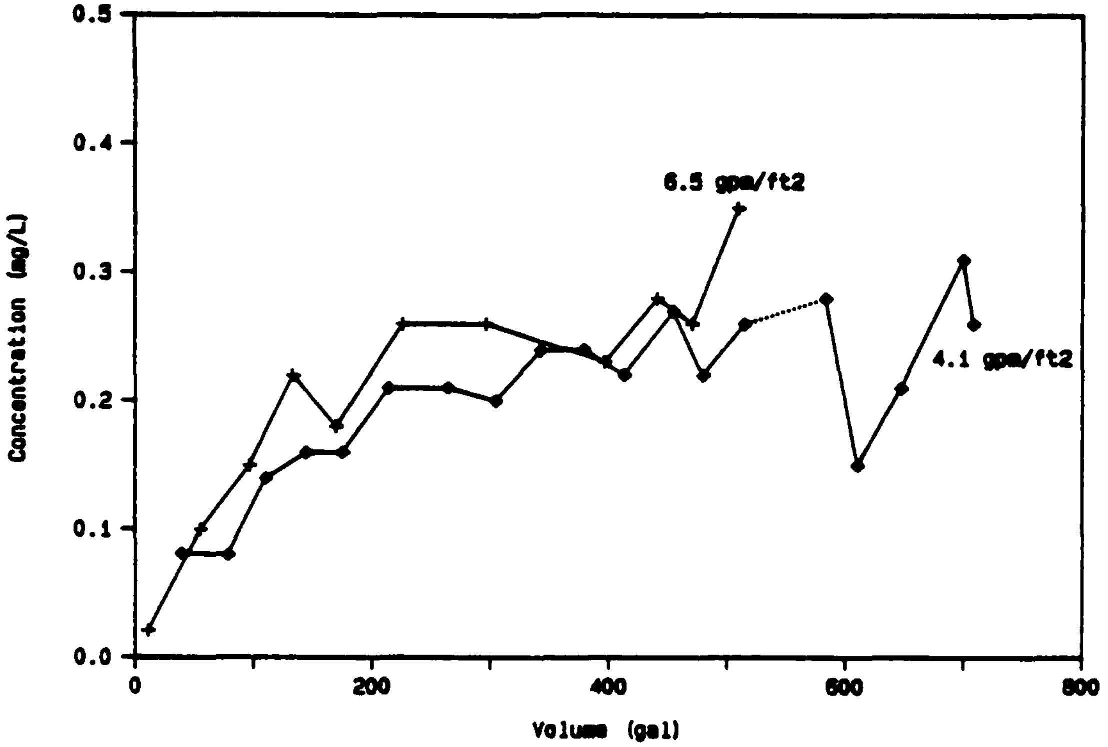

Figure 7-36. Effect of hydraulic loading rate on TNT concentration (4.5-4.8 min contact time).

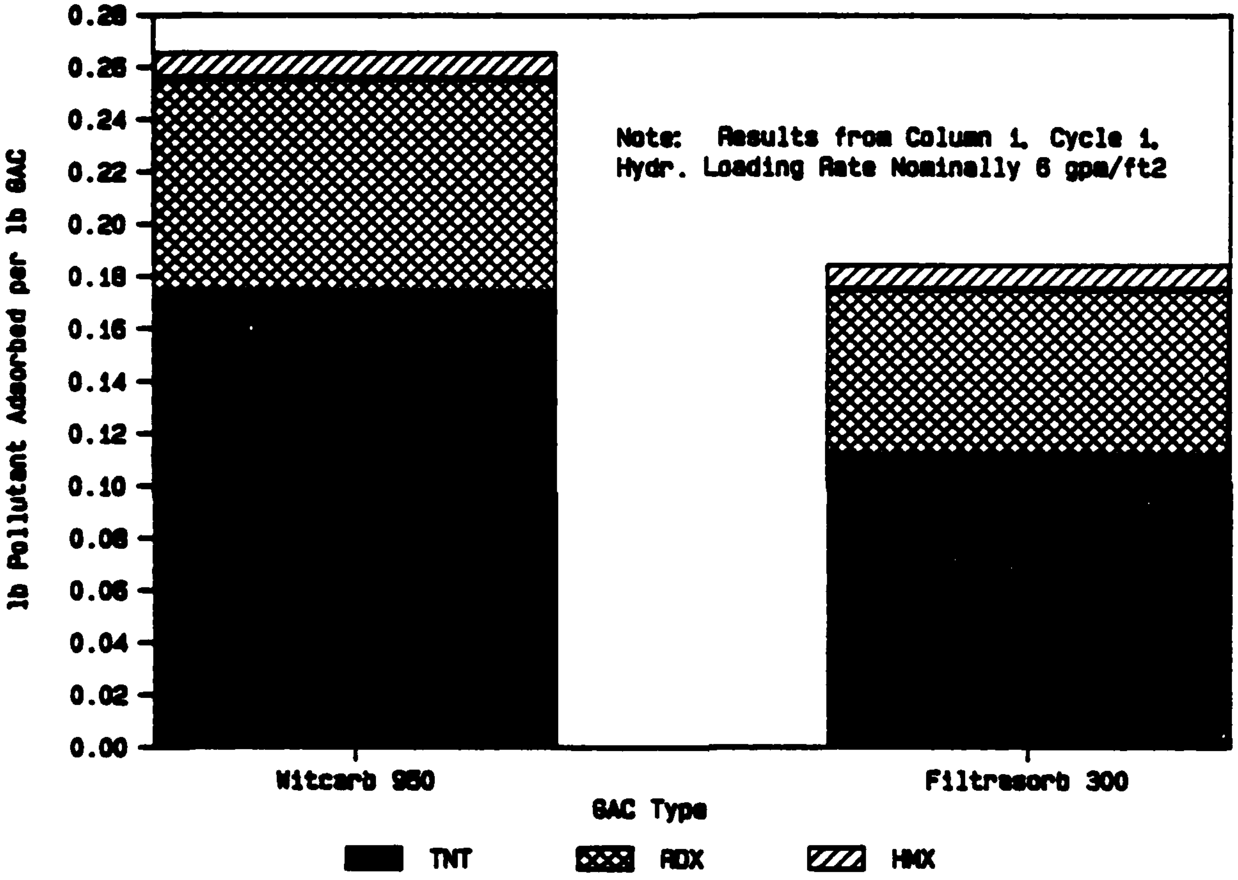

Figure 7-37. Comparison of nitrobody loading on Witco and Calgon GACs.

TABLE 7-1. Overall Test Conditions and Results for Four-in-Series GAC Column Tests.

Condition	Test Cycle No.								
	A1	B1	B2	D1	C1	C2	C3	C4	F1
Test start date	Nov. 5	Nov. 7	Nov. 9	Nov. 11	Nov. 13	Nov. 16	Nov. 18	Nov. 19	Nov. 20
GAC type[a]	W950	W950	W950	W950	W950	W950	W950	W950	F300
Bed depth, in.	11.75	11.75	11.75	15.75	15.75	15.75	15.75	15.75	11.75
GAC weight per column, lb	1.18	1.18	1.18	1.64	1.64	1.64	1.64	1.64	1.62
Average flow rate,[b] gpm	0.46	0.32	0.33	-	0.20	0.23	0.21	0.24	0.28
Hydraulic loading rate, gpm/ft²	9.4	6.5	6.7	-	4.1	4.7	4.3	4.9	5.8
Contact time per column, min	0.78	1.13	1.10	-	2.41	2.08	2.26	2.02	1.27
Test duration, hr	24.0	26.8	13.9	24	59	36.0	39.3	19.6	21.5
Total wastewater volume trtd., gal.	662	510	273	460	708	500	502	280	366
Total No. of bed volumes	1,841	1,417	2,176	954	1,469	1,037	1,042	581	1,018
Prior No. of bed volumes									
Column I	0	0	1,417	0	0	1,469	2,506	3,548	0
Column II	0	0	1,417	0	0	1,469	2,506	2,079	0
Column III	0	0	1,417	0	0	1,469	1,037	1,042	0
Column IV	0	0	0	0	0	0	0	0	0
No. of sampling times	9	12	8	8	22	12	14	6	12
Pink water tank No.	1	2	2	-	2	1	2	1	2
pH of pink water composite	-	-	6.8	-	6.97	7.02	7.18	7.04	-
Average Temperature, °F	63	60	61	60	63	62	63	63	62
Influent concentration,[b] mg/L									
RDX	42	34	44	-	34	56	39	91[c]	53
HMX	5.1	4.6	6.6	-	4.7	8.5	5.4	13[c]	7.6
DNT	0.035	0.064	0.11	-	0.094	0.14	0.067	0.21[c]	0.094
TNT	68	61	69	-	55	77	61	120[c,d]	75
Final breakthrough, Column I, %									
RDX	89	78	78	-	77	78	77	69	80
HMX	90	84	81	-	78	79	80	70	75
DNT	h	34	30	-	29	28	38	14[i]	44
TNT	74	53	51	-	44	44	44	35	48
Maximum effluent conc.,[e] mg/L									
RDX	< MDL	0.028	0.046	-	0.026	0.036	0.021	0.072	0.088[f]
HMX	ND	< MDL	0.035	-	ND	ND	ND	0.021	0.041[g]
DNT	ND	ND	ND	-	ND	ND	ND	ND	ND
TNT	0.036	0.35	0.55	-	0.32	0.26	0.26	0.30	0.48

NOTE: ND = Not detected.
< MDL = Less than minimum detection limit.
\- = Not available or not analyzed.

[a] W950 = Witco Witcarb 950, 18 x 40 mesh; F300 = Calgon Filtrasorb 300.

[b] Time-weighted average.

[c] See Table 7-8, footnote c.

[d] See Table 7-8, footnote f.

[e] Maximum value as determined by direct injection analysis (generally was final sample taken in cycle).

[f] Based upon field analysis (0.24 mg/L based upon final lab analysis).

[g] Based upon field analysis (0.065 mg/L based upon final lab analysis).

[h] Cannot quantitate (< MDL from Column I).

[i] Calculated using results immediately preceding final sample set.

TABLE 7-2. Cycle A1 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [A1 -]	Test time (hr)	Volume of wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
0 (T1) - 1	0.0	0.0	N/A	8.7	1.4	0.032	11
0 (T1) - 2	0.5	31.5	N/A	36	5.4	0.11	48
0 (T1) - 3	1.5	55.3	N/A	38	5.4	0.099	54
0 (T1) - 4	3.5	115.5	N/A	41	5.2	0.069	62
0 (T1) - 5	5.5	168.0	N/A	42	5.1	0.046	66
0 (T1) - 6	8.5	243.5	N/A	43	5.1	0.032	69
0 (T1) - 7	11.5	316.6	N/A	43	5.0	0.024	71
0 (T1) - 8	17.5	494.0	N/A	44	5.0	0.016	73
0 (T1) - 9	24.0	662.0	N/A	44	5.1	0.012	74
Average influent concentration[b]				42	5.1	0.035	68
1 (A1) - 1	0.0	0.0	0	1.4	0.36	ND	1.4
1 (A1) - 2	0.5	31.5	88	3.1	0.72	< MDL	3.3
1 (A1) - 3	1.5	55.3	154	5.8	1.2	ND	6.1
1 (A1) - 4	3.5	115.5	321	11	1.7	ND	11
1 (A1) - 5	5.5	168.0	467	16	2.2	< MDL	16
1 (A1) - 6	8.5	243.5	677	23	2.9	< MDL	25
1 (A1) - 7	11.5	316.6	881	31	3.7	0.011	40
1 (A1) - 8	17.5	494.0	1,374	35	4.1	0.0071	47
1 (A1) - 9	24.0	662.0	1,841	39	4.6	< MDL	55
2 (B1) - 1	0.0	0.0	0	ND	ND	ND	0.027
2 (B1) - 2	0.5	31.5	88	ND	ND	ND	0.027
2 (B1) - 3	1.5	55.3	154	0.015	ND	ND	0.035
2 (B1) - 4	3.5	115.5	321	0.097	0.037	ND	0.11
2 (B1) - 5	5.5	168.0	467	0.31	0.086	ND	0.23
2 (B1) - 6	8.5	243.5	677	0.75	0.17	ND	0.49
2 (B1) - 7	11.5	316.6	881	4.8	0.75	ND	3.8
2 (B1) - 8	17.5	494.0	1,374	14	1.7	ND	10
2 (B1) - 9	24.0	662.0	1,841	26	3.0	ND	22
3 (C1) - 1	0.0	0.0	0	ND	ND	ND	0.032
3 (C1) - 2	0.5	31.5	88	ND	ND	ND	0.026
3 (C1) - 3	1.5	55.3	154	ND	ND	ND	0.031
3 (C1) - 4	3.5	115.5	321	ND	ND	ND	0.019
3 (C1) - 5	5.5	168.0	467	ND	ND	ND	0.020
3 (C1) - 6	8.5	243.5	677	ND	ND	ND	0.028
3 (C1) - 7	11.5	316.6	881	0.032	0.016	ND	0.039
3 (C1) - 8	17.5	494.0	1,374	0.20	0.056	ND	0.095
3 (C1) - 9	24.0	662.0	1,841	1.3	0.23	ND	0.50
4 (D1) - 1	0.0	0.0	0	ND	ND	ND	ND
4 (D1) - 2	0.5	31.5	88	ND	ND	ND	0.020
4 (D1) - 3	1.5	55.3	154	ND	ND	ND	0.028
4 (D1) - 4	3.5	115.5	321	ND	ND	ND	0.018
4 (D1) - 5	5.5	168.0	467	ND	ND	ND	0.036
4 (D1) - 6	8.5	243.5	677	< MDL	ND	ND	0.025
4 (D1) - 7	11.5	316.6	881	ND	ND	ND	0.025
4 (D1) - 8	17.5	494.0	1,374	ND	ND	ND	< MDL
4 (D1) - 9	24.0	662.0	1,841	ND	ND	ND	0.019
4 (D1) - 9 - TE	Trace enrichment analysis			-	-	ND (< 0.47 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.

[b] Time-weighted averages.

TABLE 7-3. Cycle B1 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [B1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
0 (T2) - 1	0.0	0.0	N/A	45	5.3	0.016	72
0 (T2) - 2	0.5	11.0	N/A	43	5.1	0.020	70
0 (T2) - 3	2.5	55.4	N/A	39	5.0	0.049	67
0 (T2) - 4	4.5	96.6	N/A	37	4.9	0.054	64
0 (T2) - 5	6.5	133.2	N/A	36	4.8	0.066	63
0 (T2) - 6	8.5	169.7	N/A	35	4.6	0.063	62
0 (T2) - 7	11.5	226.2	N/A	34	4.6	0.066	61
0 (T2) - 8	14.5	296.6	N/A	33	4.5	0.073	61
0 (T2) - 9	20.5	397.1	N/A	32	4.5	0.073	59
0 (T2) - 10	22.8	441.0	N/A	32	4.5	0.072	58
0 (T2) - 11	24.8	470.9	N/A	32	4.5	0.071	58
0 (T2) - 12	26.8	509.7	N/A	32	4.4	0.073	58
Average influent concentration[b]				34	4.6	0.064	61
1 (A1) - 1	0.0	0.0	0	ND	ND	ND	0.044
1 (A1) - 2	0.5	11.0	30	0.0096	ND	ND	0.085
1 (A1) - 3	2.5	55.4	154	0.17	0.043	ND	0.35
1 (A1) - 4	4.5	96.6	269	0.64	0.15	ND	0.73
1 (A1) - 5	6.5	133.2	370	2.0	0.38	ND	1.9
1 (A1) - 6	8.5	169.7	472	4.9	0.84	ND	4.4
1 (A1) - 7	11.5	226.2	629	10	1.6	ND	10
1 (A1) - 8	14.5	296.6	825	18	2.7	0.015	20
1 (A1) - 9	20.5	397.1	1,104	20	2.9	0.0092	20
1 (A1) - 10	22.8	441.0	1,226	24	3.5	0.026	28
1 (A1) - 11	24.8	470.9	1,310	25	3.7	0.027	31
1 (A1) - 12	26.8	509.7	1,417	25	3.7	0.025	31
2 (B1) - 1	0.0	0.0	0	ND	ND	ND	0.022
2 (B1) - 2	0.5	11.0	30	< MDL	ND	ND	0.053
2 (B1) - 3	2.5	55.4	154	< MDL	ND	ND	0.13
2 (B1) - 4	4.5	96.6	269	0.0088	ND	ND	0.19
2 (B1) - 5	6.5	133.2	370	< MDL	ND	ND	0.30
2 (B1) - 6	8.5	169.7	472	0.013	ND	ND	0.26
2 (B1) - 7	11.5	226.2	629	0.038	0.014	ND	0.39
2 (B1) - 8	14.5	296.6	825	0.11	0.023	ND	0.37
2 (B1) - 9	20.5	397.1	1,104	0.21	0.060	ND	0.44
2 (B1) - 10	22.8	441.0	1,226	0.94	0.22	ND	0.86
2 (B1) - 11	24.8	470.9	1,310	1.3	0.29	ND	0.95
2 (B1) - 12	26.8	509.7	1,417	1.9	0.40	ND	1.3

TABLE 7-3. Concluded.

Sample No. [B1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
3 (C1) - 1	0.0	0.0	0	ND	ND	ND	< MDL
3 (C1) - 2	0.5	11.0	30	ND	ND	ND	0.034
3 (C1) - 3	2.5	55.4	154	0.0079	ND	ND	0.12
3 (C1) - 4	4.5	96.6	269	0.010	ND	ND	0.17
3 (C1) - 5	6.5	133.2	370	< MDL	ND	ND	0.26
3 (C1) - 6	8.5	169.7	472	< MDL	ND	ND	0.21
3 (C1) - 7	11.5	226.2	629	0.023	< MDL	ND	0.32
3 (C1) - 8	14.5	296.6	825	0.017	ND	ND	0.27
3 (C1) - 9	20.5	397.1	1,104	0.015	ND	ND	0.27
3 (C1) - 10	22.8	441.0	1,226	0.021	< MDL	ND	0.36
3 (C1) - 11	24.8	470.9	1,310	0.017	ND	ND	0.28
3 (C1) - 12	26.8	509.7	1,417	0.025	ND	ND	0.41
4 (D1) - 1	0.0	0.0	0	ND	ND	ND	ND
4 (D1) - 2	0.5	11.0	30	ND	ND	ND	0.021
4 (D1) - 3	2.5	55.4	154	< MDL	ND	ND	0.10[c]
4 (D1) - 4	4.5	96.6	269	0.017	ND	ND	0.15[c]
4 (D1) - 5	6.5	133.2	370	0.015	ND	ND	0.22[c]
4 (D1) - 6	8.5	169.7	472	< MDL	ND	ND	0.18[c]
4 (D1) - 7	11.5	226.2	629	0.016	< MDL	ND	0.26[c]
4 (D1) - 8	14.5	296.6	825	0.018	ND	ND	0.26[c]
4 (D1) - 9	20.5	397.1	1,104	0.017	ND	ND	0.23[c]
4 (D1) - 10	22.8	441.0	1,226	-	ND	ND	0.28[c]
4 (D1) - 11	24.8	470.9	1,310	0.017	ND	ND	0.26[c]
4 (D1) - 12	26.8	509.7	1,417	0.028	< MDL	ND	0.35[c]
4 (D1) - 12 - TE	Trace enrichment analysis			-	-	d	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.
[b] Time-weighted averages.
[c] Final effluent concentration exceeds criterion.
[d] Sample lost during preparation.

TABLE 7-4. Cycle B2 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [B2 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
0 (T2) - 1	0.3	4.4	N/A	32	4.6	-	54
0 (T2) - 2	2.3	47.1	N/A	38	5.8	0.10	62
0 (T2) - 3	4.4	88.4	N/A	42	6.3	0.11	66
0 (T2) - 4	6.3	126.6	N/A	44	6.6	0.12	69
0 (T2) - 5	8.3	170.2	N/A	47	7.0	0.12	71
0 (T2) - 6	10.3	206.0	N/A	48	7.2	0.13	73
0 (T2) - 7	12.3	235.2	N/A	49	7.5	0.15	75
0 (T2) - 8	13.9	272.8	N/A	49	7.3	0.13	73
Average influent concentration[b]				44	6.6	0.11	69
1 (B1) - 1	0.3	4.4	1,429	1.4	0.30	ND	1.5
1 (B1) - 2	2.3	47.1	1,548	4.6	0.97	ND	3.4
1 (B1) - 3	4.4	88.4	1,663	12	2.2	ND	9.6
1 (B1) - 4	6.3	126.6	1,769	19	3.3	0.011	15
1 (B1) - 5	8.3	170.2	1,890	26	4.2	0.016	22
1 (B1) - 6	10.3	206.0	1,990	28	4.6	0.028	23
1 (B1) - 7	12.3	235.2	2,071	29	4.7	0.021	22
1 (B1) - 8	13.9	272.8	2,176	38	5.9	0.039	37
2 (C1) - 1	0.3	4.4	1,429	0.020	ND	ND	0.29
2 (C1) - 2	2.3	47.1	1,548	0.035	0.055	ND	0.36
2 (C1) - 3	4.4	88.4	1,663	0.085	0.11	ND	0.42
2 (C1) - 4	6.3	126.6	1,769	0.25	0.15	ND	0.52
2 (C1) - 5	8.3	170.2	1,890	0.63	0.36	ND	0.85
2 (C1) - 6	10.3	206.0	1,990	0.54	0.23	ND	0.65
2 (C1) - 7	12.3	235.2	2,071	0.49	0.24	ND	0.59
2 (C1) - 8	13.9	272.8	2,176	2.9	0.79	ND	2.1
3 (D1) - 1	0.3	4.4	1,429	0.015	ND	ND	0.27
3 (D1) - 2	2.3	47.1	1,548	0.017	0.017	ND	0.28
3 (D1) - 3	4.4	88.4	1,663	0.19[c]	0.058[c]	ND[c]	0.43[c]
3 (D1) - 4	6.3	126.6	1,769	0.029	0.034	ND	0.36
3 (D1) - 5	8.3	170.2	1,890	0.032	0.072	ND	0.46
3 (D1) - 6	10.3	206.0	1,990	0.027	0.017	ND	0.40
3 (D1) - 7	12.3	235.2	2,071	0.022	0.018	ND	0.33
3 (D1) - 8	13.9	272.8	2,176	0.061	0.078	ND	0.67
4 (E1) - 1	0.3	4.4	12	< MDL	ND	ND	0.24[d]
4 (E1) - 2	2.3	47.1	131	0.019	ND	ND	0.25[d]
4 (E1) - 3	4.4	88.4	246	0.023	0.0097	ND	0.28[d]
4 (E1) - 4	6.3	126.6	352	0.025	0.024	ND	0.33[d]
4 (E1) - 5	8.3	170.2	473	0.032[d]	0.035[d]	ND	0.40[d]
4 (E1) - 6	10.3	206.0	573	0.026	0.030	ND	0.31[d]
4 (E1) - 7	12.3	235.2	654	0.020	0.021	ND	0.28[d]
4 (E1) - 8	13.9	272.8	759	0.046[d]	0.031[d]	ND	0.55[d]
4 (E1) - 8 - TE	Trace enrichment analysis			-	-	ND (< 0 .47 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.

[b] Time-weighted averages.

[c] RDX concentration appeared artificially high, so reanalyzed later in laboratory. Later results were 0.22, 0.092, ND, and 0.26 for RDX, HMX, 2,4-DNT, and TNT, respectively.

[d] Final effluent concentration exceeds criterion.

TABLE 7-5. Cycle C1 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [C1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
0 (T2) - 1	0.0	0.0	N/A	34	4.8	0.21	44
0 (T2) - 2	1.0	13.2	N/A	34	4.7	0.073	51
0 (T2) - 3	3.0	38.9	N/A	34	4.7	0.076	53
0 (T2) - 4	6.2	78.2	N/A	35	4.8	0.088	56
0 (T2) - 5	9.0	110.2	N/A	34	4.8	0.079	56
0 (T2) - 6	12.0	144.4	N/A	34	4.8	0.075	57
0 (T2) - 7	15.0	174.7	N/A	34	4.8	0.081	56
0 (T2) - 8	18.0	213.9	N/A	33	4.8	0.071	56
0 (T2) - 9	21.3	264.0	N/A	33	4.8	0.10	56
0 (T2) - 10	23.0	304.0	N/A	33	4.8	0.13	56
0 (T2) - 11	27.0	342.6	N/A	32	4.6	0.11	54
0 (T2) - 12	30.0	379.1	N/A	33	4.6	0.11	55
0 (T2) - 13	33.0	412.6	N/A	33	4.4	0.075	54
0 (T2) - 14	36.4	454.5	N/A	33	4.6	0.11	54
0 (T2) - 15	39.0	479.3	N/A	33	4.4	0.11	54
0 (T2) - 16	42.0	514.7	N/A	33	4.5	0.10	54
0 (T2) - 17	45.0	548.1	N/A	33	4.3	0.081	53
0 (T2) - 18	48.0	583.2	N/A	34	4.9	0.073	55
0 (T2) - 19	51.1	609.9	N/A	32	4.4	0.11	53
0 (T2) - 20	54.0	646.5	N/A	37	5.4	0.11	57
0 (T2) - 21	58.0	699.5	N/A	40	5.5	0.094	59
0 (T2) - 22	59.0	708.0	N/A	44	6.7	0.10	63
Average influent concentration[b]				34	4.7	0.094	55
1 (A1) - 1	0.0	0.0	0	< MDL	ND	ND	0.099
1 (A1) - 2	1.0	13.2	27	< MDL	ND	ND	0.11
1 (A1) - 3	3.0	38.9	81	< MDL	ND	ND	0.12
1 (A1) - 4	6.2	78.2	162	< MDL	ND	ND	0.19
1 (A1) - 5	9.0	110.2	229	0.016	< MDL	ND	0.24
1 (A1) - 6	12.0	144.4	300	0.031	0.0091	ND	0.31
1 (A1) - 7	15.0	174.7	362	0.032	0.014	ND	0.32
1 (A1) - 8	18.0	213.9	444	0.27	0.086	ND	0.44
1 (A1) - 9	21.3	264.0	548	1.1	0.25	ND	0.91
1 (A1) - 10	23.0	304.0	631	1.7	0.39	ND	1.1
1 (A1) - 11	27.0	342.6	711	2.6	0.48	ND	1.4
1 (A1) - 12	30.0	379.1	787	3.7	0.56	ND	1.9
1 (A1) - 13	33.0	412.6	856	5.0	0.48	ND	2.6
1 (A1) - 14	36.4	454.5	943	10	1.4	ND	6.9
1 (A1) - 15	39.0	479.3	995	12	2.1	ND	9.5
1 (A1) - 16	42.0	514.7	1,068	12	1.8	ND	7.0
1 (A1) - 17	45.0	548.1	1,137	15	2.1	ND	9.2
1 (A1) - 18	48.0	583.2	1,210	18	2.6	0.0096	13
1 (A1) - 19	51.1	609.9	1,265	16	2.3	< MDL	8.7
1 (A1) - 20	54.0	646.5	1,341	25	3.9	0.010	19
1 (A1) - 21	58.0	699.5	1,451	32	5.0	0.022	26
1 (A1) - 22	59.0	708.0	1,469	34	5.2	0.029	28
2 (B1) - 1	0.0	0.0	0	ND[c]	ND[c]	ND[c]	ND[c]
2 (B1) - 2	1.0	13.2	27	-	-	-	-
2 (B1) - 3	3.0	38.9	81	ND	ND	ND	0.081
2 (B1) - 4	6.2	78.2	162	ND	ND	ND	0.080
2 (B1) - 5	9.0	110.2	229	< MDL	ND	ND	0.14
2 (B1) - 6	12.0	144.4	300	< MDL	ND	ND	0.16
2 (B1) - 7	15.0	174.7	362	< MDL	ND	ND	0.16
2 (B1) - 8	18.0	213.9	444	0.012	ND	ND	0.21
2 (B1) - 9	21.3	264.0	548	< MDL	ND	ND	0.21
2 (B1) - 10	23.0	304.0	631	0.011	ND	ND	0.20

TABLE 7-5. Continued.

Sample No. [C1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
2 (B1) - 11	27.0	342.6	711	< MDL	ND	ND	0.24
2 (B1) - 12	30.0	379.1	787	0.008	ND	ND	0.24
2 (B1) - 13	33.0	412.6	856	< MDL	ND	ND	0.22
2 (B1) - 14	36.4	454.5	943	0.013	ND	ND	0.27
2 (B1) - 15	39.0	479.3	995	ND	ND	ND	0.22
2 (B1) - 16	42.0	514.7	1,068	ND	ND	ND	0.26
2 (B1) - 17	45.0	548.1	1,137	-	-	-	-
2 (B1) - 18	48.0	583.2	1,210	0.011	< MDL	ND	0.28
2 (B1) - 19	51.1	609.9	1,265	0.012	ND	ND	0.15
2 (B1) - 20	54.0	646.5	1,341	0.017	0.015	ND	0.21
2 (B1) - 21	58.0	699.5	1,451	0.046	0.020	ND	0.31
2 (B1) - 22	59.0	708.0	1,469	0.082[c]	0.052[c]	ND[c]	0.26[c]
3 (C1) - 1	0.0	0.0	0	ND[c]	ND[c]	ND[c]	ND[c]
3 (C1) - 2	1.0	13.2	27	-	-	-	-
3 (C1) - 3	3.0	38.9	81	ND	ND	ND	0.055
3 (C1) - 4	6.2	78.2	162	ND	ND	ND	0.078
3 (C1) - 5	9.0	110.2	229	< MDL	ND	ND	0.087
3 (C1) - 6	12.0	144.4	300	< MDL	ND	ND	0.14
3 (C1) - 7	15.0	174.7	362	< MDL	ND	ND	0.13
3 (C1) - 8	18.0	213.9	444	< MDL	ND	ND	0.11
3 (C1) - 9	21.3	264.0	548	< MDL	ND	ND	0.15
3 (C1) - 10	23.0	304.0	631	< MDL	ND	ND	0.17
3 (C1) - 11	27.0	342.6	711	< MDL	ND	ND	0.19
3 (C1) - 12	30.0	379.1	787	0.015	ND	ND	0.18
3 (C1) - 13	33.0	412.6	856	< MDL	ND	ND	0.15
3 (C1) - 14	36.4	454.5	943	< MDL	ND	ND	0.17
3 (C1) - 15	39.0	479.3	995	0.011	ND	ND	0.17
3 (C1) - 16	42.0	514.7	1,068	ND	ND	ND	0.16
3 (C1) - 17	45.0	548.1	1,137	-	-	-	-
3 (C1) - 18	48.0	583.2	1,210	< MDL	ND	ND	0.18
3 (C1) - 19	51.1	609.9	1,265	< MDL	ND	ND	0.15
3 (C1) - 20	54.0	646.5	1,341	0.010	ND	ND	0.18
3 (C1) - 21	58.0	699.5	1,451	0.013	ND	ND	0.21
3 (C1) - 22	59.0	708.0	1,469	0.034[c]	ND[c]	ND[c]	0.16[c]
4 (D1) - 1	0.0	0.0	0	ND	ND	ND	ND
4 (D1) - 2	1.0	13.2	27	ND	ND	ND	0.013
4 (D1) - 3	3.0	38.9	81	ND	ND	ND	0.049[d]
4 (D1) - 4	6.2	78.2	162	ND	ND	ND	0.054[d]
4 (D1) - 5	9.0	110.2	229	< MDL	ND	ND	0.12[d]
4 (D1) - 6	12.0	144.4	300	< MDL	ND	ND	0.12[d]
4 (D1) - 7	15.0	174.7	362	< MDL	ND	ND	0.14[d]
4 (D1) - 8	18.0	213.9	444	< MDL	ND	ND	0.10[d]
4 (D1) - 9	21.3	264.0	548	< MDL	ND	ND	0.12[d]
4 (D1) - 10	23.0	304.0	631	< MDL	ND	ND	0.13[d]
4 (D1) - 11	27.0	342.6	711	< MDL	ND	ND	0.16[d]
4 (D1) - 12	30.0	379.1	787	< MDL	ND	ND	0.22[d]
4 (D1) - 13	33.0	412.6	856	0.016	ND	ND	0.16[d]
4 (D1) - 14	36.4	454.5	943	< MDL	ND	ND	0.14[d]
4 (D1) - 15	39.0	479.3	995	ND	ND	ND	0.12[d]
4 (D1) - 16	42.0	514.7	1,068	ND	ND	ND	0.16[d]
4 (D1) - 17	45.0	548.1	1,137	< MDL	ND	ND	0.16[d]
4 (D1) - 18	48.0	583.2	1,210	0.017	ND	ND	0.26[d]
4 (D1) - 19	51.1	609.9	1,265	< MDL	ND	ND	0.11[d]
4 (D1) - 20	54.0	646.5	1,341	ND	ND	ND	0.15[d]

TABLE 7-5. Concluded.

Sample No. [C1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
4 (D1) - 21	58.0	699.5	1,451	< MDL	ND	ND	0.21[d]
4 (D1) - 22	59.0	708.0	1,469	0.026	ND	ND	0.32[d]
4 (D1) - 22 - TE	Trace enrichment analysis			-	-	ND (< 0.23 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.
[b] Time-weighted averages.
[c] Analysis performed later in laboratory.
[d] Final effluent concentration exceeds criterion.

TABLE 7-6. Cycle C2 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [C2 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
0 (T1) - 1	0.0	0.0	N/A	45	6.7	0.15	58
0 (T1) - 2	4.0	43.7	N/A	49	6.9	0.14	66
0 (T1) - 3	9.0	100.2	N/A	52	7.6	0.13	71
0 (T1) - 4	14.8	186.2	N/A	57	8.4	0.14	80
0 (T1) - 5	20.3	269.3	N/A	59	8.7	0.14	83
0 (T1) - 6	22.0	293.8	N/A	59	9.4	0.15	83
0 (T1) - 7	25.0	334.1	N/A	59	9.4	0.13	83
0 (T1) - 8	28.0	384.4	N/A	59	9.4	0.15	82
0 (T1) - 9	30.5	420.8	N/A	59	9.3	0.16	82
0 (T1) - 10	33.5	465.0	N/A	59	9.5	0.13	82
0 (T1) - 11	35.0	486.7	N/A	-	-	-	-
0 (T1) - 12	36.0	499.7	N/A	60	9.7	0.14	86
Average influent concentration[b]				56	8.5	0.14	77
1 (B1) - 1	0.0	0.0	1,469	0.068	< MDL	ND	0.42
1 (B1) - 2	4.0	43.7	1,560	0.13	0.060	ND	0.35
1 (B1) - 3	9.0	100.2	1,677	0.84	0.27	ND	0.60
1 (B1) - 4	14.8	186.2	1,855	9.1	1.7	ND	4.8
1 (B1) - 5	20.3	269.3	2,028	22	3.7	0.0072	13
1 (B1) - 6	22.0	293.8	2,079	25	4.2	0.0051	14
1 (B1) - 7	25.0	334.1	2,162	29	4.9	0.015	17
1 (B1) - 8	28.0	384.4	2,267	40	6.5	0.024	29
1 (B1) - 9	30.5	420.8	2,342	42	7.0	0.030	32
1 (B1) - 10	33.5	465.0	2,434	45	7.4	0.032	34
1 (B1) - 11	35.0	486.7	2,479	47	7.6	0.037	37
1 (B1) - 12	36.0	499.7	2,506	47	7.7	0.039	38
2 (C1) - 1	0.0	0.0	1,469	0.046[c]	ND[c]	ND[c]	0.078[c]
2 (C1) - 2	4.0	43.7	1,560	-	-	-	-
2 (C1) - 3	9.0	100.2	1,677	< MDL	ND	ND	0.20
2 (C1) - 4	14.8	186.2	1,855	< MDL	ND	ND	0.23
2 (C1) - 5	20.3	269.3	2,028	0.031	0.012	ND	0.28
2 (C1) - 6	22.0	293.8	2,079	0.036	0.018	ND	0.33
2 (C1) - 7	25.0	334.1	2,162	0.043	0.018	ND	0.34
2 (C1) - 8	28.0	384.4	2,267	0.071	0.033	ND	0.30
2 (C1) - 9	30.5	420.8	2,342	0.15	0.066	ND	0.33
2 (C1) - 10	33.5	465.0	2,434	0.28	0.10	ND	0.41
2 (C1) - 11	35.0	486.7	2,479	-	-	-	-
2 (C1) - 12	36.0	499.7	2,506	0.48[c]	0.18[c]	ND[c]	0.37[c]

TABLE 7-6. Concluded.

Sample No. [C2 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
3 (D1) - 1	0.0	0.0	1,469	0.073[c]	ND[c]	ND[c]	0.05[c]
3 (D1) - 2	4.0	43.7	1,560	-	-	-	-
3 (D1) - 3	9.0	100.2	1,677	< MDL	ND	ND	0.18
3 (D1) - 4	14.8	186.2	1,855	< MDL	ND	ND	0.17
3 (D1) - 5	20.3	269.3	2,028	0.024	ND	ND	0.22
3 (D1) - 6	22.0	293.8	2,079	0.020	ND	ND	0.31
3 (D1) - 7	25.0	334.1	2,162	0.026	< MDL	ND	0.24
3 (D1) - 8	28.0	384.4	2,267	0.015	ND	ND	0.18
3 (D1) - 9	30.5	420.8	2,342	0.018	ND	ND	0.23
3 (D1) - 10	33.5	465.0	2,434	< MDL	ND	ND	0.19
3 (D1) - 11	35.0	486.7	2,479	-	-	-	-
3 (D1) - 12	36.0	499.7	2,506	0.046[c]	ND[c]	ND[c]	0.27[c]
4 (E1) - 1	0.0	0.0	0	ND	ND	ND	ND
4 (E1) - 2	4.0	43.7	91	ND	ND	ND	0.12[d]
4 (E1) - 3	9.0	100.2	208	< MDL	ND	ND	0.15[d]
4 (E1) - 4	14.8	186.2	386	< MDL	ND	ND	0.11[d]
4 (E1) - 5	20.3	269.3	559	0.020	ND	ND	0.22[d]
4 (E1) - 6	22.0	293.8	610	0.020	ND	ND	0.26[d]
4 (E1) - 7	25.0	334.1	693	0.020	ND	ND	0.26[d]
4 (E1) - 8	28.0	384.4	798	< MDL	ND	ND	0.16[d]
4 (E1) - 9	30.5	420.8	873	< MDL	ND	ND	0.21[d]
4 (E1) - 10	33.5	465.0	965	< MDL	ND	ND	0.19[d]
4 (E1) - 11	35.0	486.7	1,010	-	-	-	-
4 (E1) - 12	36.0	499.7	1,037	0.036[c,d]	ND	ND[c]	0.24[c,d]
4 (E1) - 12 - TE	Trace enrichment analysis			-	-	ND - (< 0.23 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
\- = Not analyzed or not available.

[a] Cumulative for specific column.
[b] Time-weighted averages.
[c] Analysis performed later in MRI laboratory.
[d] Final effluent concentration exceeds criterion.

TABLE 7-7. Cycle C3 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [C3 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
0 (T2) - 1	0.3	3.2	N/A	59	9.3	0.14	82
0 (T2) - 2	3.8	46.6	N/A	-	-	-	-
0 (T2) - 3	6.8	88.3	N/A	44	6.5	0.088	66
0 (T2) - 4	9.8	125.5	N/A	41	6.0	0.078	62
0 (T2) - 5	12.8	165.3	N/A	39	5.4	0.070	61
0 (T2) - 6	15.8	200.8	N/A	37	5.3	0.064	59
0 (T2) - 7	18.8	237.5	N/A	37	5.1	0.061	58
0 (T2) - 8	21.8	281.0	N/A	36	4.9	0.058	57
0 (T2) - 9	24.8	318.8	N/A	36	4.5	0.057	56
0 (T2) - 10	27.8	356.6	N/A	35	4.3	0.048	56
0 (T2) - 11	30.8	391.3	N/A	35	4.3	0.054	56
0 (T2) - 12	33.8	425.7	N/A	35	4.2	0.050	55
0 (T2) - 13	36.8	466.7	N/A	35	4.2	0.031	55
0 (T2) - 14	39.3	502.3	N/A	35	4.4	0.042	55
Average influent concentration[b]				39	5.4	0.067	61
1 (C1) - 1	0.3	3.2	2,513	0.15	0.058	ND	0.38
1 (C1) - 2	3.8	46.6	2,603	1.1[c]	0.30[c]	ND[c]	0.66[c]
1 (C1) - 3	6.8	88.3	2,689	2.8	0.63	ND	1.7
1 (C1) - 4	9.8	125.5	2,766	4.6	0.90	ND	2.3
1 (C1) - 5	12.8	165.3	2,849	6.0	1.0	ND	3.0
1 (C1) - 6	15.8	200.8	2,923	8.1	1.3	ND	4.0
1 (C1) - 7	18.8	237.5	2,999	11	1.7	ND	6.4
1 (C1) - 8	21.8	281.0	3,089	15	2.2	ND	9.6
1 (C1) - 9	24.8	318.8	3,167	17	3.4	ND	12
1 (C1) - 10	27.8	356.6	3,246	20	2.1	ND	14
1 (C1) - 11	30.8	391.3	3,318	21	2.8	0.0039	15
1 (C1) - 12	33.8	425.7	3,389	22	2.3	0.0044	16
1 (C1) - 13	36.8	466.7	3,474	26	3.1	0.0027	22
1 (C1) - 14	39.3	502.3	3,548	27	3.5	0.016	24
2 (D1) - 1	0.3	3.2	2,513	< MDL	ND	ND	0.22
2 (D1) - 2	3.8	46.6	2,603	-	-	-	-
2 (D1) - 3	6.8	88.3	2,689	< MDL	ND	ND	0.21
2 (D1) - 4	9.8	125.5	2,766	0.010	ND	ND	0.17
2 (D1) - 5	12.8	165.3	2,849	< MDL	ND	ND	0.13
2 (D1) - 6	15.8	200.8	2,923	0.0084	< MDL	ND	0.23
2 (D1) - 7	18.8	237.5	2,999	< MDL	ND	ND	0.19
2 (D1) - 8	21.8	281.0	3,089	< MDL	ND	ND	0.19
2 (D1) - 9	24.8	318.8	3,167	0.014	0.0088	ND	0.16
2 (D1) - 10	27.8	356.6	3,246	< MDL	< MDL	ND	0.14
2 (D1) - 11	30.8	391.3	3,318	< MDL	ND	ND	0.18
2 (D1) - 12	33.8	425.7	3,389	0.020	0.013	ND	0.14
2 (D1) - 13	36.8	466.7	3,474	0.039	0.021	ND	0.19
2 (D1) - 14	39.3	502.3	3,548	0.079	0.016	ND	0.34

TABLE 7-7. Concluded.

Sample No. [C3 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
3 (E1) - 1	0.3	3.2	1,044	< MDL	ND	ND	0.18
3 (E1) - 2	3.8	46.6	1,134	-	-	-	-
3 (E1) - 3	6.8	88.3	1,220	0.012	ND	ND	0.18
3 (E1) - 4	9.8	125.5	1,297	< MDL	ND	ND	0.14
3 (E1) - 5	12.8	165.3	1,380	0.0088	ND	ND	0.13
3 (E1) - 6	15.8	200.8	1,454	< MDL	ND	ND	0.16
3 (E1) - 7	18.8	237.5	1,530	< MDL	ND	ND	0.14
3 (E1) - 8	21.8	281.0	1,620	< MDL	ND	ND	0.14
3 (E1) - 9	24.8	318.8	1,698	< MDL	ND	ND	0.15
3 (E1) - 10	27.8	356.6	1,777	< MDL	ND	ND	0.090
3 (E1) - 11	30.8	391.3	1,849	< MDL	ND	ND	0.12
3 (E1) - 12	33.8	425.7	1,920	0.0098	ND	ND	0.10
3 (E1) - 13	36.8	466.7	2,005	< MDL	ND	ND	0.13
3 (E1) - 14	39.3	502.3	2,079	< MDL	ND	ND	0.29
4 (A2) - 1	0.3	3.2	7	0.0083	ND	ND	0.025
4 (A2) - 2	3.8	46.6	97	-	-	-	-
4 (A2) - 3	6.8	88.3	183	< MDL	ND	ND	0.12[d]
4 (A2) - 4	9.8	125.5	260	0.0076	ND	ND	0.12[d]
4 (A2) - 5	12.8	165.3	343	< MDL	ND	ND	0.10[d]
4 (A2) - 6	15.8	200.8	417	0.021	ND	ND	0.23[d]
4 (A2) - 7	18.8	237.5	493	< MDL	ND	ND	0.17[d]
4 (A2) - 8	21.8	281.0	583	0.014	ND	ND	0.18[d]
4 (A2) - 9	24.8	318.8	661	< MDL	ND	ND	0.11[d]
4 (A2) - 10	27.8	356.6	740	< MDL	ND	ND	0.084[d]
4 (A2) - 11	30.8	391.3	812	0.016	ND	ND	0.16[d]
4 (A2) - 12	33.8	425.7	883	< MDL	ND	ND	0.17[d]
4 (A2) - 13	36.8	466.7	968	< MDL	ND	ND	0.15[d]
4 (A2) - 14	39.3	502.3	1,042	< MDL	ND	ND	0.26[d]
4 (A2) - 14 - TE	Trace enrichment analysis			-	-	ND (< 0.23 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.

[b] Time-weighted averages.

[c] Analysis performed later in MRI laboratory.

[d] Final effluent concentration exceeds criterion.

TABLE 7-8. Cycle C4 Results -- Four-in-Series GAC Column Test Using Witco Witcarb 950.

Sample No. [C4 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
0 (T1) - 1	0.3	3.2	N/A	35	4.8	0.029	55[f]
0 (T1) - 2	8.8	131.7	N/A	94	13	0.21	130[f]
0 (T1) - 3	11.3	166.6	N/A	100	13	0.27	130[f]
0 (T1) - 4	14.3	206.6	N/A	100	14	0.24	130[f]
0 (T1) - 5	17.0	244.5	N/A	100	14	0.23	130[f]
0 (T1) - 6	19.6	280.0	N/A	96	13	-	130[f]
Average influent concentration[b,c]				91	13	0.21	120[f]
1 (D1) - 1	0.3	3.2	3,555	0.23	0.098	ND	0.47
1 (D1) - 2	8.8	131.7	3,821	11	2.3	ND	5.3
1 (D1) - 3	11.3	166.6	3,894	24	4.1	ND	11
1 (D1) - 4	14.3	206.6	3,977	42	7.8	ND	24
1 (D1) - 5	17.0	244.5	4,055	56	8.0	0.032	37
1 (D1) - 6	19.6	280.0	4,129	66	9.1	g	46
2 (E1) - 1	0.3	3.2	2,086	0.039[d]	ND[d]	ND[d]	0.19[d]
2 (E1) - 2	8.8	131.7	2,352	0.052[d]	ND[d]	ND[d]	0.33[d]
2 (E1) - 3	11.3	166.6	2,425	-	-	-	-
2 (E1) - 4	14.3	206.6	2,508	0.066[d]	0.032[d]	ND[d]	0.40[d]
2 (E1) - 5	17.0	244.5	2,586	-	-	-	-
2 (E1) - 6	19.6	280.0	2,660	0.12[d]	0.066[d]	ND[d]	0.38[d]
3 (A2) - 1	0.3	3.2	1,049	0.044[d]	ND[d]	ND[d]	0.15[d]
3 (A2) - 2	8.8	131.7	1,315	0.040[d]	ND[d]	ND[d]	0.24[d]
3 (A2) - 3	11.3	166.6	1,388	-	-	-	-
3 (A2) - 4	14.3	206.6	1,471	0.052[d]	ND[d]	ND[d]	0.24[d]
3 (A2) - 5	17.0	244.5	1,549	-	-	-	-
3 (A2) - 6	19.6	280.0	1,623	0.048[d]	ND[d]	ND[d]	0.22[d]
4 (B2) - 1	0.3	3.2	7	0.036[d,e]	ND[d]	ND[d]	-[h]
4 (B2) - 2	8.8	131.7	273	0.069[e]	0.021	ND	0.16[e]
4 (B2) - 3	11.3	166.6	346	0.049[d,e]	ND[d]	ND[d]	-[h]
4 (B2) - 4	14.3	206.6	429	0.072[d,e]	ND[d]	ND[d]	-[h]
4 (B2) - 5	17.0	244.5	507	0.039[e]	ND	ND	0.30[e]
4 (B2) - 6	19.6	280.0	581	0.036[d,e]	ND[d]	ND[d]	0.18[e,h]
4 (B2) - 6 - TE	Trace enrichment analysis			-	-	ND (< 0.23 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.

[b] Time-weighted averages.

[c] Arbitrarily adjusted time-weighting so first interval is equivalent to 3 hr instead of 8.5 hr to avoid undue weighting to startup values, presumably low due to carryover from previous test cycle.

[d] Analysis performed later in MRI laboratory.

[e] Final effluent concentration exceeds criterion.

[f] Value derived from analyses of first sample and composite sample.

[g] Too poorly resolved to quantitate.

[h] Analyzed later in laboratory. Results were 0.092, ND, 0.036, and 0.015 for Sample Nos. 1, 3, 4, and 6, respectively. These values were suspect and were not used for data analysis.

TABLE 7-9. Cycle F1 Results -- Four-in-Series GAC Column Test Using Calgon Filtrasorb 300.

Sample No. [F1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L)			
				RDX	HMX	2,4-DNT	TNT
0 (T2) - 1	0.0	0.0	N/A	93	12	-	91
0 (T2) - 2	1.5	26.0	N/A	80	11	0.16	58
0 (T2) - 3	3.5	59.7	N/A	66	8.8	-	-
0 (T2) - 4	5.5	95.9	N/A	59	8.7	0.12	87
0 (T2) - 5	7.5	131.4	N/A	-	-	-	-
0 (T2) - 6	9.5	163.4	N/A	49	7.1	0.093	78
0 (T2) - 7	11.5	193.9	N/A	-	-	-	-
0 (T2) - 8	13.5	226.4	N/A	43	6.3	0.083	71
0 (T2) - 9	15.5	261.3	N/A	43	6.4	0.081	72
0 (T2) - 10	17.5	293.8	N/A	42	6.1	0.063	71
0 (T2) - 11	19.5	330.1	N/A	43	6.4	0.066	75
0 (T2) - 12	21.5	365.9	N/A	40	5.7	0.043	67
Average influent concentration[b]				53	7.6	0.094	75
1 (A1) - 1	0.0	0.0	0	0.72	0.095	ND[c]	0.34[c]
1 (A1) - 2	1.5	26.0	72	1.4	0.10	ND	0.85
1 (A1) - 3	3.5	59.7	166	4.3	0.45	ND	1.7[c]
1 (A1) - 4	5.5	95.9	267	11	1.2	-	5.6
1 (A1) - 5	7.5	131.4	365	16[c]	1.6[c]	ND[c]	7.4[c]
1 (A1) - 6	9.5	163.4	454	20	2.1	ND	12
1 (A1) - 7	11.5	193.9	539	23[c]	2.5[c]	ND[c]	14[c]
1 (A1) - 8	13.5	226.4	630	26	3.3	0.021	19
1 (A1) - 9	15.5	261.3	727	29	3.8	0.021	26
1 (A1) - 10	17.5	293.8	817	31	4.0	0.020	25
1 (A1) - 11	19.5	330.1	918	32	4.3	0.019	31
1 (A1) - 12	21.5	365.9	1,018	32	4.3	0.019	32
2 (B1) - 1	0.0	0.0	0	0.029[c]	ND[c]	ND[c]	ND[c]
2 (B1) - 2	1.5	26.0	72	-	-	-	-
2 (B1) - 3	3.5	59.7	166	0.045[c]	ND[c]	ND[c]	0.32[c]
2 (B1) - 4	5.5	95.9	267	-	-	-	-
2 (B1) - 5	7.5	131.4	365	-	-	-	-
2 (B1) - 6	9.5	163.4	454	0.27[c]	0.044[c]	ND[c]	0.35[c]
2 (B1) - 7	11.5	193.9	539	-	-	-	-
2 (B1) - 8	13.5	226.4	630	-	-	-	-
2 (B1) - 9	15.5	261.3	727	1.6[c]	0.16[c]	ND[c]	0.68[c]
2 (B1) - 10	17.5	293.8	817	-	-	-	-
2 (B1) - 11	19.5	330.1	918	-	-	-	-
2 (B1) - 12	21.5	365.9	1,018	5.2	0.50	-	2.1

TABLE 7-9. Concluded.

Sample No. [F1 -]	Test time (hr)	Volume wastewater (gal.)	No. of bed volumes[a]	Concentration (mg/L) RDX	HMX	2,4-DNT	TNT
3 (C1) - 1	0.0	0.0	0	ND[c]	ND[c]	ND[c]	ND[c]
3 (C1) - 2	1.5	26.0	72	-	-	-	-
3 (C1) - 3	3.5	59.7	166	0.032[c]	ND[c]	ND[c]	ND[c]
3 (C1) - 4	5.5	95.9	267	-	-	-	-
3 (C1) - 5	7.5	131.4	365	-	-	-	-
3 (C1) - 6	9.5	163.4	454	0.028[c]	ND[c]	ND[c]	0.18[c]
3 (C1) - 7	11.5	193.9	539	-	-	-	-
3 (C1) - 8	13.5	226.4	630	-	-	-	-
3 (C1) - 9	15.5	261.3	727	0.052[c]	ND[c]	ND[c]	0.20[c]
3 (C1) - 10	17.5	293.8	817	-	-	-	-
3 (C1) - 11	19.5	330.1	918	-	-	-	-
3 (C1) - 12	21.5	365.9	1,018	0.032	-	-	0.28
4 (D1) - 1	0.0	0.0	0	0.022	ND	ND	0.037
4 (D1) - 2	1.5	26.0	72	0.070[d]	ND	ND	0.14[d]
4 (D1) - 3	3.5	59.7	166	0.088[d]	< MDL	ND	0.19[d]
4 (D1) - 4	5.5	95.9	267	0.20[d]	0.041[d]	ND	0.48[d]
4 (D1) - 5	7.5	131.4	365	0.24[c,d]	0.065[c,d]	ND[c]	0.31[c,d]
4 (D1) - 6	9.5	163.4	454	0.16[d]	0.027	ND	0.40[d]
4 (D1) - 7	11.5	193.9	539	-	-	-	-
4 (D1) - 8	13.5	226.4	630	0.060[d]	< MDL	ND	0.31[d]
4 (D1) - 9	15.5	261.3	727	-	-	-	-
4 (D1) - 10	17.5	293.8	817	0.023	ND	ND	0.15[d]
4 (D1) - 11	19.5	330.1	918	-	-	-	-
4 (D1) - 12	21.5	365.9	1,018	0.030	ND[c]	ND[c]	0.28[c,d]
4 (D1) - 12 - TE	Trace enrichment analysis			-	-	ND (< 0.23 μg/L)	-

NOTE: ND = Not detected.
< MDL = Detected, but less than minimum detectable level.
N/A = Not applicable.
- = Not analyzed or not available.

[a] Cumulative for specific column.
[b] Time-weighted averages.
[c] Analysis performed later in MRI laboratory.
[d] Final effluent concentration exceeds criterion.

TABLE 7-10. Carbon Loading Rates by Test Cycle and Nitrobody.

Test	Compound	Cycle	Cumulative carbon loading by Column No. (lb/ 100 lb)						
			A1	B1	C1	D1	E1	A2	B2
A	RDX	A1	7.57	8.23	3.64	0.105	-	-	-
	HMX	A1	0.870	1.01	0.445	0.022	-	-	-
	DNT	A1	0.015	0.002	0.000	0.000	-	-	-
	TNT	A1	16.1	12.4	2.86	0.042	-	-	-
	TOTAL	A1	24.5	21.6	6.94	0.168	-	-	-
B	RDX	B1	8.14	4.27	0.097	0.000	-	-	-
		B2	-	4.76	3.54	0.081	0.005	-	-
		Total	8.14	9.03	3.64	0.081	0.005	-	-
	HMX	B1	1.02	0.635	0.023	0.000	-	-	-
		B2	-	0.655	0.567	0.034	0.004	-	-
		Total	1.02	1.29	0.590	0.034	0.004	-	-
	DNT	B1	0.020	0.003	0.000	0.000	-	-	-
		B2	-	0.021	0.002	0.000	0.000	-	-
		Total	0.020	0.024	0.002	0.000	0.000	-	-
	TNT	B1	17.5	4.67	0.063	0.012	-	-	-
		B2	-	10.2	2.87	0.049	0.013	-	-
		Total	17.5	14.8	2.93	0.061	0.013	-	-
	TOTAL	B1	26.6	9.57	0.184	0.012	-	-	-
		B2	-	15.6	6.98	0.164	0.022	-	-
		Total	26.6	25.2	7.16	0.176	0.022	-	-
C	RDX	C1	9.39	2.78	0.002	0.000	-	-	-
		C2	-	9.06	5.14	0.014	0.003	-	-
		C3	-	-	6.84	3.21	0.002	(0.001)[a]	-
		C4	-	-	-	8.35	3.38	0.002	(0.002)
		Total	9.39	11.8	12.0	11.6	3.39	0.002	0.002
	HMX	C1	1.28	0.424	0.001	0.000	-	-	-
		C2	-	1.30	0.863	0.007	0.000	-	-
		C3	-	-	0.929	0.449	0.001	0.000	-
		C4	-	-	-	1.05	0.584	0.002	(0.001)
		Total	1.28	1.72	1.79	1.50	0.585	0.002	(0.001)
	DNT	C1	0.033	0.001	0.000	0.000	-	-	-
		C2	-	0.033	0.003	0.000	0.000	-	-
		C3	-	-	0.017	0.000	0.000	0.000	-
		C4	-	-	-	0.025	0.001	0.000	0.000
		Total	0.033	0.034	0.020	0.026	0.001	0.000	0.000
	TNT	C1	17.8	1.91	0.020	0.002	-	-	-
		C2	-	16.2	3.46	0.018	0.007	-	-
		C3	-	-	13.2	2.22	0.010	0.002	-
		C4	-	-	-	13.9	2.01	0.015	0.012
		Total	17.8	18.2	16.7	16.2	2.02	0.017	0.012
	TOTAL	C1	28.5	5.11	0.022	0.002	-	-	-
		C2	-	26.6	9.47	0.039	0.010	-	-
		C3	-	-	21.0	5.88	0.013	0.002	-
		C4	-	-	-	23.4	5.97	0.020	0.009
		Total	28.5	31.7	30.5	29.3	6.00	0.022	0.009
F	RDX	F1	6.35	b	b	b	-	-	-
	HMX	F1	0.978	b	b	b	-	-	-
	DNT	F1	0.017	b	b	b	-	-	-
	TNT	F1	11.2	b	b	b	-	-	-
	TOTAL	F1	18.5	b	b	b	-	-	-

NOTE: - = Not applicable.

[a] Parentheses indicate negative value.

[b] Not determined.

8. ECONOMIC ANALYSIS

8.1 SCOPE

This section presents limited cost information that would be helpful in designing GAC systems to meet more stringent discharge levels. Direct operating costs, including GAC cost and power cost, have been projected for full-scale systems under various operating scenarios. Other operating costs, such as labor, maintenance, GAC regeneration, and capital cost considerations, are discussed conceptually, but no cost estimates have been made. Detailed engineering plans and specifications for actual plants would be needed for a thorough economic analysis, and these were not available. However, the information presented should provide a good starting point for a more detailed cost analysis.

8.2 OPERATING COSTS

8.2.1 Increased Cost of Meeting More Stringent Discharge Levels

Direct operating costs have been projected for two types of full-scale GAC systems: (1) those capable of meeting current discharge levels; and (2) those capable of meeting much more stringent discharge levels. Costs were calculated for both GAC use and for power consumption. These estimates are based upon data reported in Section 7 and upon manufacturers' curves for pressure drops. (The field data for pressure drop were not thought to be reliable for scale-up.) Numerous assumptions have been made and are documented accordingly.

8.2.1.1 GAC Cost. The cost of replacing GAC is by far the overriding operating expense. It was assumed that all GAC would be virgin. However, regeneration may be warranted if the more stringent discharge levels are adopted and if the pink water generation rate is sufficiently high. The costs of regeneration and carbon loss would need to be factored into the GAC costs in that case.

The GAC costs were based upon field data from Test Series C, a four-cycle test sequence involving Witco Witcarb 950 GAC and an average hydraulic loading rate of 4.4 GPM/ft^2. The effluent quality from the four carbon columns was generally sufficient to meet the proposed limit of 0.03 mg/L for either RDX or HMX. This level was completely met on a time-averaged basis. As discussed earlier, however, TNT levels greatly exceeded the proposed level of 0.04 mg/L. Concentrations of TNT were always less than 0.5 mg/L and usually below 0.3 mg/L. It was assumed for the cost analysis that these levels were the best achievable in a well-designed full-scale system.

A configuration of three carbon columns in series seems to be sufficient to meet the proposed limit for RDX or HMX, although more columns may be required at higher hydraulic loading rates. As a design safety factor, it was assumed that four columns in series would be needed.

Costs were determined for three different scenarios, as defined below:

Scenario	Requirements	No. of columns
A	Meets current discharge standards (1.0 mg/L RDX, HMX, or TNT)	1
B	Meets current discharge standards (1.0 mg/L RDX, HMX, or TNT)	2
C	Meets proposed discharge standards (0.03 mg/L RDX or HMX, 0.3 mg/L TNT)	4

Scenario A would meet the current discharge standards with only a single GAC column. The column would always start with fresh GAC, and when breakthrough occurred, the GAC would be discarded and replaced. Scenario B would meet the same standards, but would use two columns in series, so that the leading column can become saturated with pollutants prior to rotation. Scenario C uses four columns in series to meet the more stringent effluent standards. Regardless of the number of columns used for treatment, however, there should be at least one column on standby, an important factor for capital costs.

Current discharge standards vary by site and by state NPDES permit levels. It was assumed that 1.0 mg/L maximum level of any nitrobody would represent current requirements. For proposed discharge standards it was assumed that RDX or HMX would remain below 0.03 mg/L on a time-averaged basis, while average TNT levels would remain below 0.3 mg/L. Presumably, the 2,4-DNT limit of 0.0007 mg/L would be net, but insufficient data are available to strongly support that premise.

Full-scale GAC columns currently in use typically contain 900 lb GAC. Based upon the dimensions of the carbon bed used for pilot tests, a full-scale system was conceptually designed to perform the economic analysis. The specifications are shown below.

Full-Scale Column Specifications

Length/diameter ratio for GAC bed = 5.25
Diameter = 2 ft
Length = 10.5 ft
Total length (including 2 ft freeboard) = 12.5 ft
Volume = 33 ft^3
GAC weight--Witco Witcarb 950 = 1,023 lb
--Calgon Filtrasorb 300 = 875 lb

It is assumed that the column will operate in an upflow, packed bed configuration. The bed weights were calculated using the midpoint of manufacturer reported ranges of bulk density ("apparent density of 29 to 33 lb/ft^3" for Witcarb 950; "backwashed and settled bulk density of 26 to 27 lb/ft^3" for Filtrasorb 300).

Carbon utilization rates were determined on the basis of pink water volume. However, due to the variations in nitrobody concentration it is difficult to compare one test cycle to another. The data were therefore normalized according to "average" pink water characteristics. Time-weighted average concentrations of influent pink water over the entire sequence of "C" tests are shown below.

	Test cycle				
	C1	C2	C3	C4	Average
Time (hr)	59.0	36.0	39.3	19.6	-
Concentration (mg/L)					
RDX	34	56	39	91	47.7
HMX	4.7	8.5	5.4	13	6.8
RDX/HMX	38.7	64.5	44.4	104	54.5
2,4-DNT	0.094	0.14	0.067	0.21	0.11
TNT	55	77	61	120	70

Breakthrough curves in Section 7 show that RDX and HMX exhaust GAC adsorptive capacity nearly simultaneously, well ahead of TNT or DNT. The combined level of RDX and HMX is apparently the main limiting factor affecting GAC utilization, although TNT concentration is probably important as well. The average combined RDX and HMX level for this test series was 55 mg/L, or 0.45 lb/1,000 gal. The breakthrough volumes were normalized using the average RDX/HMX concentration and the concentrations for each test cycle, as shown in Table 8-1.

When the data are normalized, there is little difference in carbon utilization rates, although cycle C3 seems somewhat out of line with the other cycles. One would expect to see a trend of increasing utilization (decreasing breakthrough volumes) as the system goes from all virgin carbon at startup to progressively more prior history in the leading column. However, results in Section 7 showed that little loading occurs except in the first and second columns. Thus, it is not surprising that the values in Table 8-1 are fairly close.

The average carbon utilization rate for cycles C1 to C4 (3.2 lb/1,000 gal) was used to compute carbon costs for scenario C. The figure is close to the normalized value for cycle C4, which represents operating data for a stabilized, four column in series system. Cycle C2 represents a two column in series system that meets existing standards. Effluent from the second column easily met existing standards for RDX, HMX, and TNT, and the breakthrough volume in the first column models a stabilized, two column system. The utilization rate for cycle C2 was 2.8 lb/1,000 gal., but since this did not appear to be significantly different than in cycle C4, the average value of 3.2 lb/1,000 gal was used to calculate GAC costs for scenario B as well.

Although it may at first seem odd that GAC would be utilized at the same rate (3.2 lb/1,000 gal.) to meet either current standards (Scenario B) or proposed standards (Scenario C), it must be remembered that the operating systems are quite different, with a four in series system being much more costly to install and maintain than a two in series system.

The GAC utilization rate for scenario A was determined by using data for cycle C1, where the lead column is filled with virgin GAC. To simulate a single column system, it was assumed that breakthrough occurred when 1.0 mg/L was exceeded for any pollutant. In cycle C1, this occurred at 21.3 hr, or a breakthrough volume of 264 gal., when the column 1 effluent contained 1.1 mg/L RDX and 0.91 mg/L TNT. The normalized GAC utilization rate was determined in the same manner as for the other cycles.

Costs were projected for the three scenarios described previously. Carbon usage and costs are presented below in several units.

GAC Costs

Scenario	No. of columns	GAC util. (lb/1,000 gal.)	GAC util. (lb/day)	Average breakthrough time (days)	GAC cost ($/1,000 gal.)	GAC cost ($/day)
A	1	8.7	173	5.9	7.90	157
B	2	3.2	64	16	2.90	58
C	4	3.2	64	16	2.90	58

The breakthrough times and daily costs assume a carbon bed weight of 1,020 lb and a hydraulic loading rate of 4.4 gpm/ft^2, or a flowrate of 13.8 gpm (19,900 gal/day). The cost is based upon $0.91/lb for Witcarb 950 (as of January 1985).

8.2.1.2 Power Cost. The cost of electrical power consumed in operating a pump was estimated for the same three scenarios. This cost is very minor in comparison to the GAC cost. It is based upon pressure heads for pumping pink water through GAC beds as well as ancillary equipment. Information on pressure heads is presented to help specify a pump for design of a full-scale system. Manufacturer's curves on pressure heads were used, and typical resistance factors for various components were obtained from other sources.[6,10] The equation for converting to electrical power is:[7]

$$\text{kW} = \frac{0.75 \times \text{gpm} \times \text{psi}}{1{,}714 \times e}$$

where e is the combined pump and motor efficiency.

It was assumed that the pump efficiency is 60% and the electric motor efficiency is 75%, for a combined efficiency of 45% ($e = 0.45$). The cost of electricity was assumed to be $0.08/kW-hr. The flowrate was assumed to be 13.8 gpm. Pressure heads were converted from feet of water to psi by dividing by 2.31.

The manufacturer's curves for Witcarb 940, 18 x 40 mesh, show a head loss of 5.2 in. W.C./ft bed depth for 4.4 gpm/ft^3 and 68°F. For a bed depth of 10.5 ft, the head loss is thus 4.6 ft W.C. per column.

Resistance coefficients (K) were calculated based upon assumed components. The "K" values were then summed and converted into pressure heads. The assumed components for determining head losses are listed below. A prefilter should be included as well, but no information on pressure drops was available for diatomaceous earth filters.

Head losses	
Ancillary equipment	Each GAC column
• 100 ft, 1-1/2 in. Schedule 40 steel pipe	• 25 ft, 1-1/2 in. Schedule 40 steel pipe
• 2 diaphragm valves	• 1 diaphragm valve
• 4 standard 90 degree elbows	• 2 standard 90 degree elbows
• disk-type flowmeter	• 3 tees, with flow through branch
• exit loss	• entrance loss
	• exit loss

Pumping costs were estimated based upon the preceding information. This is summarized in Table 8-2. A 6 ft elevation between the pump and the discharge point was assumed.

8.2.1.3 Other Operating Costs. In addition to GAC replacement, other operating costs are important factors. The cost of labor and maintenance will vary according to configuration and complexity of the treatment system. If regeneration is used, it will impact overall operational costs considerably. These factors are briefly discussed below.

The greater the number of columns in series, the greater the number of components that will need to be maintained or replaced periodically. To properly assess performance, multiple column systems require more attention. For example, additional samples may need to be taken and more instruments must be read, with impact on labor costs for operators, analytical chemists and technicians, and facility engineers. All of these factors should be addressed in a thorough economic analysis.

If a regeneration system is installed, it will help to offset the GAC costs, but the operating costs must be factored in as well. If it is a thermal process, the fuel costs may be a large cost item. The regeneration process is not 100% efficient in terms of either quantity (recovery) or quality (adsorptive capacity). These efficiency factors must be known and factored in as well.

The estimated GAC utilization rates alone do not seem to make a strong case for regeneration. The amount of GAC used may not be greatly affected. However, capital costs for the increasing number of columns would be significant.

8.2.2 Cost Comparison of Different GAC Types

Field tests B and F were performed under similar conditions (nominally 6 gpm/ft^2 hydraulic loading rate and 11-3/4 in. bed depth), but used two GAC types (Witco Witcarb 950 and Calgon Filtrasorb 300, respectively). Effluent quality for cycle F1 was poorer than for cycle B1, but since the influent was more concentrated in cycle F1, direct comparison is difficult. A comparison of treatment costs was performed to see if any cost advantages exist when using a different GAC than is normally used. This is summarized in Table 8-3.

There are no dramatic differences in either GAC utilization or cost between the two types, although the Calgon product seems to be slightly less cost-efficient. Pumping costs would be less for the Calgon product due to lower pressure heads (1.7 in. W.C./ft bed depth versus 5.2 in. W.C./ft bed depth), but since pumping costs were shown in Section 8.2.1.2 to be minor compared to GAC replacement, these costs were not projected.

A rigorous series of comparative tests would be needed to determine if either product has cost advantages over the other. Other factors may be more important in the long run. For instance, Witcarb is a petroleum coke-based product, and is harder and less susceptible to attrition than Filtrasorb and other bituminous coal-based products. It may be easier to handle (less dusty) and experience less loss if regenerated. These factors should be evaluated in further testing.

8.3 CAPITAL COSTS

To effectively meet more stringent discharge standards, additional columns in series will be required. This will have a tremendous impact on capital costs, and upon siting costs as well. The economic analysis on GAC utilization rates suggest that although overall GAC consumption may not be higher, the amount of GAC in the treatment system will be much higher in order to achieve longer contact time. For testing and comparative purposes, it has been assumed that a four in series configuration will be used. However, another available option is a pulsed bed system with much greater GAC capacity than would be needed for the current standards.

Assuming that multiple column systems will be used and using Scenario B and C, at least two additional columns would be required to meet the more stringent standards. With one column available on standby, this would mean switching from three columns to five columns, so the cost of the columns, fittings, piping, valves, and so forth would be multiplied by a factor of 5/3. Siting and space requirements would be affected as well. All of these factors should be examined on a site-specific basis. Some sites may have available spare columns not currently in use and sufficient existing space. On the other hand, a completely redesigned treatment facility may be required at some plants.

8.4 SUMMARY OF ECONOMIC ANALYSIS

Based upon this economic analysis, it is expected that meeting proposed, more stringent standards of 0.03 mg/L for RDX or HMX and 0.3 mg/L for TNT will increase carbon usage costs by approximately $0.00 to $5.00/1,000 gal. and pumping costs by $0.007 to $0.009/1,000 gal. Changing GAC type from that currently used may offer limited cost advantages. These are very general cost estimates with many assumed conditions. If more precise cost estimates are required, they would need to be made for individual, site-specific designs.

Capital costs would be increased dramatically to meet the more stringent standards. Detailed engineering design data are required to accurately estimate capital costs.

Although not considered in this economic analysis, the increased costs of chemical analysis for monitoring lower effluent concentrations may be an important factor. The lower detection levels needed, particularly for 2,4-DNT, may require additional laboratory equipment and more labor intensive operations for sample preparation.

TABLE 8-1. Carbon Utilization Rates.

Cycle	Actual breakthrough vol. (gal.)	Actual GAC util.[a] (lb/1,000 gal.)	RDX/HMX conc.[b] (mg/L)	Normalized breakthrough[c] vol. (gal.)	Normalized GAC util.[a] (lb/1,000 gal.)
C1	708	2.3	39	503	3.3
C2	500	3.3	65	592	2.8
C3	502	3.3	44	409	3.9
C4	280	5.9	104	534	3.1
Average[d]	-	-	-	-	3.2
C1-A[e]	264	6.2	39	187	8.7

---

[a] Weight of carbon bed = 1.64 lb.

[b] Combined time-weighted average influent concentrations of RDX and HMX.

[c] Normalized volume = actual volume x $\frac{\text{RDX/HMX Conc.}}{\text{55 mg/L}}$

[d] Average GAC utilization for all four cycles, adjusting for normalized breakthrough volume.

[e] Assuming breakthrough of ≥ 1.0 mg/L nitrobody (single column operation).

TABLE 8-2. Pumping Costs.

	Scenario A	Scenario B	Scenario C
Number of columns	1	2	4
Total bed depth (ft)	10.5	21	42
Head loss, ancillary equipment (ft W.C.)	2.57	2.57	2.57
Head loss, column equipment (ft W.C.)	0.85	1.69	3.38
Head loss, GAC[a] (ft W.C.)	4.55	9.10	18.20
Elevation (ft W.C.)	6.00	6.00	6.00
Total head loss--(ft W.C.)	13.97	19.36	30.15
--(psi)	6.05	8.38	13.05
Power (W)	81.2	112	175
kW-hr/day	1.95	2.70	4.20
Cost[b] ($/day)	0.16	0.22	0.34
Cost[b,c] ($/1,000 gal.)	0.008	0.011	0.017

---

[a] Witco Witcarb 950; hydraulic loading rate of 4.4 gpm/ft².
[b] Assumes $0.08/kW-hr
[c] Assumes 19,900 gal/day.

TABLE 8-3. Comparison of Carbon Utilization Rates and Costs for Two GAC Types.

	W950	F300
Test cycle	B1	F1
Hydraulic loading rate (gpm/ft^2)	6.5	5.8
Measured GAC weight per column (lb)	1.18	1.62
Breakthrough volume (gal.)	510	366
Actual GAC utilization (lb/1,000 gal.)	2.3	4.4
RDX/HMX concentration[a] (mg/L)	38.6	60.6
Normalized breakthrough volume (gal.)	361	407
Normalized GAC util. (lb/1,000 gal.)	3.3	4.0
GAC cost ($/lb)	0.91	0.89
GAC cost ($/1,000 gal.)	3.00	3.60

---

[a] Combined RDX and HMX concentrations.

9. CONCLUSIONS AND RECOMMENDATIONS

This research program was geared towards providing quantitative data on the capability of GAC to remove the nitrobodies TNT, 2,4-DNT, RDX, and HMX from pink water under typical AAP conditions. This objective was achieved through a multiphase study which included preliminary GAC screening, isotherm tests, preliminary column tests, four in series column tests, and an economic analysis. Conclusions arising from each of these phases are summarized in this section. Recommendations for further study are also provided.

9.1 PRELIMINARY GAC SCREENING

Property data from manufacturers and literature references were used to screen nine different GACs potentially useful for treating pink water. Five of these were selected for isotherm testing based upon the criteria of surface area, pore volume, iodine number, mean particle diamter, popular use, pressure drop, and manufacturers' recommendations. The GACs selected from this screening were Calgon Fitrasorb in the 200, 300, and 400 grades; Westvaco Nuchar WV-G; and Witco Witcarb 950.

9.2 ISOTHERM TESTS

Isotherm tests were used to select the best performing GAC for subsequent column testing and to study temperature and compositional effects.

The best performing GAC was consistently Witco Witcarb 950. The ranking of other GACs was not as well defined; the best to worst ranking appears to be Witcarb 950, Nuchar WV-G, Filtrasorb 400, Filtrasorb 300, and Filtrasorb 200.

The isotherm tests indicated that with a high enough carbon dosage equilibrium conditions can reach the desired effluent limits of 0.04 mg/L for TNT, 0.03 mg/L for RDX and HMX, and 0.0007 mg/L for 2,4-DNT. The highest carbon loading or q_e levels were obtained for TNT, followed by RDX, HMX, and 2,4-DNT.

The isotherms were nonlinear in the regions of minimum and maximum carbon dosage, particularly when all four compounds were present. Test results from varying pink water composition indicate that competitive adsorption occurs. The presence of TNT and DNT markedly reduces the adsorption of RDX and HMX, but RDX and HMX only slightly impede the adsorption of TNT and DNT.

Tests were conducted over a temperature range of 40° to 120°F, representing normal variation expected at AAPs. Temperature effects were not large enough to justify performing column tests at varying temperatures. However, results did indicate that higher temperatures do somewhat improve adsorption of TNT and DNT, whereas RDX and HMX adsorption is decreased.

Comparison tests between synthetic and actual pink water generally showed little difference in adsorption, increasing the validity of the isotherm tests performed with laboratory prepared pink water. The use of acetone as an aid in solubilizing munition compounds was seen to diminish adsorption of RDX and HMX but have little effect on TNT and DNT.

9.3 PRELIMINARY COLUMN TESTS

Preliminary column tests were performed in the laboratory to aid in planning and designing equipment for pilot scale multiple column tests. From these tests it was learned that GAC becomes saturated with respect to RDX and HMX much more rapidly than with respect to TNT and DNT. Breakthrough curves for HMX paralleled those of RDX.

TNT effluent levels were higher than the other compounds, remaining near the target level.

Carbon loading was greatest for TNT, followed by RDX, HMX, then DNT, which was the order of decreasing influent concentrations. Cumulative carbon loadings approached that of the maximum q_e values from the isotherm tests.

By comparing the volume of pink water needed to exceed the discharge levels to the volume needed to saturate a column, it was seen that fewer than five columns in series should be needed to optimize performance.

9.4 FOUR IN SERIES COLUMN TESTS

Pilot scale multiple column tests were performed on actual AAP pink water. The objectives were to determine if GAC treatment can achieve the proposed effluent limits under typical AAP conditions; to determine the carbon usage rates; and to help predict the economics of constructing and operating a full-scale system with the desired capabilities.

The desired treatment limit of 0.04 mg/L for TNT generally could not be achieved. A more realistic limit of 0.3 mg/L is proposed, with a maximum exceedance to 0.5 mg/L. TNT levels generally did not decrease significantly beyond the first column, even though other nitrobodies were further removed. Under the conditions tested, there seemed to be a practical lower limit for TNT reduction.

The effluent limit of 0.03 mg/L was generally met for both RDX and HMX. It is anticipated that this limit can be achieved in a properly designed and monitored full-scale GAC system under most conditions.

Breakthrough curves for RDX and HMX were very similar. These compounds always reached breakthrough in the first column well ahead of TNT and DNT.

The four in series column system appeared to reach steady state operation by the third rotational cycle. The maximum loading rates of total nitrobodies was only about half that obtained in the isotherm tests. Loading of TNT was much higher in the isotherm tests, while more RDX was adsorbed during the column tests.

Carbon usage is improved by using two columns in series as opposed to a single column, but little is gained by using more than two columns in series. In terms of effluent levels, however, a third or fourth column is needed to reach desired RDX and HMX levels.

All other things being equal, increasing the hydraulic loading rate apparently improves the effluent quality, but at the expense of poorer carbon utilization. The desired TNT effluent limit may be achievable with a hydraulic loading rate approaching 10 gpm/ft^2.

Comparison tests between Witcarb 950 and Filtrasorb 300 were not conclusive, but did suggest that the Witcarb GAC may produce a better quality effluent while more efficiently adsorbing nitrobodies.

9.5 ECONOMIC ANALYSIS

A limited economic analysis was performed to study the cost impact of treating pink water to much lower levels.

By increasing the level of GAC treatment from current standards to proposed standards of 0.03 mg/L for RDX or HMX and 0.3 mg/L for TNT, carbon costs are expected to increase by up to $5.00/1,000 gal. and pumping costs by up to $0.009/1,000 gal. Changing GAC type from that currently in use may offer a limited cost advantage. Other operating expenses such as maintenance and labor costs are also expected to increase. Capital costs would be dramatically affected by the more stringent standards. An accurate estimate of the total cost difference requires detailed design information to be applied on a site-specific basis.

9.6 RECOMMENDATIONS

The authors recommend that the following measures be taken in subsequent studies.

- Additional effort is needed to determine why reaching low TNT levels is difficult and to better define a practical treatment objective.

- Additional column tests are needed to confirm that meeting a treatment level of 0.0007 mg/L is feasible for 2,4-DNT.

- Carbon usage rates are expected to be different when pink water contains only TNT and DNT or only RDX and HMX. Further pilot tests are needed to generate these data.

- The optimum number of carbon columns appears to be either three or four. This needs to be better resolved.

- The use of higher hydraulic loading rates appears to improve effluent quality. This could be a critical parameter for TNT levels. More study is needed to assess the effects of hydraulic loading rate.

- All laboratory and field tests were conducted with contact time in the range of 1-10 min. A two column test should be conducted with dramatically longer contact time (i.e., 30 min/column) to determine if the effluent quality can be further improved.

- GAC derived from petroleum coke appears to offer some material handling advantages (less dust and attrition due to greater hardness). This needs to be better evaluated, and additional comparative tests are needed to assess any performance differences in GAC types.

- The technique for degassing GAC and filling and packing columns could significantly affect performance. Additional research is warranted.

10. REFERENCES

The list of available GAC references is substantial. There are many texts discussing adsorption theory that are available from most technical libraries; in addition, Uhrmacher[21] cataloged 228 specific references, all of which need not be repeated here. Following is a list of selected references that were specifically consulted during this project.

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GLOSSARY

Term or symbol	Definition
C_f	Concentration of solute in effluent stream
C_o	Concentration of solute in influent stream
C_e	Concentration of solute in equilibrium with a fixed dosage of GAC in a batch isotherm system
q_e	Weight of solute adsorbed by GAC per unit weight of GAC
ΔP	Pressure drop, inches water gauge across a column
ΔP ratio	Pressure drop per unit column height (i.e., GAC bed depth), in. H_2O bed depth
L_c	GAC bed depth, ft
D_c	Column diameter, ft
LD ratio	L_c/D_c, ft of bed depth per ft of column diameter
LV	Linear velocity
Breakthrough	Condition for a GAC column when $C_f = C_o$. At breakthrough GAC has achieved its maximum adsorption capability (q_e at $C_f = C_o$)
Hydraulic loading	Volume of flow per GAC column unit area, gpm/ft^2
Initial contact time	Time for a flow front to move through a GAC column

Isotherm	Plot of q_e versus C_e
Operating line	Plot of q_e versus C_f
Pink water	For this project, a solution where the solutes are any combinations of TNT, 2,4-DNT, RDX, and HMX
Solute	A dissolved substance

APPENDIX A - ANALYTICAL METHODS

APPENDIX A - ANALYTICAL METHODS

A.1 STANDARD ANALYTICAL REFERENCE MATERIALS

Standard analytical reference materials (SARMs) were provided by USATHAMA from stocks at the U.S. Army ARDC, Dover, New Jersey. Each SARM was identified from ARDC by lot and ID number. Because they were shipped wet (except for 2,4-DNT) the SARMs were dried prior to preparation of standard solutions using the apparatus shown in Figure A-1. Each SARM was dried until constant weight versus time was reached and the dry weight recorded. Each SARM was dissolved in acetone (Burdick and Jackson) and transferred to a 100 mL volumetric flask with rinsing. The drying operation was conducted in an explosion-proof laboratory area. The SARM weights and the acetone solution concentrations were:

SARM Compound	Weight mg	Acetone solution concentration mg/L	Lot No.	ID No.
2,4-DNT	220	2,200	1147	PA1837
TNT	187	1,870	1129	PA1834
RDX	205	2,050	1217	PA1836
HMX	207	2,070	1130	PA1835

Aliquots of SARM acetone solutions were diluted with Milli-Q purified water to prepare standards of known mg/L concentrations. The following sample analysis procedures utilized these SARM standard solutions for calibrations.

A.2 HPLC SYSTEM

RDX, HMX, and TNT were analyzed at all levels of interest by direct injection with a reversed phase High Performance Liquid Chromatography (HPLC) system and ultraviolet (UV) detection. However, the lower concentration levels of 2,4-DNT (to 0.0007 mg/L) could not be detected with this method. Therefore, two separate procedures, direct injection and trace enrichment, were used to provide complete analytical results.

HPLC System:

Solvent Delivery: Varian 5020 HPLC or Waters 6000A pump
Detector: Waters 440, 254 nm, 0.005 Absorbance Units Full Scale (AUFS)
Injector: Waters WISP 710B or Precision Sampling LC241; 100 or 200 μL injection volume
Recorder: Houston Instruments Omniscribe or Heath SR-204
Electronic Integration: Nelson Analytical Model 4400 Data System or Varian CDS111L integrator
Mobile Phase: Approximately 25% acetonitrile, Fisher HPLC Grade: 75% purified water
Flow Rate: 1.3 to 2.7 mL/min
Guard Column: Whatman CO:PELL ODS, 72 x 2.3 mm ID
Column: Waters NOVA-PAK C_{18}, 150 x 3.9 mm ID, or Supelco $LC_{18}DB$, 150 x 4.6 mm ID

A.3 DIRECT INJECTION ANALYSES

Sample preparation for the direct injection analyses consisted of filtration of the aqueous samples through Gelman Acrodisk CR filters (0.45 μm) to remove particulates. An injection volume of 100 μL was used. The HPLC systems for use in the laboratory and in the field were essentially the same except for substitution of instrument components.

A.3.1 Laboratory Direct Injection Analyses

The direct inject analyses at MRI included multi-level standards bracketing the concentration levels of interest. Six mixed standard solutions were prepared, which covered six concentration levels for TNT, five levels for RDX, four levels for HMX and three levels for 2,4-DNT. Replicate injections of these standards and water blanks were interspersed throughout each sample set. For TNT, RDX, and HMX, calibration curves were calculated by breaking the full concentration range into a high and a low range in order to maintain the integrity of the lower calibration levels. The correlation coefficients for the linear regression calibrations were generally 0.999 or greater. The concentrations of the standard solutions are given below. See Figure A-2 for a typical chromatogram of Standard C.

	Standard concentrations (mg/L)					
Compound	A	B	C	D	E	F
RDX	30.8	15.4	0.616	0.0616	0.0185	-
HMX	10.4	5.20	0.208	0.0208	-	-
2,4-DNT	1.10	0.550	0.0220	-	-	-
TNT	103	51.4	2.06	0.206	0.618	0.0185

Figure A-3 shows chromatograms, at high sensitivity, of synthetic pink water prepared at MRI for the isotherm tests and actual pink water collected at Kansas Army Amunition Plant. Note that many of the extra peaks which are present in the actual pink water appeared in the synthetic pink water with time. Thus, the synthetic pink water should yield isotherm test results very comparable to actual pink water.

A.3.2 Field Direct Injection Analyses

The direct injection analyses in the field were performed using a single point, mid-range calibration standard. The mid-range standard and a low standard (approximately 20 ppb of each compound) were alternated with each set of seven samples during the assay. A water blank was also analyzed with each set. The standard concentrations are listed below. See Figures A-4 and A-5 for chromatograms of the mid-range and low standards. Figure A-6 shows a typical chromatogram of the actual pink water influent analyzed at IAAP. Figures A-7 and A-8 show typical chromatograms of effluent from columns 1 and 4, respectively.

	Standard concentrations (mg/L)			
Standard	RDX	HMX	DNT	TNT
Mid-level	15.4	5.18	0.110	46.8
Low level (~ 20 ppb)	0.0205	0.0207	0.0220	0.0187

A.4 TRACE ENRICHMENT ANALYSES

In order to analyze for 2,4-DNT to sub-ppb concentrations it was necessary to trace enrich the samples prior to injection into the HPLC system. This was generally accomplished by loading 50 mL of a filtered aqueous sample onto a mini-column using a Waters 6000A pump operating at 5 mL/min. The mini-column consisted of a stainless steel guard column assembly, 72 x 2.3 mm ID, packed with Waters Porapak S GC column packing material. After reversing the mini-column, the compounds of interest were eluted with approximately 5 mL of acetone (Burdick and Jackson) at 1 mL/min. The eluate was reduced in volume with a stream of purified, inert gas, transferred to a 1 mL volumetric flask and brought up to volume with Milli-Q purified water. Enriched samples were then injected (200 µL) into the HPLC system described previously along with standards. The recovery values for all four compounds were between 80 and 100%. Porapak S was chosen as the mini-column packing based on research evaluating solid sorbents.* Figure A-9 shows chromatograms of a deionized water sample spiked with the four compounds of interest, both before and after trace enrichment.

Trace enrichment analysis of the samples brought back to MRI from IAAP did not indicate any presence of 2,4-DNT above 0.0007 mg/L. There is, however, some concern for the integrity of the samples while they were stored at MRI prior to analysis. During the direct injection re-analyses which preceded this trace enrichment work, there was one sample which was expected to contain 2,4-DNT, but none was detected. DNT had been detected in this sample during the original analysis in the field. No chromatographic system problems were observed, therefore, the integrity of the samples upon storage is in doubt. No degradation of the nominal 20 ppb standard was observed, but the samples are a much more complex matrix than the standards and so might have different degradation or binding possibilities.

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* Anspach, G.L.; Jones III, W. E. and Kitchens, J. F. (1982, "Evaluation of Solid Sorbents for Sampling and Analysis of Explosives from Water," Atlantic Research Corporation, Prepared for USATHAMA, DRXTH-TE-CR-82142.

A.4.1 Trace Enrichment Standards

The two standards analyzed with the trace enrichment samples had 2,4-DNT concentrations of 0.0275 and 1.10 mg/L which bracketed the levels of interest. Assuming a recovery of 81%, as was obtained with the trace enrichment analysis of the IAAP samples, these levels are equivalent to 0.00068 and 0.027 mg/L in samples prior to enrichment.

A.5 CONFIRMATION OF TNT

It was desired to confirm that the peak quantitated as TNT in samples eluting from the multiple column apparatus at IAAP was indeed TNT. High Resolution Gas Chromatography analysis was used for confirmation. An aliquot of the aqueous sample, C1-4-8, was extracted with 2x the sample volume twice with toluene and brought to a final volume equivalent to a 1 to 10 dilution of the original sample. Recovery for the extraction was between 95 and 100%. An aliquot of the sample extract was spiked with TNT. The sample extract, spiked sample extract, and an internal standard blank were injected in the GC system described below. See Figure A-10 for chromatograms of the three injections. The C1-4-8 sample extract did yield a peak at the expected retention time for TNT. The spiked sample extract produced a homogeneous peak of increased size at the same retention time. The internal standard blank showed no peak at the retention time of TNT. Thus the presence of TNT in this sample was confirmed.

A.5.1 GC System

The following High Resolution Gas Chromatographic system was used for the confirmation of TNT.

Instrument: Varian 3700 Gas Chromatograph
Column: J & W DB-5, 0.25 micron thickness, 30 meter
Detector: ^{63}Ni Electron capture, 64 x 1, attenuation x range
Injector: Grob-type capillary, splitless mode, splitter on after 30 seconds
Carrier Gas: Helium

Make-up Gas: Nitrogen, 30 mL/min
Injector Temperature: 240°C
Detector Temperature: 360°C
Column Temperature Program: 100° to 280° C at 15°/min
Injection Volume: 1.5 µL
Internal Standard: Lindane
Retention Times: TNT - 7.78 min
Internal Standard - 8.37 min

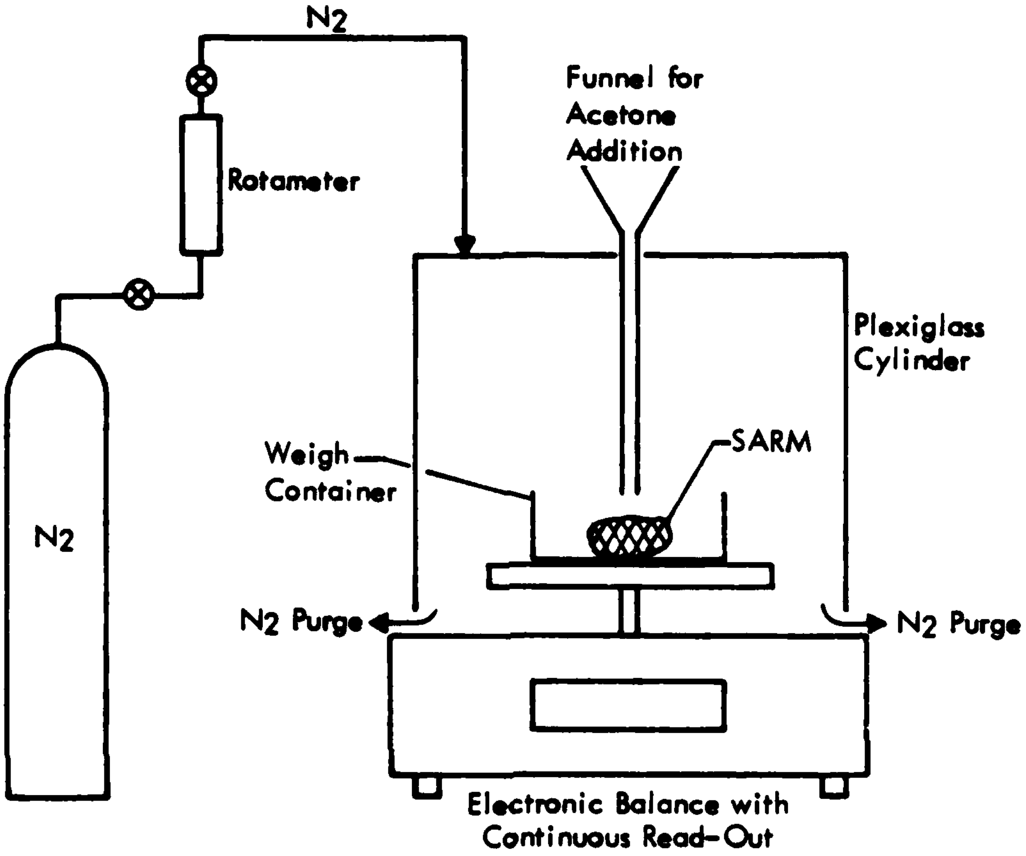


Figure A-1. Apparatus for drying and weighing SARMs.

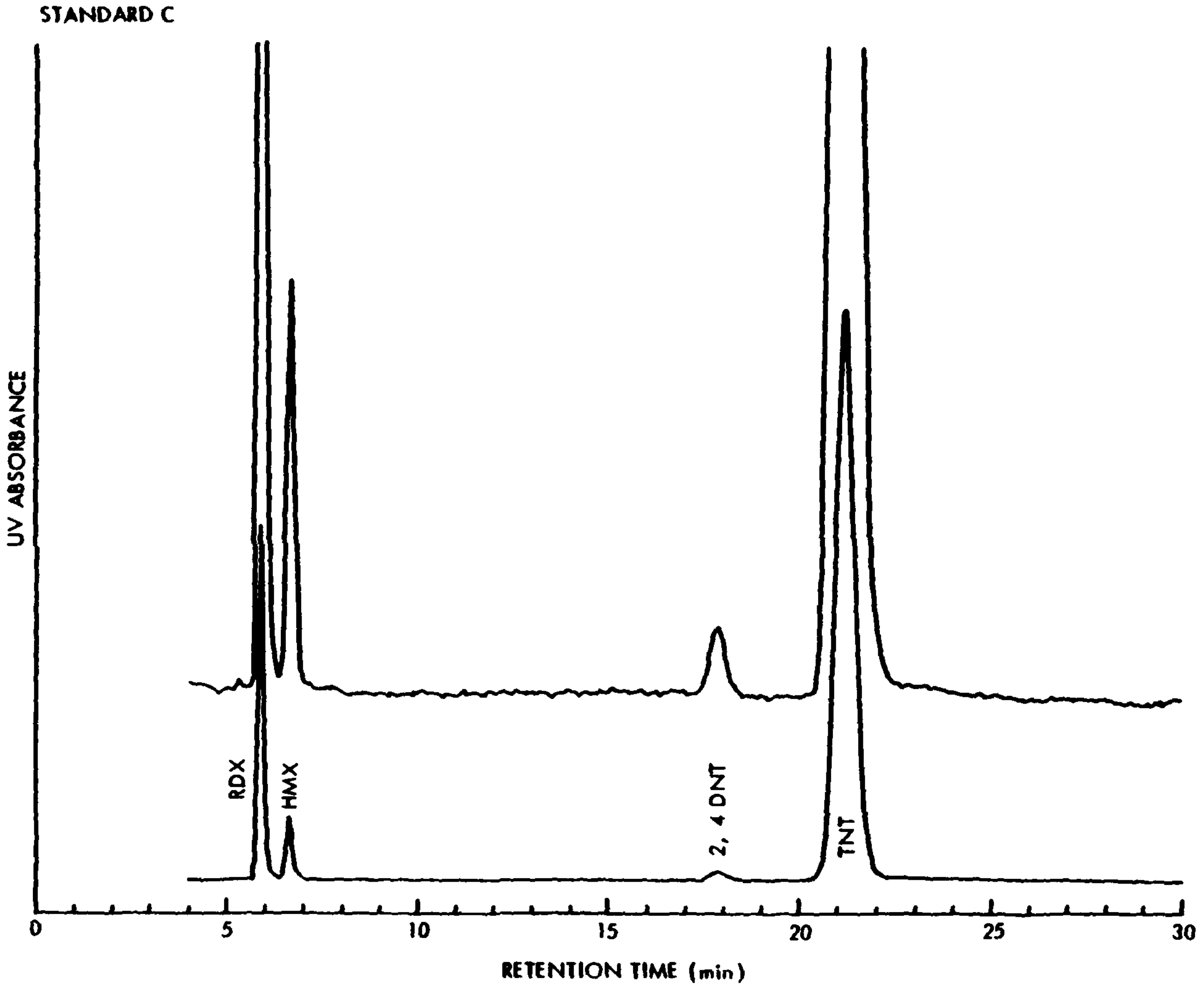


Figure A-2. HPLC chromatogram of standard C.

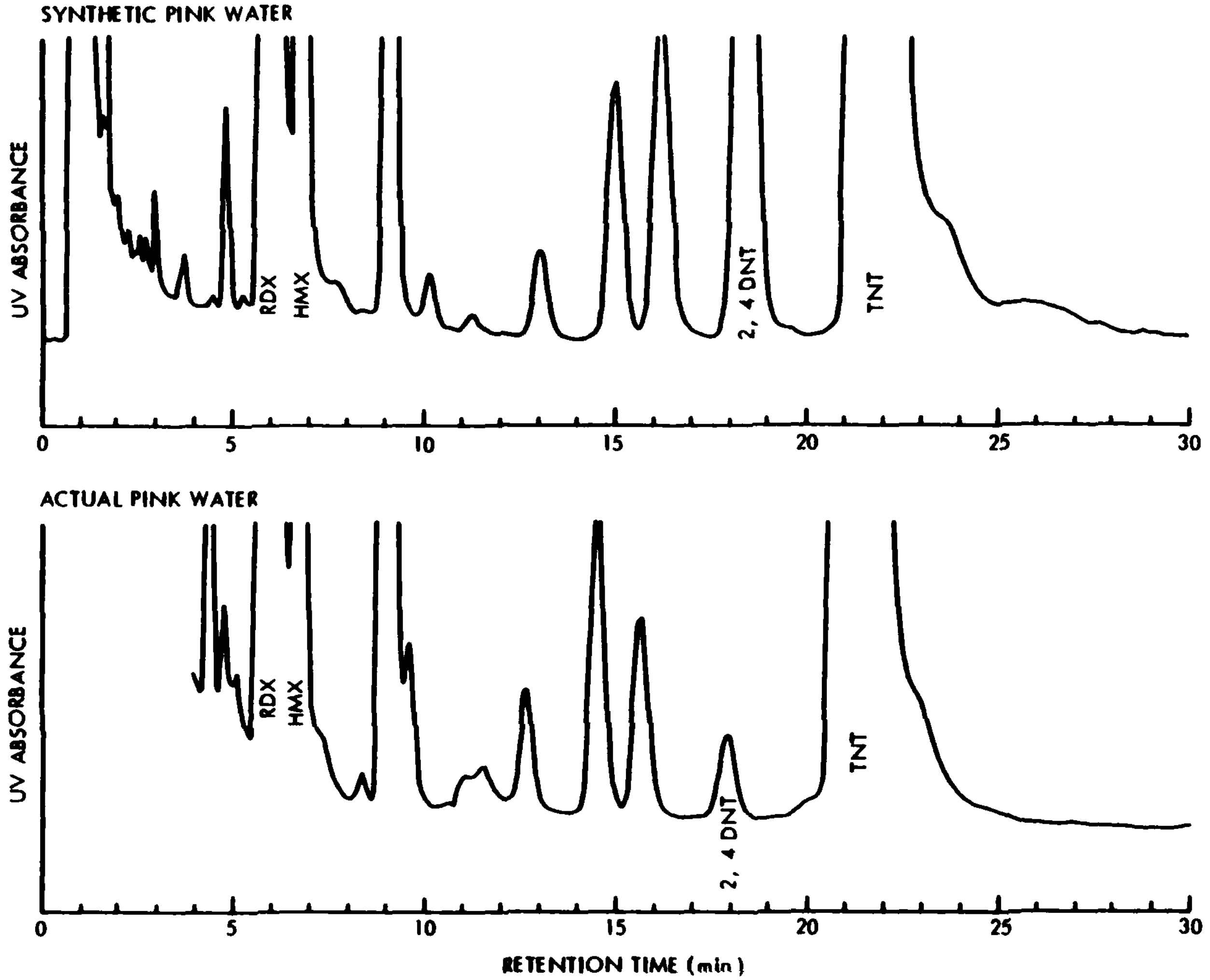


Figure A-3. Comparison of synthetic pink water and actual pink water by HPLC.

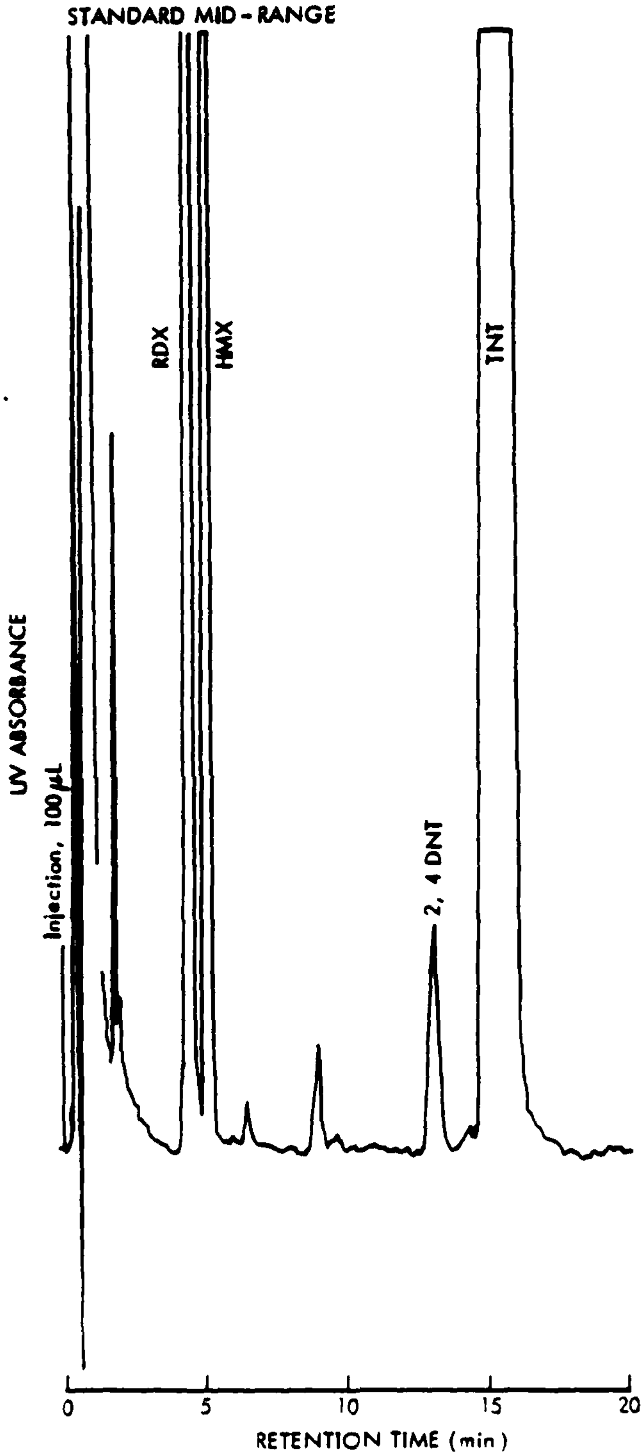


Figure A-4. HPLC chromatogram of midrange standard.

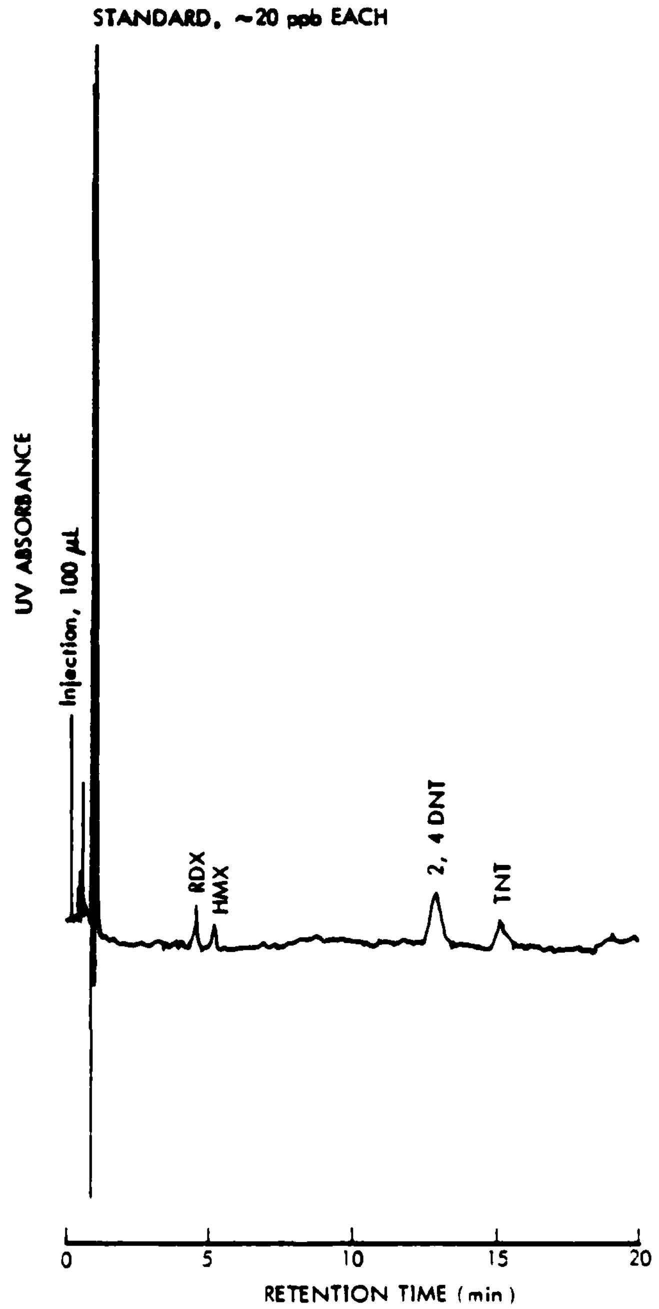


Figure A-5. HPLC chromatogram of low standard.

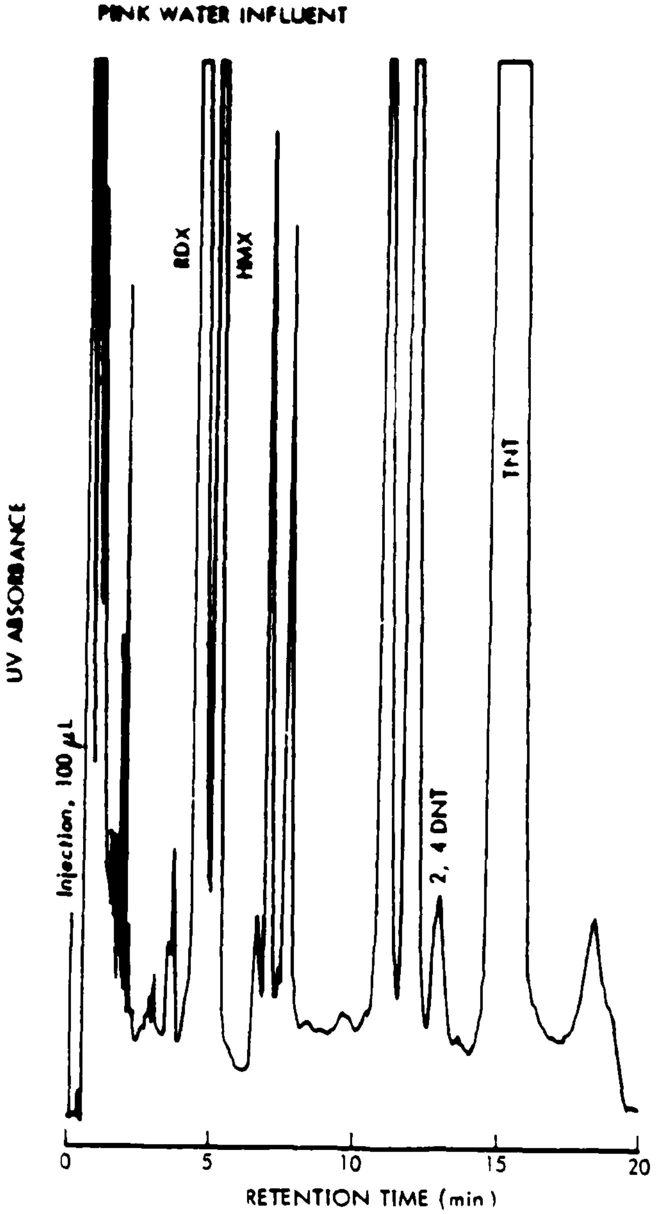


Figure A-6. Pink water influent by HPLC.

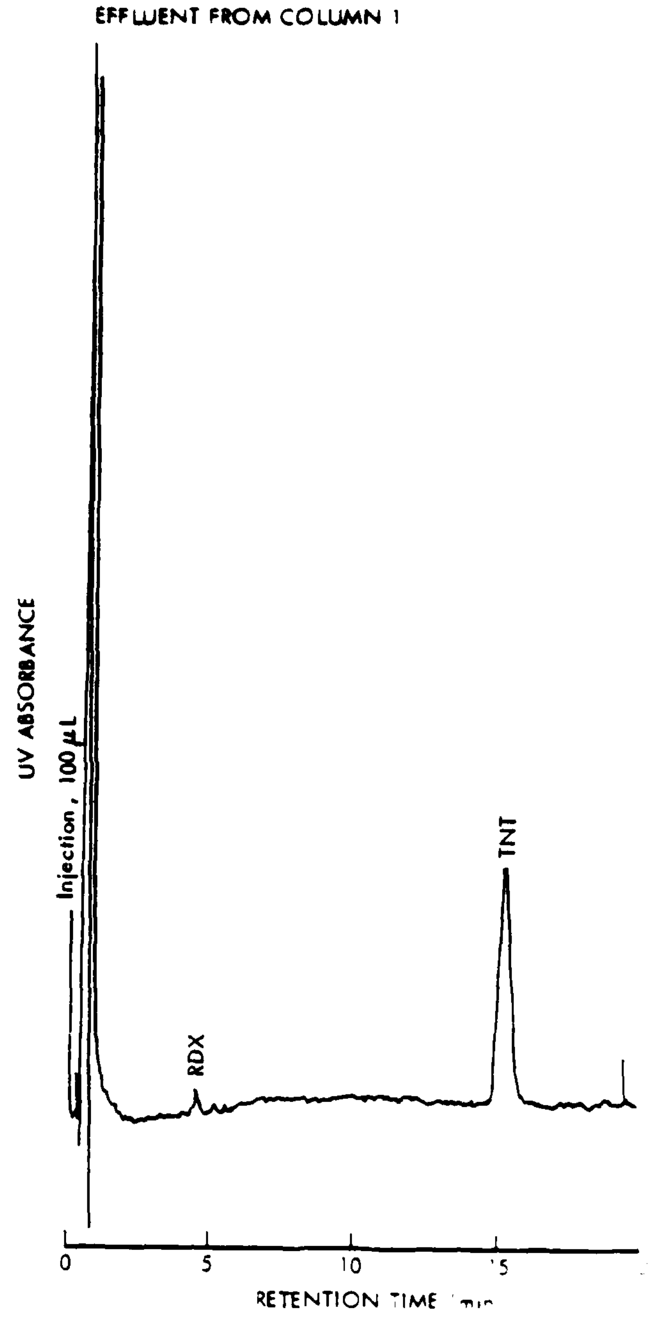


Figure A-7. Effluent from column [illegible]

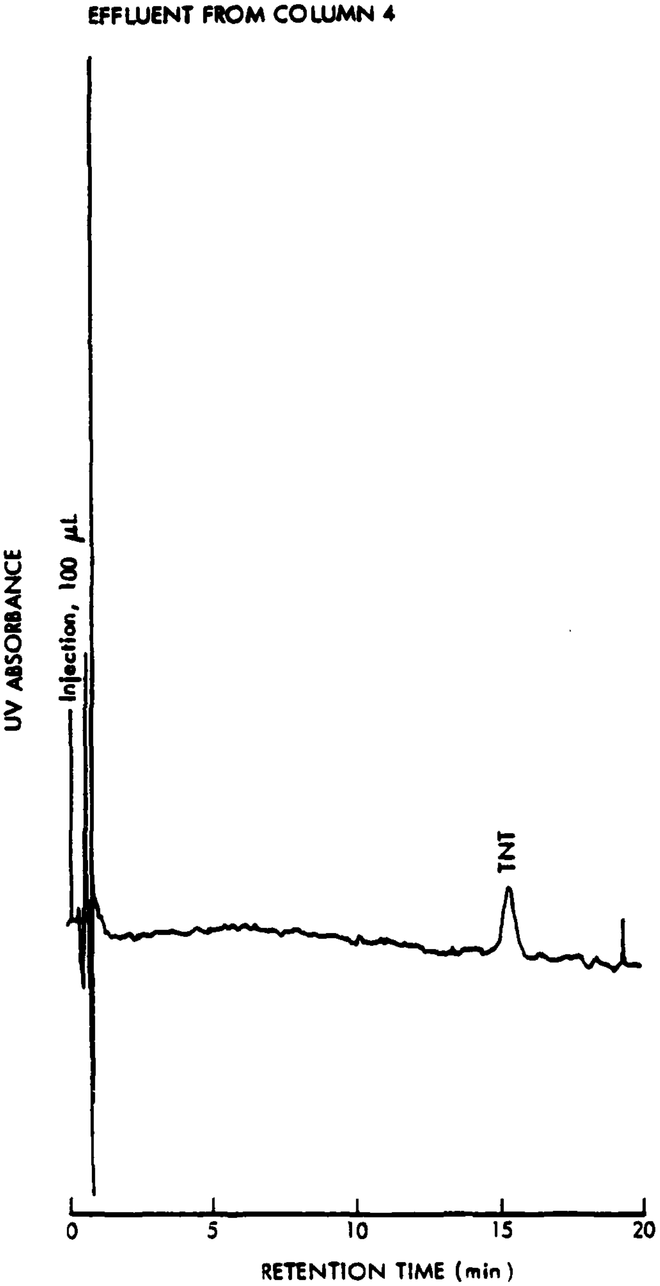


Figure A-8. Effluent from column 4 by HPLC.

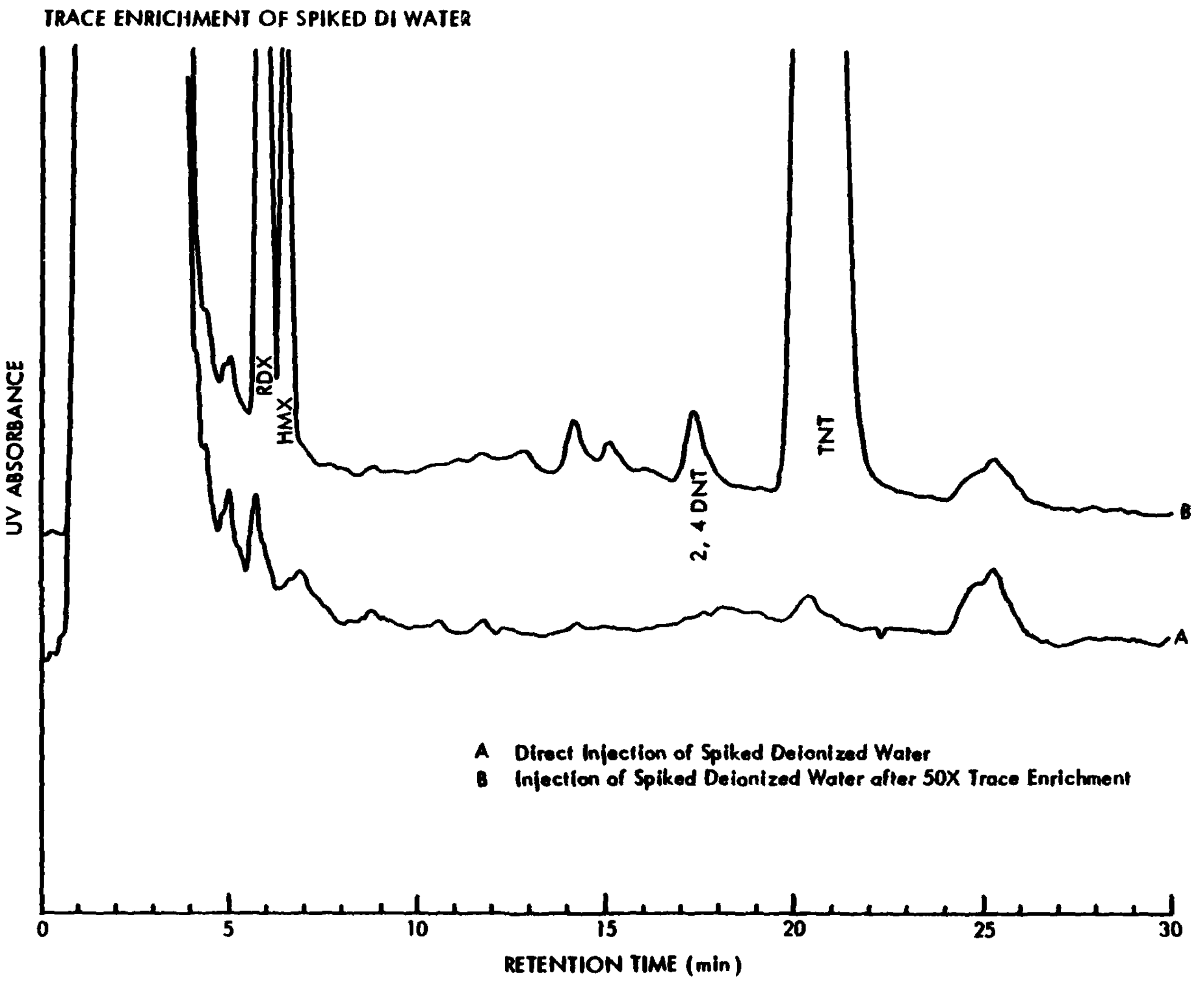
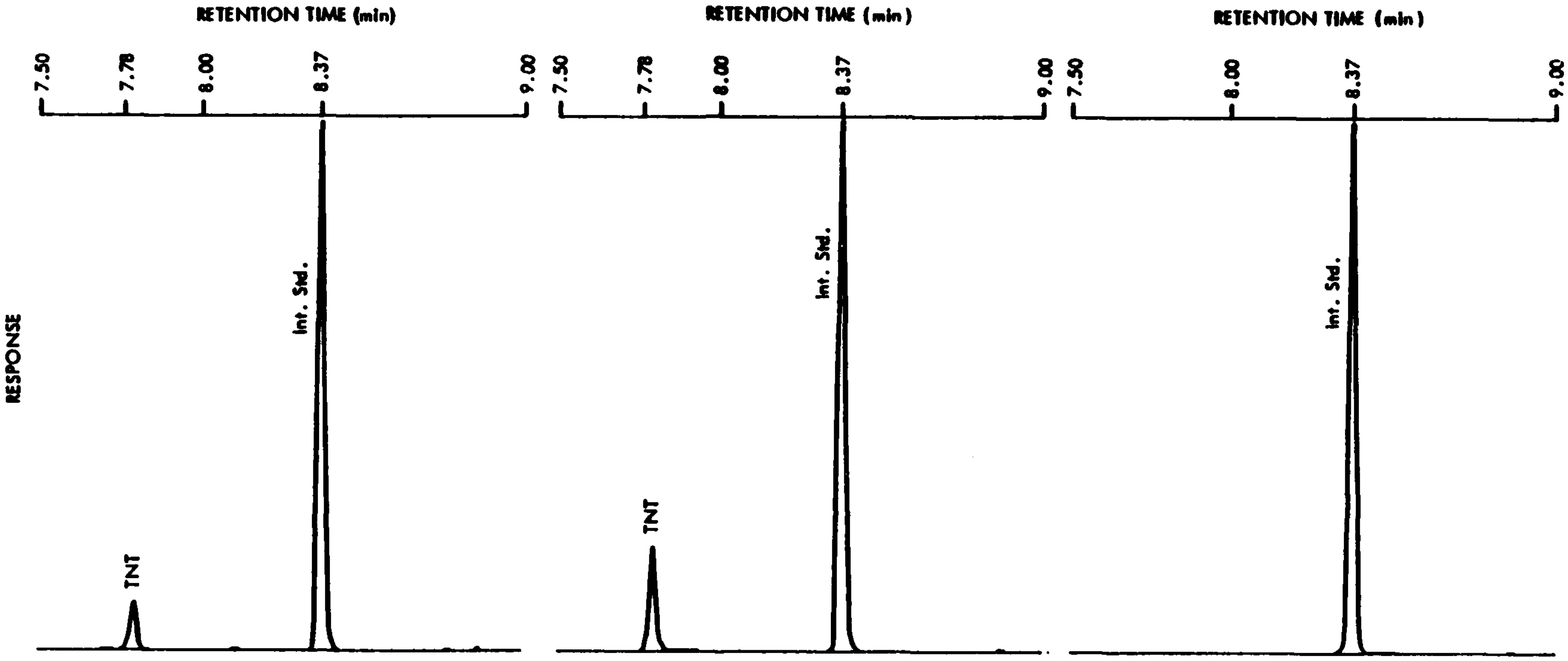


Figure A-9. Trace enrichment of spiked DI water.



Sample C1-4-8

Sample C1-4 - 8 Spiked with TNT

Internal Standard Blank

Figure A-10. Confirmation of TNT by GC.

APPENDIX B - FIELD OPERATION OF FOUR IN SERIES COLUMN TEST ASSEMBLY

APPENDIX B - FIELD OPERATION OF FOUR IN SERIES COLUMN

B.1 GAC PRETEST CONDITIONING

B.1.1 Preliminary Tests - Cycles A1, B1, and B2

The columns were filled with dry carbon, approximately 18 ounces (oz) to maintain a 12-in. carbon bed when fully assembled. The columns were charged with potable water to wet the carbon. Then the carbon beds were washed by passing water up through each column, allowing the carbon beds to expand to within 6 in. of the top of each column. The wash process serves to expel fine carbon particles. The columns were then equipped with their respective top glass bead screens and polyethylene spacers. Again potable water was used to check the system. Noticeable pressure drops occurred from one column to the next. The pressure drops were attributed to fine carbon particles blocking the screens in the brass caps. The problem were resolved by using filter sections containing Pyrex glass wool at the top and bottom of each column.

B.1.2 Final Tests - Cycles C1, C2, C3, C4, and F1

An alternative method to condition the carbon is used in this series of tests to ensure more complete wetting of the carbon. Dry carbon was placed in a series of vacuum flasks. A vacuum was applied to the flasks for 1 hr. Then, hot tap water was bled into the flasks over the dry carbon. While under vacuum, the hot water/carbon mixture boiled for 1 hr. The conditioned carbon was then stored under water until it was to be used. The columns were loaded volumetrically with the carbon/water slurry, maintaining a 16-in. carbon bed when fully assembled. Due to an additional 4 in. in the carbon beds, the polyethylene spacers were removed. Then the carbon beds were washed as previously mentioned.

B.2 CALIBRATION OF FLOWMETER AND WATER METER

Prior to initiating tests, the flowmeter and water meter were calibrated at the nominal rate intended for tests. Potable water was passed through the carbon columns in series, while monitoring the meters and measuring the actual discharge volume against time. Data collected were as follows:

Water meter (gal.)			Discharge (gal.)	Time (sec)	Effluent flowmeter (gpm)	Calculated flow rate (gpm)
V_i	V_f	ΔV	V_d	t	F_a	F_c
449.50	450.40	0.90	0.95	122.4	0.47	0.47

Calculated flow rate: $V_d/t = F_c$

Correction factor for total volume: $V_d/\Delta V$, $0.95/0.90 = 1.06$

Therefore, the ΔV from the water meter would be multiplied by 1.06 to determine the actual discharge volume.

The same procedure was conducted at the conclusion of all tests at nominal flow rates of 0.20 and 0.28 gpm, resulting in correction factors of 0.94 and 1.08, respectively. Because of the variance in correction factors, it was assumed that 1.0 (i.e., no correction) was the best value.

B.3 OPERATING PROCEDURES

1. Prior to the start of each test, a pink water sample was extracted from the supply tank for that test.

2. Upon the start of each test, adjustments were made to the diaphragm pump between the supply tank and the multiple column test unit, to operate at the desired flow rate.

3. Draw pink water samples and recorded meter (flow, water, pressure) readings at regular intervals.

4. The pink water samples are taken to the HPLC lab for analysis.

5. The four in series tests were operated until the first carbon column was at or near breakthrough.

6. After the completion of a test, the fresh carbon column was brought on-line; the original first column was taken off-line and prepared for later use; the original second column now becomes the first in series.

7. Pyrex glass wool in the filter section was changed as necessary, usually before a new test or as pressure drops occurred.