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Removal of Extremely Low Levels of Munitions  
in a Drinking Water Supply

R. Mark Bricka<sup>1</sup> and Wayne Sharp<sup>2</sup>

Abstract

Past military operations have resulted in the contamination of soils by chemical munitions such as RDX, HMX and TNT (contaminant description, page 2). The migration of water through the soils can transport the contaminants into groundwater and contaminate drinking water sources. Many military munitions are known or suspected to be carcinogenic and, therefore, must be removed from drinking water.

This paper addresses the removal of RDX and HMX from a drinking water source at levels of less than 6 parts per billion (ppb) using activated carbon (AC). While the use of AC has been found to be effective in treating wastewater contaminated with levels of munitions from 10 - 100 parts per million (ppm), few studies have addressed the removal of these compounds at ppb levels. The effectiveness of several different types of carbons were compared using batch isotherms. Two of the most effective carbons were studied in pilot carbon tests. The results of the isotherm tests are presented here.

Introduction

Site Description. The site of interest is a military base that was established in the late 1800's. In its early history this facility was used as a powder depot to fill projectiles with miximite (a propellant). Since World War I, this facility was used to produce artillery ammunition, bombs, high explosives, pyrotechnics and other ordinances. Weapons production at this facility has ceased, but as a result of the past activities at this facility contaminants are migrating into the groundwater.

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One source of drinking water for this installation is a screened well in a stratified-drift aquifer system at a depth of 75-85 feet below land surface. In the 1980's sampling of this well revealed low level contamination of trichloroethylene (TCE), RDX and HMX. TCE levels exceeded drinking water standards and an air stripping column was installed to remove the TCE. RDX and HMX concentrations were below drinking water standards. Health Advisory (HA) levels for RDX and HMX were published by the U.S. Environmental Protection Agency (USEPA) in November 1988. The lifetime HA levels are 2 ppb and 400 ppb for RDX and HMX, respectively (McLellan et. al. 1988a, and McLellan et. al. 1988 b). It is expected that continuous withdrawals from this well will increase RDX and HMX concentrations. In addition, it is believed that future USEPA regulations will adapt the HA as a drinking water standard. In an effort to have an appropriate cost effective technology to meet any such standard, this study was initiated.

RDX and HMX. RDX and HMX are military explosives. RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) is a code name for Research Department Explosive. This explosive is described as a white crystalline solid with about 1.3 times the explosive power of trinitrotoluene (TNT). RDX is classified as a EPA Group C compound: Possible Human Carcinogen (McLellan et. al. 1988a). HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is a code name for High Melting Explosive. This explosive is described as a colorless crystalline solid with about 1.3 times the explosive power of TNT. HMX is classified as a EPA Group D compound: Not Classified as to Human Carcinogenicity (McLellan et. al. 1988b).

Objective of Investigation. The objective of this investigation was to determine the feasibility of using granular activated carbon (GAC) to remove low levels of RDX from a drinking water source. The target treatment level in this investigation was to remove RDX to less than 1 ppb in the treated water.

Historical Treatment of HMX and RDX. Until recently, the main concern for the treatment of HMX and RDX was associated with solid waste or wastewater from processing and manufacturing facilities. GAC treatment of these wastes has been know to be effective in removing HMX and RDX from these highly contaminated waste streams to limits which permit discharge. One recently conducted isotherm study by Hinshaw (Hinshaw et. al. 1987), investigated the treatment of synthetic and actual "pink water" (wastewater containing explosive) at HMX and RDX concentration levels around 5 ppm and 20ppm, respectively. At carbon dosages of around 10 mg/l this study indicated little or no removal of the contaminants. In fact substantial treatment did not occur until the carbon dosage exceeded 1000 mg/l.

Another study conducted by Roy F. Weston Inc. (Weston 1990) investigated the use of GAC to treat RDX and TNT contaminated

wastewater from Milan Army Ammunition Plant (MAAP) using isotherm tests. The waste water contained RDX concentration in excess of 450 ppb. Isotherm tests indicated only about 50% removal of the RDX at carbon dosage levels of 10 mg/l. Effective treatment was not achieved until the wastewater was dosed with carbon concentrations in excess of 200 mg/l. At this dosage (200 mg/l) the RDX concentration in the treated effluent was in excess of 3 ppb.

No studies could be found on removing explosives from water which contained low levels (<10ppm) of explosive contaminant. Foust and Aly (1987) reported that "adsorbed quantities at equilibrium usually increase with an increase in the solute concentration." Based on this information and the information from the more concentrated explosive wastewater studies, it was decided that carbon dosages that were higher than those used in the previous studies would be appropriate.

#### Method

Prior to testing 40 gallons of ground water was collected in HPDE plastic containers (5 gallons each). Immediately after collection this sample was transported to a laboratory where were equal portions from each 5 gallon container were transferred to 40 amber glass containers (1 gallon each). A representative sample was collected from two of the containers and was shipped to an offsite lab for analysis. The purpose of this sample was to verify the presence of explosive contaminants. Table 1 presents typical explosive concentrations found in water supply samples used in this evaluation. Samples were stored in amber glass bottles at room temperature for 3 days prior to the initiation of the isotherm tests.

Table 1. Typical Water Supply Explosive Concentration

Explosive Contaminant	Concentration (ppb)
1,3,5-TNB	<DL
1,3-DNB	<DL
2,4,6-TNT	<DL
2,4-DNT	<DL
2,6-DNT	<DL
HMX	1.4
NB	<DL
RDX	5.5
TETRYL	<DL

Five carbons investigated for the adsorption of RDX and HMX are listed in Table 2. These carbons were pulverized by the manufactures prior to testing. To assure that equilibrium

conditions would be obtained at a faster rate. Pulverizing the carbon has no significant effect on its adsorption capacity (Weston 1990). A known weight of dry carbon was added to 1 liter amber glass bottles and 850 ml of contaminated water were added to each bottle. The nominal carbon to water dosage consisted of 10, 100, 500, 1000, and 10,000 mg/l. Due to the low concentration of explosives in the groundwater and possible analytical error, all tests were performed in triplicate and a blank sample was carried through the isotherm tests for each carbon type. In addition, the pH of one set of the Filtrasorb 400 carbon was lowered to 4.0 to investigate the effects of pH on adsorption. After the carbon and water was placed in the containers, the containers were placed on a shaker table and shaken in the horizontal position at 120 cycles per minute for 24 hours.

Table 2. Carbon Types Evaluated in the Isotherm Tests

Manufacture	Carbon Type	Base Material
Westates Carbon Inc.	CC-601	Coconut Shell
Calgon Carbon Corp.	Filtrasorb 200	Bituminous Coal
Calgon Carbon Corp.	Filtrasorb 400	Bituminous Coal
American Norit Co.	Norit ROW 0.8	Extruded Coal
American Norit Co.	Hydrodarco 4000	Lignite Coal

Upon the completion of the 24 hour contact period, samples were removed and the carbon was allowed to settle. The carbon was separated from the liquid using by passing it through a Millipore 0.45 micron filter using vacuum. The filtered samples were placed in 1-liter amber glass jars, sealed with teflon caps, packed in ice, and shipped to an offsite lab for analysis.

### Results

The results of the isotherm tests were averaged for the three runs and are presented in Table 3. All the carbons at each dosage tested, produced results below the detection limit of 0.617 ppb for RDX and 0.869 ppb for HMX. Normally in isotherm testing the data are modeled with either Lagmuir, BET or Freundlich equations. This type of examination provides an estimate of the ultimate adsorption capacity the carbon has for the contaminant (Weber 1972, Clark and Lykins 1989). Unfortunately, since all the data points were below the detection limit, these data did not permit this type of data analysis.

Table 3. Results of the Isotherm Tests

Concentrations		
Carbon (mg/l)	HMX (ppb)	RDX (ppb)
F-200		
BL	1.62	5.77
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617
F-400		
BL	1.88	6.04
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617
pH=4.0	1.630	5.48
BL	<0.869	<0.617
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617
CC-601		
BL	0.523	4.53
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617
ROW 0.8		
BL	1.38	5.78
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617
H-4000		
BL	1.72	5.42
10	<0.869	<0.617
100	<0.869	<0.617
500	<0.869	<0.617
1000	<0.869	<0.617
10,000	<0.869	<0.617

Where: F-200 = Filtrasorb 200  
F-400 = Filtrasorb 400  
Row 0.8 = Norit ROW 0.8  
H-4000 = Hydrodarco 4000

### Conclusions

All carbons evaluated appear to be effective in the removal of low levels of explosives. While it would be beneficial to perform this testing with lower carbon dosages in order to determine carbon loading at equilibrium, substantial data are provided to allow the study to proceed to the pilot column phase. Pilot testing is necessary because adsorption isotherm data only present the maximum carbon loading that can be achieved. Generally, the carbon loading will be lower in pilot column testing, due to fact that this is a dynamic system and the carbon may not achieve equilibrium conditions prior to breakthrough. Pilot column testing, has been initiated and the results of this testing will be presented in a later paper.

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