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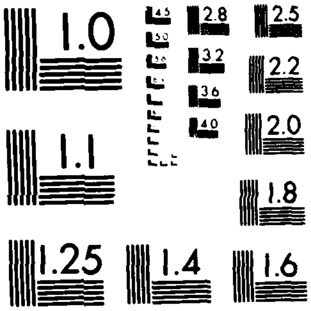
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Contractor Report No. DRXTH-TE-CR-~~88323~~ 83223

GRANULAR ACTIVATED CARBON
PERFORMANCE CAPABILITY AND AVAILABILITY

CARLTECH ASSOCIATES, INC.

JUNE 1983

FINAL REPORT

Distribution Unlimited

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Submitted to:

Commander
U.S. Army Toxic & Hazardous Materials Agency
Attn: DRXTH-TE-D
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The U.S. Army currently uses granular activated carbon (GAC) at Army Ammunition Plants (AAPs) to remove nitrobodies from pink water prior to discharge. The AAPs operate at low production rates and are meeting established effluent limits. However, production rates may increase drastically at full mobilization and future effluent limits may be more strict.

In response to Army needs, an information search/survey was performed to determine operating characteristics of GAC columns for reduction of effluent nitrobody concentrations from pink water. Data were obtained and reported on GAC pollutant removal capacity; competitive adsorption, feasibility to achieve stringent effluent limitations; research required to fill information gaps; and commercial GAC availability.

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CARLTECH
ASSOCIATES,
INC.

GRANULAR ACTIVATED CARBON

PERFORMANCE CAPABILITY AND AVAILABILITY

SECTION 1 -- SUMMARY

The U.S. Army currently uses granular activated carbon (GAC) at Army ammunition plants (AAPs) to remove nitrobodies from pink water prior to discharge to local surface waters. The AAPs currently operate at low production rates and are meeting established effluent limits. However, production rates may increase significantly and future effluent limits may be more strict. The Army, therefore, requires evaluation of:

- GAC capability to remove pink water pollutants
  - at increased operational rates, and
  - to meet more stringent discharge limits, and
- the commercial availability of GAC to supply Army requirements.

In response to Army needs, CARLTECH ASSOCIATES, INC. has performed an information search/survey to determine the operating characteristics of GAC columns for reduction of effluent nitrobody concentrations from pink water process streams. Specifically, the following areas of concern were addresses:

- GAC capacity to remove TNT, RDX, HMX, and 2,4-DNT from pink water at various flow rates and volumes of pink water processed,
- effect of influent temperature on the above,
- competitive adsorption demonstrated by the pollutants mentioned in above and resultant desorption effects on treated effluent pollutant concentrations, and
- feasibility of GAC to treat pink water such that the following effluent concentrations will be obtained:

TNT	0.04 ppm
RDX	0.03 ppm
HMX	0.03 ppm
2,4-DNT	0.0007 ppm.

There was no data found supporting achievement of the specified effluent limits for TNT, 2,4-DNT, RDX, and HMX that were suitable for design use.

Data suitable for design use were found supporting the following pink water treatment effluent limits with good confidence:

			Value Listed in Contract
TNT	0.1	mg/l,	.04
RDX/HMX	0.25	mg/l.	.03

Increasing influent flow rate in existing treatment units would raise effluent concentrations of TNT, 2,4-DNT, RDX and HMX and would decrease time before breakthrough. Temperature has no measurable effect on GAC removal of TNT in the ranges evaluated. We estimate, based on solubility data, that RDX/HMX removal should decrease sharply with increasing temperature.

TNT is preferentially adsorbed over RDX when both are present in pink water. Influent raw waste TNT concentrations of as low as 20 mg/l can decrease column RDX capacity by 20 to 40 percent. In addition, TNT will displace RDX that is already adsorbed in GAC columns. We expect that 2,4-DNT and HMX would behave similarly to TNT and RDX, respectively. Several methods exist for extrapolation of commercial data; however, they are not suitable for this case because the competitive adsorption behavior of the system is unique.

GAC manufacturers have adequate current capacity to meet Army needs at total mobilization. In the unlikely event that stringent drinking water regulations are imposed within the next decade, available GAC capacity will be exceeded. However, time-phasing of drinking water needs is likely and in the worst case, 6 to 12 months (net) would be required to increase GAC production to meet increased demand.

Thirteen AAPs have potential for stream dilution credit and we have developed an equation to calculate allowable effluent concentrations based on that credit.

Data gaps requiring additional GAC research were identified in the following areas:

- Feasibility of GAC to achieve contract specified effluent limits,
- Competitive adsorption (kinetic and equilibrium effects, breakthrough phenomena),
- Extrapolation methods,
- Effects of temperature on adsorption over a large temperature range, and
- Reliability of measured concentrations at high dilution.

The amount and cost of additional research can be lowered by performance of complete GAC modeling analysis of the TNT/RDX system using existing laboratory-scale data.

Available data do not indicate that AAPs can achieve contract-specified effluent limits using GAC treatment. AAPs should be able to achieve alternative effluent limits with a moderate certainty, given sufficient GAC capacity. More data are needed to address whether AAPs can achieve current effluent limitations at full mobilization.

Future work on this study should include complete modeling of competitive adsorption and evaluation of the feasibility of combining biotreatment with GAC treatment to eliminate design problems caused by competitive adsorption.

SECTION 2 -- INTRODUCTION

2.1 BACKGROUND

The U.S. Army manufactures ordnance at several locations in the United States. A major waste stream called "pink water" arises from these operations, primarily from the washdown of land assembly and package (LAP) facilities. The principal components of pink water are the following explosives and their byproducts:

- 2,4,6-Trinitrotoluene (TNT);
- 2,4-Dinitrotoluene (2,4-DNT);
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); and
- Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX).

Collectively, these chemicals are called "nitrobodies". Additionally, pink water may also contain acetylated derivatives of RDX and HMX:

- 1-Acetyl-1,2,3,4,5,6-hexhydro-3,5-dinitro-1,3,5-triazine (TAX) and

- 1-Acetyl-1,2,3,4,5,6,7,8-octahydro-3,5,7-tritro-1,3,5,7-tetraazocine (SEX).

The Army uses granular activated carbon (GAC) to treat wastewater in order to remove the nitrobodies from pink water prior to discharge into the environment. This wastewater treatment is adequate to meet current EPA and NPDES permit requirements; however, future requirements are likely to be more stringent.

2.2 PURPOSE

The purpose of this study is to determine whether it is feasible to use GAC to treat pink water at current and maximum production rates to the following discharge levels:

- TNT 0.04 mg/1
- 2,4-DNT 0.0007 mg/1
- RDX 0.03 mg/1
- HMX 0.03 mg/1.

In addition, there is a question of what impact, if any, Army full production needs would have on the available supply of GAC. Therefore, availability of GAC from domestic commercial manufacturers, as well as quantification of Army needs, must be determined.

2.3 ORGANIZATION OF REPORT

This report is organized in the following manner. Section 1 contains a summary of the contents of this report. Section 2 is the introduction. Section 3 describes the methodology used during this study both to locate and analyze relevant literature. Section 4 presents results of this study, and Section 5 presents conclusions and recommendations drawn based on those results. Section 6 presents future work. The appendices contain a detailed bibliography (Appendix A) and other supporting materials.

SECTION 3 -- METHODOLOGY

3.1 INTRODUCTION

In this section we discuss how GAC data were obtained from the literature and how the data were compiled, examined, evaluated, and analyzed. CARLTECH ASSOCIATES, INC. conducted both computerized and manual literature searches and supplemented these with unpublished data. Knowledgeable individuals were also surveyed and interviewed.

3.2 LITERATURE REVIEW

Information was collected on the following subjects:

- GAC capacity to remove TNT, 2,4-DNT, RDX, and HMX pollutants from pink water at varying flow rates;
- The effect of influent temperature on pollutant removal by GAC;
- Competitive adsorption between major pollutants [TNT and its byproducts; RDX and its byproducts; HMX; and 2,4-DNT];
- The feasibility of GAC to achieve the following effluent limits:
    - TNT 0.04 mg/l,
    - 2,4-DNT 0.0007 mg/l,
    - RDX 0.03 mg/l,
    - HMX 0.03 mg/l;
- The commercial availability of sufficient GAC to meet projected Army needs including a scenario of stringent drinking water regulations requiring massive GAC usage;
- Stream dilution effects including surface water flows at the AAPs.

Available literature was reviewed in domestic and foreign publications and abstracts of foreign sources published in English, German, or French were evaluated. A more detailed description of our approach is presented below.

3.2.1 Preliminary Literature Search

The following abstract services were surveyed to determine availability of data and to develop a strategy for later computerized searches:

- Chemical Abstracts;
- Engineering Abstracts;
- Environmental Abstracts; and
- Selected Water Resources Abstracts.

3.2.2 Computerized Literature Search

The following computerized databases were searched:

- NTIS;
- COMPENDEX;
- POLLUTION ABSTRACTS;
- ENVIROLINE;
- ENVIRONMENTAL BIBLIOGRAPHY;
- CAS On-line; and
- ISMEC.

The searches used combinations of keywords such as pink water; ammunition; munitions; activated carbon; pollution abatement; pollution control; azo; nitrobodies; TNT, DNT, RDX and HMX; as well as actual compound names: 2,4,6-trinitrotoluene, 2,4-dinitrotolutene, triazacyclohexane and tetranitrotetraazacyclooctane. We also included a U.S. Army database, PLASTEC, by scanning its printout. Promising citations were identified and references located at the following libraries: Library of Congress, U.S. Department of Agriculture Library, Johns Hopkins University Library, and libraries of the University of Maryland.

3.2.3 Manual Literature Search

An indepth manual search was designed based on results of the previous literature searches. In addition to screening the abstract services listed above, we searched the following publications from 1970 to present:

- Chemical Abstracts;
- Engineering Abstracts;
- Environmental Abstracts;
- Selected Water Resources Abstracts;
- Pollution Abstracts; and
- the U.S. Government Reports Index.

We surveyed the libraries listed above and the Rutgers University Library. The year 1970 was chosen as the earlier delimiter because preliminary manual and computer searches showed few publications prior to 1970.

3.2.4 Other Sources

We interviewed individuals at the U.S. Army Toxic and Hazardous Materials Agency; the U.S. Army Large Calibre Weapons Systems Laboratory; the U.S. EPA; individual U.S. Army bases; the U.S. Navy; and a number of private individuals and companies. These individuals were asked to provide data on recently performed work in areas such as GAC adsorption capacity, competitive adsorption of nitrated pollutants, industrial GAC manufacturing capacity, and potential demand for GAC.

3.3 ANALYSIS

Publications were reviewed by the project staff to determine relevance to the project, types of chemicals addressed, and scientific and engineering methods used. Publications were also reviewed for quality and consistency with the bulk of available data.

Because of the large number of publications to be reviewed, we built a computerized database of citations using a microcomputer database management system. The database was used to produce reports of literature citations relevant to the various tasks performed during this project.

3.4 CAPACITY TO REMOVE NITROBODIES FROM PINK WATER

The capacity of GAC to remove waterborne nitrobodies was assessed. The following data were extracted and examined.

- Organic adsorption capacity;
- Engineering design data (M-03);
- Effects of temperature on pollutant removal;
- Effect of competitive adsorption on pollutant removal; and
- Effect of flow rate on existing GAC treatment units.

3.5 STREAM MIXING EFFECTS

Stream mixing effects at 17 AAPs were assessed using the AEHA formula published in Reference 0-20. This formula estimates the permitted waste loadings in accordance with stream requirements. Loadings were then used to produce equations which calculated allowable concentration as a function of effluent flow rate. Certain receiving waters had a "zero" ten year low flow; therefore, discharge waters must meet stream standards; no credit could be taken for dilution.

3.6 AVAILABILITY OF REQUIRED GRANULAR ACTIVATED CARBON

Data was obtained from the U.S. EPA concerning availability and projected demand for GAC. The EPA data were based on studies performed in 1976 and updated in 1979. We further updated the EPA studies by interviewing key GAC manufacturers. Data obtained from industry sources were compared to data obtained from EPA and journal articles. Results were used to project GAC availability in the 1983 to 1990 time frame.

Data on full production demand for GAC were obtained from U.S. Army publications (Q-01). These data contained estimated pink water flows for the following munitions production levels:

- Current production estimated to be 2 million gallons per day and;
- Full mobilization estimated to be 900 million gallons per day.

GAC use is roughly linearly proportional to effluent flow rate. Therefore, in the event of partial mobilization, GAC needs can be estimated by interpolation between the two levels mentioned above.

SECTION 4 -- RESULTS

4.1 INTRODUCTION

In this section CARLTECH ASSOCIATES, INC. presents results of applying the methodology discussed in Section 3. The results are divided by topic and presented below. More than 200 publications (Appendix A) were examined, approximately 60 were found to be relevant to this project. Although our sources were primarily public databases, the great bulk of publications found were issued by the U.S. Army.

4.2 CAPACITY TO REMOVE NITROBODIES FROM PINK WATER

4.2.1 Effect of Flow Rate

Studies by Mason and Hanger (M-03) and by Eskelund et al (E-02) have proposed models for kinetics of adsorption of pink water organics by activated carbon. Both models are basically similar in nature and propose that mass transfer from the water phase to the carbon phase is the rate-limiting step in the wastewater treatment.

Based on theoretical considerations described in those studies by Eskelund, we estimate that the effluent concentration from an existing GAC column will vary proportionally with increasing influent flow rate as approximated in the equation below:

$$(1) \quad \frac{Cd_2}{Cd_1} = \frac{e^{(1/F_2^{0.5})}}{e^{(1/F_1^{0.5})}}.$$

Models discussed by Eskelund (E-02), combined with mass transfer correlations contained in standard handbooks (P-15), also predict that the volume treated before breakthrough would vary inversely as the square root of influent flow rate:

$$(2) \quad \frac{Vt_2}{Vt_1} = \frac{(A - B\ F_2^{0.5})}{(A - B\ F_1^{0.5})}.$$

Where: Cd_2, Cd_1 = Discharge concentration of pollutant at conditions 1 and 2, respectively.

Vt_2, Vt_1 = Volume of water treated at the point when pollutant breakthrough occurs.

And, A is a constant equal to:

$$\frac{\pi\ R^2 WeDb}{Ci}$$

Where: R = Carbon column radius
We = Saturation capacity of GAC (pounds/pound)
Db = Bed depth
Ci = Influent concentration of pollutants,

And, B is a constant equal to:

$$\frac{\pi R^2 \mathrm{Ln}\,[(Ci/Cb)-1]}{Ci[Alpha]},$$

Where: R = Carbon column radius
Cb = Breakthrough concentration of pollutants
Ci = Influent concentration of pollutants,

$$Alpha = \frac{2.62(Df/S)^{0.5}}{dp^{1.5}},$$

Where: Df = Diffusion coefficient of effluent water
S = Cross section area of column
dp = Average carbon particle diameter.

A crude approximation of this equation produces:

$$(3) \quad \frac{Vt_2}{Vt_1} = \frac{F_1^{0.5}}{F_2^{0.5}}.$$

An increase of 25 percent in influent flow rate should increase the effluent nitrobody concentration by approximately 11 percent and should decrease the volume treated before breakthrough by 11 percent. An increase of 50 percent in influent flow rate should increase the nitrobody discharge concentration by 20 percent and should decrease the volume treated before breakthrough by 18 percent.

Therefore, increasing the influent flow rate to an operating GAC treatment column would raise the effluent concentration of TNT, 2,4-DNT, RDX and HMX; and would lower the time before TNT or RDX breakthrough.

4.2.2 Effect of Temperature on Removal Capacity

We found little available data on the effect of temperature on removal of nitrobodies. Castorina et al, (C-05) studied the effect of temperature on adsorption of TNT over a narrow range (25 to 45 degrees Celsius) and observed no effect on the ability of the carbon to adsorb TNT.

Studies (H-02) have shown that RDX, HMX, SEX, and TAX are physisorbed. Past studies of physisorption (S-28) have shown an inverse relationship between carbon adsorption and water solubility. Therefore, in the absence of data on effects of temperature on adsorption of RDX, HMX, etc., we can extrapolate temperature effects by analogy with water solubility.

Studies have reported that the solubility of RDX in water increases rapidly with temperature by a factor of almost 200 from 25 to 83 degrees Celsius (P-03). Therefore, we believe that adsorption of RDX, HMX, SEX, and TAX may decrease by as much as two orders of magnitude if influent temperatures increase from 25 to 85 degrees Celsius. This result, however, is theoretical, and should be verified via bench scale laboratory studies.

Study P-03 also mentions instances of RDX bearing streams cooling and causing flow blockages and plugging in waste pipes and treatment columns. If hot water (higher than 80 degrees Celsius) is used in RDX washdown operations, plugging may occur in carbon columns if the waste stream should cool. Protection against plugging is achieved in most waste treatment plants through use of holding capacity (i.e. a basin or tank) ahead of the carbon treatment unit. This type of holding capacity is fairly standard in most wastewater treatment plant designs. Should the raw waste stream average more than 70 degrees Celsius and contain appreciable amounts of RDX and its byproducts, then thermal buffering should be considered in the design of holding capacity for the carbon treatment unit.

Hence, temperature was shown to have no measurable effect on TNT adsorption in the 25 to 45 degree Celsius temperature range. Removal of RDX and HMX is projected to decrease sharply with increasing temperature.

4.2.3 Effect of Competitive Adsorption

Vlahakis in a recent study (V-02) evaluating GAC for domestic use noted that TNT was preferentially adsorbed over RDX with a resulting loss of 40 percent in RDX adsorption capacity. At an influent concentration of 60 mg/l of TNT the capacity was decreased from 0.125 g RDX/g carbon to 0.076 g RDX/g of carbon. Presence of TNT also accelerated RDX breakthrough on GAC columns studied. Vlahakis also found that in solutions containing TNT and RDX the important factor affecting RDX adsorption is the ratio of concentrations of TNT to RDX.

An engineering study for the Milan AAP (M-03) showed that TNT was the preferred species of adsorption and that competitive adsorption reduced the overall GAC treatment capacity. Saturation capacities for a single component system are reported to be 0.55 pound of TNT per pound of carbon and 0.125 pound of RDX per pound of carbon. For a mixture containing 108 mg/l TNT and 89 mg/l RDX, the capacities were reduced to 0.181 pound TNT per pound of carbon and 0.090 pound of RDX per pound of carbon respectively (M-03). No explanation was given for the sharp drop in adsorption capacity.

A report compiled in 1976 by Layne and Tash (L-01) and quoted by Burrows (B-07) states that "...each compound interfered with adsorption of the other and TNT was preferentially adsorbed ... an exception to the general rule ... (that) in a mixture a compound is more readily adsorbed." Layne and Tash report finding the plot of Freudlich isotherms for TNT/RDX mixtures were nonlinear. Patterson et al (P-03) noted that, although there is interference between RDX and TNT, a carbon system could be designed to be useful until RDX breakthrough occurred, although it significantly raised treatment costs and gave an overcapacity for TNT.

The most recently published study by Burrows (B-07) examined a five-component mixture that included TNT, RDX and HMX and additionally 1-Acetyl-1,2,3,4,5,6-hexahydro-3,5-dinitro-1,3,5-triazine (TAX) and 1-Acetyl-1,2,3,4,5,6,7,8-octahydro-3,5,7-trinitro-1,3,5,7-tetraazocine (SEX) which are acetyl derivatives of RDX and HMX. Burrows reported that total nitrobody adsorption in the mixture is significantly less efficient than adsorption of TNT and no more efficient than adsorption of HMX and SEX. Burrows also reported that HMX and RDX may also compete for GAC adsorption sites.

In the summary to this work, Burrows states that further research on GAC treatment "must depend on continuous tests using GAC columns and authentic or synthetic wastewaters containing nitramines and nitrobodies, so that both kinetic and equilibrium effects can be evaluated...since they indicate that the nitramines will be adsorbed in a series of bands (as in chromatography) at the tail end of the column and will be progressively displaced by TNT well before TNT achieves breakthrough."

We found no data on the effect of competition on the adsorption of 2,4-DNT or conversely the effect of 2,4-DNT on the adsorption of other nitrobodies. The data available indicate that competitive adsorption of nitrobodies is a well established phenomenon and must be seriously considered as a drawback to a treatment system that uses only GAC.

Thus, the literature shows that influent TNT concentrations of as little as 20 mg/l can decrease carbon column capacity for RDX and related chemicals by at least ten percent.

4.3 FEASIBILITY TO ACHIEVE REQUIRED EFFLUENT LIMITS

Results of examination of available data on treatment of pink waters by GAC is presented in Exhibit 4-1. These results show that available field data support the achievement of the following low levels of pink water treatment at good levels of confidence:

- TNT 0.01 mg/l and
- RDX/HMX <0.2 mg/l.

We found no effluent data on 2,4-DNT. However, since we believe it to be as strongly adsorbed as TNT, we expect 2,4-DNT would be treatable to the same degree as TNT.

4.3.1 Analytical Methods

Questions have been raised concerning the capability of current analytical methods to analyze effluent concentrations in the range of ten micrograms per liter (0.01 mg/l) or less. Several methods are available for chemical analysis of pink water pollutants in dilute water matrices. These analytical methods were not generally available until 1982 (Appendix B) so that measurement of the desired concentrations was not achievable until recently.

4.3.2 Use of Extrapolation Methods

Several good extrapolation methods are available for predicting adsorption of organic materials by carbon. In S-25 (soon to be published as an American Chemical Society Monograph), Strier has produced a tailored method using thermodynamic and other physical properties to estimate theoretical treatability (effluent concentration) of organic materials by GAC. We are nonetheless hesitant to use any of these methods because the unusual competitive adsorption behavior between TNT, RDX, and their byproducts places this system outside the ranges of the extrapolation methods.

4.4 STREAM MIXING EFFECTS

Available data on stream mixing effects at 17 Army ammunition plants have been analyzed. Results are presented in Appendix C. These data show that effluents would have to meet stream standards at four AAPs. Coefficients are given for equations in Exhibit 4-2 for those AAPs reporting measurable low stream flows. These equations estimate allowable treated effluent concentrations of TNT, 2,4-DNT, RDX, and HMX in milligrams per liter as a function of effluent flow rate at each AAP.

4.5 AVAILABILITY OF REQUIRED GRANULAR ACTIVATED CARBON

Data on Army, municipal and commercial, requirements for GAC were evaluated and compared to existing GAC production capacity. Examination of data supplied by EPA (P-02) shows that current GAC manufacturing capacity is 200 million pounds per year and the industry is operating at 50 to 60 percent of capacity. This leaves an excess capacity of approximately 100 million pounds of GAC per year.

The Army is estimated to require 60 to 165 million (Appendix D) pounds per year of GAC at full mobilization and 130 to 400 thousand pounds per year at current discharge rates. Therefore, there should be sufficient GAC capacity to meet full mobilization requirements within a reasonable time period.

Telephone interviews of GAC vendors have verified that conclusions mentioned in the 1979 report (P-02) are still current and that excess capacity exists for the types of carbon currently being ordered by the Army. Telephone discussions with EPA personnel have indicated that stringent water treatment regulations (the basis for the large GAC manufacturing capacity) have been tabled and are not expected to be implemented. Should current regulatory thinking be reconsidered, GAC demand is not expected to increase dramatically before the late 1980's or early 1990's.

Should full mobilization occur simultaneously with imposition of strict water treatment regulations, the following scenario would apply:

- Water treatment would consume 240 million pounds of additional GAC for initial fill and an additional 240 million pounds per year for makeup (P-02).

- This demand exceeds the available supply and the EPA report suggests phasing in of water treatment for that reason.

- Vendor contacts indicate that delays of as much as 18 months could be encountered in bringing additional capacity on-line.

Available information indicates that 6 to 12 months would be required to reactivate AAPs that are currently inactive. Thus, delays of 6 to 12 months (net) could be experienced in delivery of GAC should this scenario materialize. However, a portion of this projected GAC demand (50-60 million pounds per year) is used to decolorize sugar, a process which does not affect food safety. Therefore, during a period of full mobilization, we believe that this GAC demand could be subordinated to wastewater treatment, thus, freeing an additional 50 to 60 million pounds of GAC per year.

In summary, these results show that, barring a rapid phase-in of stringent drinking water regulations, there is enough GAC manufacturing capacity to meet Army full mobilization requirements. In the event of imposition of drinking water regulations, there may be a temporary time lag in development of sufficient GAC capacity. It is extremely unlikely, however, that there will be significant demand for drinking water treatment before 1990.

4.6 INFORMATION GAPS

Gaps in the available data were identified via analyses performed and discussed in previous sections of this report. Gaps made data unsuitable for use in GAC process design and were identified in the following areas (Exhibit 4-3):

- Feasibility to achieve contract-specified effluent limitiations via GAC treatment;

- Competitive adsorption;

- Extrapolation methods; and

- Effects of temperature.

These gaps can be filled by performance of laboratory and pilot-scale research in GAC adsorption on TNT, 2,4-DNT, RDX, and HMX at low effluent concentrations and at widely varying temperatures. The amount (and cost) of the required environmental program can be lowered by using available laboratory-scale data to formulate a complete adsorption model of the TNT-RDX-byproducts system. Available data is adequate for modeling purposes. Experiments, then, would be performed to validate the model in the low effluent concentration region. If validated, the model would be suitable for use in designing future GAC treatment systems.

EXHIBIT 4-1

LOWEST LEVEL REPORTED IN LITERATURE

TNT

LOWEST LEVEL REPORTED/mg/l TNT	2,4-DNT	RDX	HMX	DEMONSTRATIONS STATUS	NUMBER OF OBSERVATIONS AT CONCENTRATIONS	TOTAL NUMBER OF OBSERVATIONS	CONFIDENCE LEVEL	SOURCE
0.04	0.0007	0.03	0.03	Contract Goal				
0.05	0.025	0.25	(2)	Alternative Goal(4)				P-13
<0.1(1)	---	0.1	0.07	Laboratory	1	12	Low	B-07
---	---	<0.05	---	Laboratory	0	0	N/A	V-02
0.005	---	0.066	---	Laboratory	3	10	Moderate	V-02
<0.2	---	<0.2	---	Laboratory	21	36	Moderate	L-02
<0.5(3)	---	<0.02	---	Laboratory	Unknown	Unknown	N/A	P-09
0.1	---	<0.11	---	Pilot	8	8	Good	K-03
<0.005	---	0.02	---	Pilot/Field	2	7	Moderate	R-06
0.3	---	<0.2	---	Field	1	1	Low	0-08
0.3	---	1.0	---	Field	Unknown	Unknown	N/A	S-05
3.7	---	19.0	---	Field	Unknown	Unknown	N/A	T-01
0.1	---	---	---	Field	Unknown	Unknown	N/A	S-05
0.008	---	---	---	Field	Unknown	Unknown	N/A	S-05
0.1	---	<0.1	---	Field	544	967	Good	S-11

RDX

LOWEST LEVEL REPORTED, mg/l TNT	2,4-DNT	RDX	HMX	DEMONSTRATIONS STATUS	NUMBER OF OBSERVATIONS AT CONCENTRATIONS	TOTAL NUMBER OF OBSERVATIONS	CONFIDENCE LEVEL	SOURCE
0.04	0.0007	0.03	0.03	Contract Goal				
0.05	0.025	0.25	(2)	Alternative Goal(4)				P-13
<0.1(1)	---	0.1	0.07	Laboratory	1	7	Low	B-07
---	---	<0.05	---	Laboratory	3	40	N/A	V-02
0.005	---	0.066	---	Laboratory	3	10	Moderate	V-02
<0.2	---	<0.2	---	Laboratory	14	36	Moderate	L-02
<0.5(3)	---	<0.02	---	Laboratory	Unknown	Unknown	N/A	P-09
0.1	---	<0.11	---	Pilot	15	22	Good	K-03
<0.005	---	0.02	---	Pilot/Field	2	7	Moderate	R-06
0.3	---	<0.2	---	Field	1	1	Low	0-08
0.3	---	1.0	---	Field	Unknown	Unknown	N/A	S-05
3.7	---	19.0	---	Field	Unknown	Unknown	N/A	T-01
0.1	---	---	---	Field	Unknown	Unknown	N/A	S-05
0.008	---	---	---	Field	Unknown	Unknown	N/A	S-05
0.1	---	<0.1	---	Field	333	968	Good	S-11

Notes:

1. As total nitrobodies
2. Combined with RDX
3. Includes dissolved air flotation, sand filter, and GAC
4. Can be achieved with moderate confidence

EXHIBIT 4-2

COEFFICIENT, E IN

ALLOWABLE EFFLUENT CONCENTRATION EQUATION (2)

PLANTS	TNT	DNT	RDX	HMX
Badger	58.717	1.043	44.337	44.337
Holston	20.371	0.359	15.578	15.578
Indiana	155.779	2.732	117.433	117.433
Iowa	0.791	0.014 (1)	0.599	0.599
Joliet	0.003 (1)	(1)	0.002 (1)	0.002 (1)
Kansas	0.025 (1)	(1)	0.019 (1)	0.019 (1)
Milan	0.359	0.006 (1)	0.276	0.276
Newport	20.371	0.348	15.578	15.578
Picatinny	0.036 (1)	(1)	0.028 (1)	0.028 (1)
Pine Bluff	41.940	0.731	31.156	31.156
Radford				
New River	24.97	0.427	19.096	19.096
Stroubles Creek	0.216	0.004 (1)	0.002 (1)	0.002 (1)
Ravenna	0.002 (1)	(1)	0.002 (1)	0.002 (1)
Volunteer	103.054	1.800	77.889	77.889

NOTES:

1. For flows exceeding 1 MGD, plant discharge must be at stream standard.
2. Allowable concentration equation:

$$C = E/Q$$

Where: C is allowable concentration, mg/l to meet limits specified in contract

E is constant, mg/l

Q is Discharge flow, MGD

EXHIBIT 4-3

GAPS IDENTIFIED

AREA	WORK NEEDED TO FILL GAP
Feasibility of treatment of pink water to contract levels not confirmed reliably using available data.	Perform laboratory and pilot studies of pink water GAC treatment at contract-specified effluent levels
Competitive adsorption	
● Lack of complete model on competitive adsorption	● Perform modeling analysis using existing data
● Lack of data at effluent concentrations 0.1 mg/l of TNT	● Perform laboratory scale research in required concentration region
● Lack of data on competitive adsorption 2-4,DNT,HMX	● Perform laboratory scale research on competitive adsorption of 2,4-DNT and HMX
Extrapolation of existing data unadvisable because methods based on data without competitive adsorption	Perform complete modeling of TNT, RDX, HMX system
Effect of temperature on nitrobody adsorption	
● Temperature range too narrow	Conduct laboratory research on GAC adsorption of TNT, 2,4-DNT, RDX and HMX in the required temperature range
● No data on 2,4-DNT, RDX, HMX	

SECTION 5 -- CONCLUSIONS AND RECOMMENDATIONS

5.1 ACHIEVEMENT OF EFFLUENT LIMITS

No literature support was found for the following pink water effluent limits:

- 2,4-DNT 0.0007 mg/l;
- RDX 0.03 mg/l; and
- HMX 0.03 mg/l.

In addition, the majority of the available data were generated at the laboratory level. We feel that this type of data is not suitable for GAC column design to treat pink water to these discharge concentrations. Both laboratory and pilot/field experiments should be performed to establish the feasibility of achievement of these levels of GAC treatment.

Available laboratory data and one pilot data point support achievement of 0.04 mg/l as the TNT effluent concentration. Pilot/field experiments should be performed to confirm this finding.

We found literature support for the following pink water treatment effluent limits:

- TNT 0.1 mg/l;
- 2,4-DNT 0.025 mg/l; and
- RDX/HMX 0.25 mg/l.

Several methods exist for extrapolation of commercial data. However, these methods are not suitable for pink water treatment because the competitive adsorption behavior of the system is unique.

5.2 EFFECT OF FLOW RATE

Increasing the influent flow rate to a GAC treatment unit increases the effluent concentration and decreases the breakthrough time as follows:

- Effluent concentration: Increases with flow rate proportional to $_{e}(1/F^{0.5})$ and
- Time before breakthrough: Decreases with flow rate proportional to $1/F^{0.5}$.

5.3 EFFECT OF TEMPERATURE ON POLLUTANT ADSORPTION

- TNT: Available data indicate no measurable effect by temperature in the 25 to 45 degrees Celsius range studied.
- 2,4-DNT: Data were not available on 2,4-DNT. However, by analogy with TNT, temperature effects are not expected in the 25 to 45 degrees Celsius range.

- RDX and HMX: Literature data were not available. However, solubility versus temperature data suggest that adsorption would decrease sharply with increasing temperature. Literature data also suggest that plugging of carbon columns can occur if influent temperatures are consistently higher than 70 degrees Celsius. Plugging can be avoided by installing properly designed holding capacity ahead of the carbon treatment unit.

5.4 COMPETITIVE ADSORPTION

Available data indicate that TNT is much more strongly adsorbed on GAC than is RDX. Influent concentrations of TNT as low as 20 mg/l are capable of decreasing RDX adsorption capacity by as much as 40 percent. Only one unifying correlation was found to predict desorption or breakthrough. Thus, research is needed to unify the widely varying breakthrough phenomena reported.

Competitive adsorption of TNT with respect to RDX/HMX may render landfill codisposal of spent RDX and TNT carbons difficult. Physisorbed TNT may leach from spent TNT carbon and have a multiplier effect on displacement of adsorbed RDX present in the same landfill.

Specific adsorption data used in this study to estimate GAC needs were based on laboratory experiments performed at nitrobody effluent concentrations either at or above the limits discussed in this study. Thus, additional experimentation is needed using TNT-RDX-byproducts mixtures to estimate specific adsorption in the range of concentrations discussed in this study. The amount of experimentation required may be reduced by thorough adsorption modeling analysis performed before starting laboratory experimentation. This modeling could be done using existing laboratory GAC data (B-07, E-02, L-02, V-02).

5.5 STREAM MIXING

Of the 17 AAPs studied, 13 have non-zero low stream flow rates, and, may be able to take credit for dilution by discharge streams.

5.6 GAC AVAILABILITY

At the present time there is ample capacity to meet even projected full mobilization U.S. Army GAC demands of as much as 165 million pounds per year. No near term impact of drinking water regulations is anticipated. Should stringent water regulations be imposed, water treatment demands would far exceed existing GAC capacity even without Army needs. In this type of situation, the EPA recommends prioritization of demand, and Army demands should play a part in prioritization. In the worst case, AAPs may experience delays of from 6 to 18 months in receiving GAC orders, resulting in net delays of 6 to 12 months.

SECTION 6 -- FUTURE WORK

Future work on this project should include complete modeling of competitive adsorption among TNT, RDX, and their byproducts to improve extrapolation. Of necessity, estimates of GAC requirements used in this study were based on available data. These data were obtained at higher effluent concentrations than those required. Existing models neglect competitive adsorption. Thus, additional effort should include formulation of a complete model of the pink water system based upon existing data. This model would then serve to reduce the amount of additional experimentation required to develop a design basis.

Examination of available data has shown that two additional chemicals, SEX and TAX, are present in pink water mixtures. Since these chemicals are acetylated derivatives of RDX and HMX, we feel that they should be studied as part of the overall system.

Data examined during this study show that the presence of TNT and its byproducts actually decreases column capacity for adsorption of RDX and its byproducts. Thus, dual treatment of TNT and its byproducts would improve treatment of RDX. Available data suggest that certain types of biological treatment of RDX are feasible. Biotreatment of TNT has been less than satisfactory (T-01) but such treatment of RDX should be possible even in the presence of TNT (M-05). Thus, investigation of feasibility of biotreatment combined with GAC to treat TNT (and its byproducts) and RDX (and its byproducts) should be investigated.

In the course of this work, flow and concentration data were analyzed using the AEHA formula during this study. As a result, we produced a table of coefficients (Exhibit 4-2) which planners may use to estimate allowable effluent concentrations for the 13 AAPs that have potential dilution credit. Planners benefit from tables or graphs allowing them to read effluent concentration limits directly, without calculation. Thus, we suggest that future work include preparation of graphs or tables of allowable effluent concentrations for TNT, 2,4-DNT, RDX, and HMX versus effluent flow rate for each of the 13 AAPs.

We estimated carbon required for wastewater treatment assuming that 2,4-DNT was adsorbed on GAC at least as strongly as is TNT. This assumption, in turn, was based upon a trade-off between molecular attraction caused by the additional nitro group in TNT (three, versus two, for 2,4-DNT) and the negative steric effect on GAC pore diffusion caused by the nitro group. Thus, we expect the two effects to cancel one another. Accordingly, future experimentation should include a 2,4-DNT adsorption validation study in the contract-required concentration range to confirm this assumption.

APPENDIX A

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GAC SOURCES CONSULTED

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0-04		Quarterly Progress Report: Project Title: MMT 54114 Pollution Abatement Methods for P&E: fr 1 December 1976 - 28 February 1977	US Army Armament R&D Command		February 1977
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0-08		Communication to B. Jackson from Iowa AAP: Concentration of TNT and RDX in Pinkwater			March 1979
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0-10		Adsorption Literature Review	Journal of Water Pollution Control Federation		June 1978
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0-13		Wastewater Treatment by Product Type	Journal of Water Pollution Control Federation	52(6)	June 1980
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0-19		Unidentified Picture			
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0-21		Picture: Pink Water Carbon Filter Columns in Series	Mason and Hanger - Silas Mason Co Inc		
0-22		Picture: Pink Water Diatomaceous Earth Filters	Mason and Hanger - Silas Mason Co Inc		
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B-07	Burrows WD	Tech Report 8207: Tertiary Treatment of Effluent from Holston AAP Industrial Liquid Waste Treatment Facility I. Batch Carbon Adsorption Studies: TNT, RDX, HMX, TAX, and SEX	US Army Medical R&D Command		September 1982
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C-03	Carpenter D	Microbial Transformation of 14 C-Labeled 2,4,6-Trinitrotoluene in an Activated-Sludge System	Applied and Environmental Microbiology	35(5)	May 1978
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C-06	Cavagnaro D	Activated Carbon. 1975-1978 (Cites from NTIS Data Base)	NTIS		July 1980
C-07	Chen C	Carbon Reactivation by Externally-Fired Rotary Kiln Furnace	Los Angeles County Sanitation District		August 1980
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F-05	Forsten I	Pollution Abatement in a Munitions Plant	Environmental Science & Technology	7(9)	September 1973
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J-01	Jackson B	Trip Report: Place Visited-Milan AAP Milan TN, Holston AAP Kingsport TN, 9 August-13 August 1982	US Army Armament R&D Command		October 1982
J-02	Jackson B	List of Individuals to Contact for Further Information on Publications			March 1983
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J-06	Jain KK	Feasibility of Munitions Wastewater Treatment by Adsorption-Oxidation	Carbon Adsorption Handbook		1978
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APPENDIX B

ANALYTICAL METHODS

In analyzing the pink water pollution abatement problem, we have discovered a lack of chemical analysis methods that could explain the absence of data on GAC or any other pollution abatement method to treat pink water to TNT levels of <10 ppb. This lack of a reliable analytical method, has been cited as recently as May, 1982 by Donald Freeman (F-07) in his report on the use of surfactant technology.

Prior to the 1980's, the analytical methods were not validated in the range of TNT or RDX of less than 100 ug/l. Most methods used spectrophotometric techniques that required the formation of colored complexes with the nitrobodies in solution (R-05). These techniques lacked sensitivity, specificity, and generally could not distinguish between the various nitrobodies. Hoffsommer at the U.S. Naval Ordnance Laboratory first attempted to separate the components using thin-layer chromatography followed by spectrometry (H-10) or electron capture vapor-phase chromatography (H-07) respectively. However, his methods were cumbersome and difficult to replicate.

Stidham reported difficulty in using high pressure liquid chromatography to analyze effluent concentrations at the Holston AAP (S-24). The detection limit for his method was 65 ug/l which set new low limits on sensitivity. Other Army work (0-35) has shown lower levels of detection 0.01 mg/l for TNT and 2,4-DNT and 0.04 mg/l for RDX and HMX. Like the Stidham method, this method used a high pressure liquid chromatograph (HPLC). In 1981, USATHAMA proposed an HPLC method that achieved very low levels of sensitivity (for TNT, RDX and HMX and six additional compounds the precision is 0.008 mg/l).

We made a telephone contact with Ms. Karen Deere, Chemist, Louisiana Army Ammunition Works. Ms. Deere confirmed that her laboratory was using an adaptation of the USATHAMA method and claimed achievement of detection levels of 0.02 mg/l routinely on a daily basis.

Both the Army and the Environmental Protection Agency have indicated an interest in achieving even lower levels of detection for 2,4-DNT and 2,6-DNT. In 1981, a gas chromatographic method using an electron capture detector reports an extremely sensitive method for these two compounds (0-33). Claims have been made that concentrations of as low as 0.00048 and 0.00043 mg/l for 2,4-DNT and 2,6-DNT can be detected.

Most of these low concentration methods have been developed recently (1981-82). There has not been enough time for available published literature on pink water pollution abatement to reflect new analytical methods. Current work using surfactant technology for effluent treatment has incorporated these recent analytical methods (F-07).

Because of the gap in the data for low levels of pollutant concentration, all decisions on whether granulated activated carbon can reduce nitrobodies in pink water must be based on extrapolation of the data. We also believe that data reported prior to 1982 that claims 0.0 mg/l as the concentration of a species should be interpreted to mean concentrations of less than 0.1 mg/l.

APPENDIX C

STREAM MIXING EFFECTS

TECHNICAL MEMORANDUM

To : J.C. Uhrmacher

From : S.F. Rudy

Subject : Project No. 8243
Task C.3.1.4: Calculation of Site Outfall Mixing Concentrations

1. GENERAL

Allowable pollutant loadings were calculated based on the AEHA formula. The methodology was provided in a memorandum from the U.S. Army. River flows were also provided.

Pollutant loadings were based on concentrations for TNT, RDX, HMX, and 2,4-DNT provided in the project contract. Temporary guidelines for WP, NGu, and NC were provided in the U.S. Army memorandum referenced above.

This technical report includes the following sections:

1. General
2. Calculation of Loadings
3. Receiving Waters
4. Effluent Standards
5. Results
6. Discussions
7. Recommendations.

2. CALCULATION OF LOADINGS

The formula for calculating the allowable pollutant loading was provided as follows:

$$Li = 5.39362 \text{ X } Ci \text{ X } Q \qquad \text{(Equation 1)}$$

Where: Li is the maximum allowable loading of a single pollutant into a flowing stream, expressed in pounds per day (lb/day)

Ci is the maximum allowable in-stream concentration of a single pollutant, expressed in milligrams per liter (mg/l)

Q is the designated stream low flow expressed in cubic feet per second (cfs)

The coefficient (5.39362) is a composite conversion factor to convert from:

$$\frac{\text{mg} - \text{ft}^3}{\text{liter} - \text{sec}} \quad \text{to} \quad \frac{\text{lb}}{\text{day}}.$$

$$\frac{\text{mg}}{\text{liter}} \times \frac{\text{ft}^3}{\text{sec}} \times \frac{86{,}400\ \text{sec}}{\text{day}} \times \frac{28.3\ \text{liter}}{\text{ft}^3} \times \frac{1\ \text{lb}}{454\ \text{gm}} \times \frac{1\ \text{gm}}{1000\ \text{mg}} = 5.39 \quad \frac{\text{lb}}{\text{day}}$$

Therefore:

$$\text{Li} \quad \frac{\text{lb}}{\text{day}} = \text{Ci} \quad \frac{\text{mg}}{\text{l}} \times \text{Q} \quad \frac{\text{ft}^3}{\text{sec}} \times 5.39$$

The allowable loading, Li, is given in pounds of pollutant that may be discharged per day. This figure is based on a continuous discharge rate for the pollutant into the stream at low flow. Thus, the total daily loading could not be discharged into the stream in a shorter period of time or the allowable in-stream concentration level would be exceeded. (See discussion in Section 6).

In the case of streams which have a design low flow of zero, no dilution can be expected by discharge of the waste into the stream bed. Therefore, the concentration of pollutants in the effluent may not exceed the maximum allowable in-stream concentration. In this case, the loading is calculated as follows:

$$\text{Li} = 8.34517 \times \text{Ci} \times \text{Q}' \qquad \text{(Equation 2)}$$

Where: Q' = Wastewater discharge in million gallons per day (mgd)

Li and Ci are the same as for equation

The coefficient (8.34517) is a composite conversion factor to convert mixed units to pounds per day.

$$\frac{\text{mg}}{\text{liter}} \times \frac{\text{M gal}}{\text{day}} \times \frac{1\ \text{lb}}{454\ \text{gm}} \times \frac{1\ \text{gm}}{1000\ \text{mg}} \times \frac{3.785\ \text{liter}}{\text{gal}} \times \frac{10_6\ \text{gal}}{\text{M gal}} = 8.34 \quad \frac{\text{lb}}{\text{day}}$$

3. RECEIVING WATERS

Values for the design low flow were reported in the U.S. Army memorandum referenced above for the streams in question. In most cases, the 7-day low flow with a recurrence interval of 10 years (7Q10) was evaluated, using available data. In a few cases, other low flow criteria were used. In many of the streams, the design low flow was determined to be zero. The design low flow values are reported in Exhibit C-1.

4. EFFLUENT STANDARDS

The following explosives are of concern in this study:

Abbreviation	Explosive
HMX	cyclotetramethylene-tetranitramine
RMX	cyclotrimethylene-trinitramine
2,4-DNT	dinitrotoluene
TNT	trinitrotoluene
NC	nitrocellulose
NG	nitroglycernine
NGu	nitroguanidine
WP	white phosphorus.

Allowable effluent concentrations (Ci) for TNT, RDX, HMX, and 2,4-DNT were provided in the contract as follows:

Explosive	Ci (ppm = mg/l)
TNT	0.04
RDX	0.03
HMX	0.03
2,4-DNT	0.0007

Calculated loadings for these parameters are reported in Exhibit C-1.

The earlier memo provided temporary guidelines for NG, NGu, NC, WP as follows:

NG	0.04
NGu	no data
NC	no limit
WP	1.0 X 10-5

Loadings for NG and WP are also reported in Exhibit C-1. The memo also provided temporary guidelines for HMX, RDX, TNT and DNT. It was assumed that contract values superceded the temporary guidelines.

5. RESULTS

The design low-flow and allowable pollutant loadings for each of the streams are reported in Exhibit C-1.

In cases where the low flow was greater than zero, equation 1 applies, and loadings were calculated as such. In cases where the low flow was determined to be zero, no loading is reported because the loading is directly a function of wastewater flow and no wastewater flow data was provided.

In cases where the design low flow is small compared to the waste discharge, it is less restrictive to calculate the allowable loading based on the total flow in the stream bed; total flow being equal to the design low flow, Q, plus the wastewater flow, Q'.

Thus: $Li = 5.39362 \times Ci \times [Q + (1.547 \times Q')]$ (Equation 3)

Where: Li, Ci and Q are defined as in (Equation 1),

And

(1.547) is a conversion factor for discharge:

$$\frac{\text{M gal}}{\text{day}} \times \frac{\text{ft}^3}{\text{7.48 gal}} \times \frac{\text{day}}{\text{86,400 sec}} \times \frac{10^6\ \text{gal}}{\text{M gal}} = 1.547\ \frac{\text{ft}^3}{\text{sec}}$$

Note: Equation 3 is not provided in the AEHA memo.

EXHIBIT C-1

ALLOWABLE POLLUTANT LOADINGS

	Design Low Flow (cfs)	Li (lbs/day) Loading					
		TNT	RDX	HMX	2,4DNT	NG	WP
Badger:							
Wisconsin R	2290	490	370	370	8.7	490	0.12
Cornhusker:							
Silver Creek	0	*	*	*	*	*	*
Prairie Cr.	0	*	*	*	*	*	*
Holston (Area B):							
Holston R.	800	170	130	130	3.0	170	0.043
Indiana:							
Ohio R.	6040	1300	980	980	22.8	1300	0.33
Iowa:							
Brush Cr.	0	*	*	*	*	*	*
Long Cr.	0	*	*	*	*	*	*
Skunk Cr.	30.6	6.6	5.0	5.0	0.12	6.6	0.0017
Joliet:							
Grant Cr.	0	*	*	*	*	*	*
Jordan cr.	No Data	-	-	-	-	-	-
Prairie Cr.	0.1	0.022	0.016	0.016	0.00038	0.022	5×10^{-6}
Kansas:							
Labette R.	0	*	*	*	*	*	*
Neosho R.	<1.0	<0.21	<0.16	<0.16	<0.0038	<0.22	$<5 \times 10^{-5}$
Lonestar:							
Barkman Cr.	0	*	*	*	*	*	*
Aiken Cr.	0	*	*	*	*	*	*
Sulfur R.	0	*	*	*	*	*	*
Louisiana:							
Boone Cr.	0	*	*	*	*	*	*
Caney Cr.	0	*	*	*	*	*	*

EXHIBIT C-1 (cont.)

	Design Low Flow (cfs)	**Li (lbs/day) Loading**					
		TNT	**RDX**	**HMX**	**2,4DNT**	**NG**	**WP**
Bayou Dorcheat	0	*	*	*	*	*	*
Milan:							
Wolf Cr.	0	*	*	*	*	*	*
Rutherford Fork	14	3.0	2.3	2.3	0 .053	3.0	8×10^{-4}
Newport:							
Wabash R.	775	170	130	130	2.9	170	0.042
Picatinny:							
Gr.Pond Brook	1.4	0.30	0.23	0.23	0.0053	0.30	8×10^{-5}
Pine Bluff:							
Arkansas R.	1610	350	260	260	6.1	350	0.087
Radford:							
Stroubles Cr.	8.48	1.8	1.4	1.4	0.032	1.8	5×10^{-4}
New R.	950	210	150	150	3.6	210	0.051
Ravenna:							
Hinkley Cr.	0.1	0.02	0.016	0.016	0.00038	0.022	5×10^{-7}
Sand Cr.	No Data	-	-	-	-	-	-
M.Br.Mahoig	15.3	3.3	2.5	0.25	0.058	3.3	8×10^{-4}
Sunflower:							
Kill Creek	0	*	*	*	*	*	*
Spoon Cr.	0	*	*	*	*	*	*
Captain Cr.	0	*	*	*	*	*	*
Kansas Cr.	3600	780	580	580	13.	780	0.19
Volunteer:							
Tennessee R.	4000	860	650	650	15.	860	0.22

Notes:

* Design low flow = 0 CFS; plant discharge must equal stream standard.

6. DISCUSSION

Exceedance of Allowable Concentrations

Several conditions, either in the stream or due to operation of the waste treatment plant, could result in exceedance or violation of the allowable in-stream concentrations. These are:

- outfall hydraulics
- wastewater discharge rate
- stream flow less than design low flow
- existence of upstream or downstream polluters.

The outfall is the point at which the wastewater is discharged into a stream. In order that maximum concentrations are not exceeded at low flow, the wastewater should be completely mixed with the flow in the stream. Ideally, therefore, the outfall should be designed such that the effluent is evenly distributed across the stream cross-section. In practice, however, this rarely occurs. In general, a mixing length measured downstream from the outfall is the length it takes for the wastewater flow to be completely dilluted by the stream flow. Good design avoids placing outfalls in the part of the stream bed where flow is sluggish or stagnant.

The rate at which the allowable pollutant load is discharged into the stream is also significant. The Li is calculated in lbs/day, but is based on continuous discharge. If the discharge of the equivalent Li is made within a shorter period of time, this would result in a "slug" of highly concentrated waste moving down the stream. For example, if the total Li were discharged in one hour, the resulting stream concentration would be 24 times the allowable Ci. (The concentration would be less if the flow in the stream were greater than design low flow.)

In cases where the actual flow in the stream is less than the design low flow, allowable concentrations would be exceeded. It may be desireable to modify plant operation in times of severe drought to reduce waste loadings.

Li is the allowable load only if the stream concentration of Ci is zero. In the event that another plant is discharging the same pollutants into the same stream, the composite effect of two polluters can be calculated as follows:

$$C_S \; Q_S + C_E \; Q_E = C \; (Q_S + Q_E)$$

$$C = \frac{C_S \, Q_S + C_E \, Q_E}{Q_S + Q_E}$$

Where: C = concentration of the resulting mixture

C_E = waste concentration of the effluent
C_S = waste concentration of the stream
Q_E = effluent flow rate
Q_S = stream flow rate.

Identification of other sources of the same pollutants may influence what state or local standards allow.

7. RECOMMENDATIONS

Recommendations arising from this analysis are discussed below.

- It may be desirable to investigate the fate of explosives once they are discharged into the natural environment. Some questions that could be asked are:
    - Do they decay with time? If so, what is the decay rate?
    - Are they assimilated by living organisms and become more concentrated at higher levels in the food chain?
    - Do they remain dissolved in the water or are they transported to the benthos, for example, and build up local concentrations?
- Various state and local agencies may have guidelines for discharge of these pollutants. These regulations should be investigated for each locality where discharge of pollutants occurs.
- As time and budget allows, more detailed investigation of stream conditions should be pursued.
- Seasonal operation of munitions plants should be considered to reduce pollutant loadings at times in the year when stream flows are normally low. Higher concentrations may be allowed when stream flows are greater than the design low flows.

APPENDIX D

ESTIMATION OF GAC NEEDS AT DIFFERENT FLOW SCENARIOS

EXHIBIT D-1 THROUGH EXHIBIT D-4

EXHIBIT D-1

ESTIMATION OF GAC NEEDS AT FULL MOBILIZATION

STRINGENT EFFLUENT GUILDEINES

POLLUTANT	FREUNDLICH PARAMETERS (1) K	1/N	CONCENTRATION mg/l	SPECIFIC ADSORPTION lbs/lb carbon	SOURCE	REMARKS
TNT	0.337	0.184	0.04	0.182	B-07	
TNT	0.304	0.174	0.04	0.173 (2)	L-01	In mixture with RDX
RDX	0.043	0.18	0.03	0.023 (2)	V-02	In mixture with TNT; Lowest RDX conc. in data 0.9 mg/l
RDX	0.042	0.519	0.03	0.007 (2)	L-01	In mixture with TNT
MIXTURE	0.0248	0.368	0.1017	0.107	B-07	TNT, DNT, RDX, HMX

POLLUTANT	INFLUENT FLOW MGD	INFLUENT CONCENTRATION mg/l	EFFLUENT CONCENTRATION mg/l	REMOVAL mg/l	SPECIFIC ADSORPTION lbs/lb carbon	GAC REQUIREMENT M lbs/yr
TNT	900	150	0.04	149.96	0.173	6.49
2,4-DNT	900	30	0.0007	29.9993	0.173 (3)	1.30
RDX	900	120	0.03	119.97	0.007	129.83
HMX	900	25	0.03	24.97	0.007	27.02
TOTAL						164.64

Notes:

1. From the Freundlich Equation: $(X/m) = KC^{1/N}$
   Where: X/m = specific adsorption, lbs/lb carbon
   K = Constant
   1/N = Constant
   C = Effluent concentration, mg/l
2. Calculated using formula presented in reference.
3. Assume adsorption behavior analogous to that of TNT.

EXHIBIT D-2

ESTIMATION OF GAC NEEDS AT FULL MOBILIZATION

ALTERNATIVE EFFLUENT GUILDEINES

	FREUNDLICH PARAMETERS (1)					
POLLUTANT	K	1/N	TARGET CONCENTRATION mg/l	SPECIFIC ADSORPTION lbs/lb carbon	SOURCE	REMARKS
TNT	0.337	0.184	0.05	0.194	B-07	
TNT	0.288	0.175	0.05	0.171 (2)	L-01	In mixture with RDX
RDX	0.043	0.18	0.25	0.034 (2)	V-02	In mixture with TNT: Lowest RDX conc. in data 0.9 mg/l
RDX	0.043	0.519	0.25	0.021 (2)	L-01	In mixture with TNT
MIXTURE	0.249	0.368	0.325	0.164	B-07	TNT, DNT, RDX, HMX

POLLUTANT	INFLUENT FLOW MGD	INFLUENT CONCENTRATION mg/l	EFFLUENT CONCENTRATION mg/l	REMOVAL mg/l	SPECIFIC ADSORPTION lbs/lb carbon	GAC REQUIREMENT M lbs/yr
TNT	900	150	0.04	149.96	0.170	6.60
2,4-DNT	900	30	0.0007	30.00	0.171 (3)	1.32
RDX/HMX	900	145	0.25	144.75	0.021	51.70
TOTAL						59.62

Notes:

1. From the Freundlich Equation: $(X/m) = KC^{1/N}$
   Where: X/m = specific adsorption, lbs/lb carbon
   K = Constant
   $1/N$ = Constant
   C = Effluent concentration, mg/l

2. Calculated using formula presented in reference.

3. Assume adsorption behavior analogous to that of TNT.

EXHIBIT D-3

ESTIMATION OF GAC NEEDS AT CURRENT FLOW RATES

STRINGENT EFFLUENT GUILDEINES

	FREUNDLICH PARAMETERS (1)					
POLLUTANT	K	1/N	CONCENTRATION mg/l	SPECIFIC ADSORPTION lbs/lb carbon	SOURCE	REMARKS
TNT	0.337	0.184	0.04	0.186	B-07	
TNT	0.305	0.175	0.04	0.173 (2)	L-01	In mixture with RDX
RDX	0.043	0.18	0.03	0.023 (2)	V-02	In mixture with TNT: Lowest RDX conc. in data 0.9 mg/l
RDX	0.043	0.519	0.03	0.007 (2)	L-01	In mixture with TNT
MIXTURE	0.025	0.368	0.101	0.107	B-07	TNT, DNT, RDX, HMX

POLLUTANT	INFLUENT FLOW MGD	INFLUENT CONCENTRATION MG/l	EFFLUENT CONCENTRATION MG/l	REMOVAL mg/l	SPECIFIC ADSORPTION lbs/lb carbon	GAC REQUIREMENT M lbs/yr
TNT	2	150	0.04	149.96	0.173	0.01
2,4-DNT	2	30	0.0007	30.00	0.173 (3)	0.01
RDX	2	120	0.03	119.97	0.007	0.29
HMX	2	25	0.03	24.97	0.007	0.06
TOTAL						0.37

Notes:

1. From the Freundlich Equation: $(X/m) = KC^{1/N}$
   Where: X/m = specific adsorption, lbs/lb carbon
   K = Constant
   1/N = Constant
   C = Effluent concentration, mg/l

2. Calculated using formula presented in reference.

3. Assume adsorption behavior analogous to that of TNT.

EXHIBIT D-4

ESTIMATION OF GAC NEEDS AT CURRENT FLOW RATES

ALTERNATIVE EFFLUENT GUILDEINES

POLLUTANT	FREUNDLICH PARAMETERS (1) K	1/N	TARGET CONCENTRATION mg/l	SPECIFIC ADSORPTION lbs/lb carbon	SOURCE	REMARKS
TNT	0.337	0.104	0.05	0.194	B-07	
TNT	0.288	0.175	0.05	0.171 (2)	L-01	*In mixture with RDX*
RDX	*0.043*	*0.18*	0.25	0.034 (2)	V-02	*In mixture with TNT; Lowest* RDX conc. in data 0.9 mg/l
RDX	0.043	0.519	0.25	0.021 (2)	L-01	In mixture with TNT
MIXTURE	*0.249*	*0.368*	0.325	0.164	B-07	TNT, DNT, RDX, HMX

POLLUTANT	INFLUENT FLOW MGD	INFLUENT CONCENTRATION MG/l	EFFLUENT CONCENTRATION mg/l	REMOVAL mg/l	SPECIFIC ADSORPTION lbs/lb carbon	GAC REQUIREMENT M lbs/yr
TNT	2	150	0.05	149.95	0.171	0.01
2,4-DNT	2	30	0.025	30.00	0.171 (3)	0.01
RDX/HMX	2	145	0.25	144.75	0.021	0.11
TOTAL						0.13

Notes:

1. From the Freundlich Equation: $(X/m) = KC^{1/N}$
   Where: X/m = specific adsorption, lbs/lb carbon
   K = Constant
   $1/N$ = Constant
   C = Effluent concentration, mg/l
2. Calculated using *formula* presented in reference.
3. Assume adsorption behavior analogous to that of TNT.

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