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## **PART V: Environmental Fate**

### **Chapter 12**

#### **EFFECTS OF REDUCING CONDITIONS ON THE FATE AND TRANSPORT OF RDX IN GROUNDWATER; A MULTIVARIATE APPROACH**

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#### **ABSTRACT**

Groundwater investigations conducted at the Massachusetts Military Reservation (MMR) show the impact of historic activities on the development of groundwater contaminant plumes emanating from military ranges. Several of the plumes, located on the southeastern side of the reservation, contain elevated concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). In most cases, these plumes show continuity from the source to the leading edge, indicating that very little attenuation of RDX is occurring in the aquifer. Interesting exceptions to this trend are locations where plumes consisting of RDX and perchlorate intercept part of the aquifer that was previously impacted by a fuel spill; reducing conditions due to biological activity resulted from this spill. RDX concentrations show a significant positive correlation with both dissolved oxygen and oxidation-reduction potential, and a significant negative correlation with specific conductivity. The distribution of RDX is more consistent upgradient from the oxygen depleted zone and implies that RDX is degrading in the aquifer near the fuel spill. A factor analysis yielded two geochemical (44 percent variability explained) and two contaminant (30 percent variability explained) factors. This suggests that the geochemical nature of the aquifer is the primary source of groundwater parameter variability determined by this investigation.

Keywords: RDX, perchlorate, groundwater contamination, correlation matrix, factor analysis

#### **1. INTRODUCTION**

Investigations of groundwater chemistry and contamination have been conducted on the Massachusetts Military Reservation (MMR) since the mid-1970s. These studies have focused on

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characterization and remediation of contaminated groundwater. The groundwater plumes are located in a sole source aquifer called the Sagamore Lens that occupies the northwestern portion of Cape Cod (Figure 1). The Sagamore Lens is an unconfined aquifer that occupies a series of glacial deposits primarily consisting of outwash as thick as 400 feet over bedrock. The sandy nature of the glacial deposits has created a groundwater setting that is highly transmissive. Therefore, much of the remediation for MMR contamination has focused on source control and groundwater plume extraction and treatment. Efforts to characterize these plumes are of particular interest to this study.

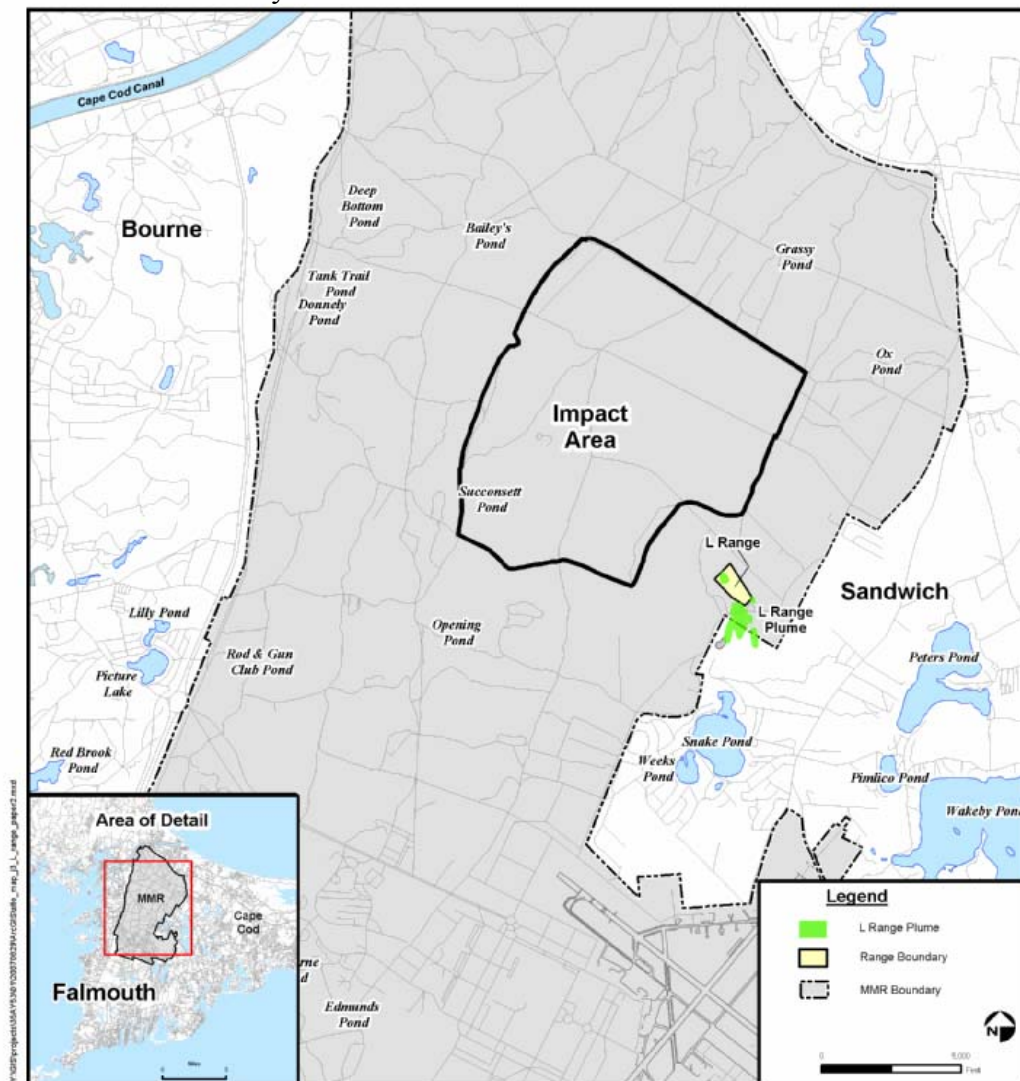


Figure 1. Location of L Range and L Range Plumes on the Massachusetts Military Reservation.

Both the MMR and areas outside the reservation are replete with groundwater wells. These wells have been placed to characterize contaminants in groundwater. Because these wells represent a heavily biased sampling, it is reasonable to ask what these wells are actually characterizing. The example in this investigation consists of a series of contaminant plumes emanating from a military test range on the MMR. This range exhibits groundwater contamination from the explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-

1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and from the propellant perchlorate. Since the groundwater monitoring network was designed to capture the variability of these three contaminants in the aquifer, it is reasonable to ask if this is actually what is shown within the groundwater data set. The purpose of this investigation is to explore what variability is actually characterized and what factors are responsible for this variability.

## **1.1 Site Setting**

The MMR is a military training facility located in the western portion of Cape Cod that covers approximately 22,000 acres (Figure 1). The military began using portions of the MMR in the early 1900s; however, the majority of activity has occurred since 1935. The most intensive military activity at the MMR occurred during World War II.

The geologic setting of the MMR is dominated by Late Pleistocene deposits from processes attributed to the Late Wisconsinan ice front advance and retreat. Deposits on Cape Cod normally date no older than 18,000 to 22,000 years ago when the Laurentide Ice Sheet reached its maximum southward extent to the islands of Martha's Vineyard and Nantucket (Oldale, 2001; Dyke and Prest, 1987; Fletcher, 1993). The geology of the MMR is dominated by an outwash plain known as the Mashpee Pitted Plain. The Mashpee Pitted Plain was formed by streams that drained the Buzzards Bay and Cape Cod Bay glacial lobes (Oldale, 2001). The MMR is located within the Sagamore Lens of the Western Cape Cod aquifer. The Sagamore Lens is an unconfined freshwater aquifer bounded on three sides by salt water: Cape Cod Bay and Cape Cod Canal to the north, Buzzards Bay to the west, and Vineyard Sound to the south.

The L Range was primarily and most recently used as a grenade launcher range. The southern end of the range contains a berm upon which eight firing points are located along the southeastern boundary. The range extends northwest from the berm and there are multiple targets positioned at varying distances around the northern portion of the range. The L Range had been used historically as an infiltration range in the 1940s and 1950s and was converted to a grenade launcher range in the late 1970s. From the late 1980s the L Range was used exclusively as a grenade launcher range until activities were discontinued in 1997. These military activities resulted in the development of groundwater contamination plumes containing elevated levels of perchlorate and RDX downgradient from the range. The top of the groundwater mound is located a short distance northwest of the L Range and the general flow direction is south-southeast from the L Range. The perchlorate and RDX groundwater plumes are diffuse and occur as isolated, noncontiguous zones or lobes detached from upgradient source areas. The maximum perchlorate and RDX concentrations detected in the plumes are 2.8 µg/L and 9.2 µg/L, respectively. HMX has been detected at and less than 1 µg/L. The spatial and temporal distribution of perchlorate and RDX concentrations indicate very stable and attenuating plumes. The varying distance and depth of contamination lobes relative to the L Range footprint between the two primary contaminants suggest that there were multiple source areas, multiple release events, or differences in the chemical-specific subsurface migration and attenuation rates. The data do not indicate a continuing source. These plumes are believed to have been formed from low order detonations of grenades near target areas and subsequent particulate deposition of explosives across the soil surface (ECC, 2005). This particulate deposition has been noted in other range studies (Jenkins et al., 2000a; 2000b; 2001a; 2001b).

An interesting compounding factor is the development of the FS-12 plume. This plume was formed when an aviation fuel pipeline was breached and approximately 70,000 gallons of fuel leaked into the aquifer just south of the L Range. This plume consists primarily of ethylene dibromide and benzene with minor amounts toluene, ethylbenzene, and xylenes (AFCEE, 2001). The L Range plume is co-mingling with the FS-12 plume remnants, and the biological interaction between the former and latter plumes creates a unique geochemical environment that may influence the nature and extent of the L Range plume.

Once in the groundwater, perchlorate, RDX, and HMX are variably subject to transformations based on geochemical conditions. Perchlorate is relatively soluble and is not easily transformed once it reaches the aquifer. Susarla et al. (1999) has shown that the distribution coefficient ( $K_d$ ) values for perchlorate range from 8.91 L/kg to 0.76 L/kg based on the type of organic matter and particle size in the matrix. Perchlorate does not adsorb readily to the soil matrix mineral fraction or organic fraction, and its transport is relatively rapid when it reaches groundwater. Perchlorate is not readily degraded by chemical or biological means. There is some indication of microbial reduction of perchlorate (Logan et al., 2001), but conditions in nature are relatively rare. In some bench scale tests, perchlorate has been shown to biodegrade under anaerobic conditions (AFCEE, 2002a). Regardless, perchlorate is a compound that migrates rapidly through groundwater with little degradation and is the most mobile contaminant in groundwater at the MMR.

RDX and HMX are not readily retained in the soil fraction and migrate to groundwater relatively rapidly. Reported  $K_d$  values for RDX under variable soil conditions ranged from 0 to 6.75 L/kg (Selim and Iskander, 1995; Townsend and Meyers, 1996; McGrath, 1995), and  $K_d$  values for HMX ranged from 0 to 13.25 L/kg (Townsend and Meyers, 1996). The highest  $K_d$  values for HMX are associated with reducing environments (Price et al., 2001). RDX and HMX are transformed anaerobically in the groundwater environment (Price et al., 1998; McCormick 1984). RDX and HMX are cyclic nitrogen-containing compounds that are moderately resistant to aerobic degradation and undergo ring cleavage and extensive mineralization (Hawari, 2000). Anaerobic degradation of RDX and HMX involves direct microbial reduction of the nitro functional groups on the cyclic structure. This process has been used to develop remedial strategies employing microbial degradation to address RDX and HMX contamination in groundwater (Kwon and Finneran, 2006; Young et al., 2006; Morley et al., 2002; Doppalapudi et al., 2002).

## 1.2 Background

Samples from the L Range groundwater study area were initially investigated using a correlation assessment. Correlation is a statistic that measures the strength of a relationship between two variables, quantified by the correlation coefficient ( $r$ ). The correlation coefficient is a linear association between variables  $x$  and  $y$ . Correlation coefficients range from -1.0 to 1.0 with these extremes being the strongest negative and positive correlations respectively. No correlation between two variables would be represented by a correlation coefficient of 0.0. These correlation coefficients are then arranged in a correlation matrix to provide an overall perspective of how all of the variables in a dataset relate to each other. Correlation analyses are

sensitive to non-normality, and mathematical transforms are recommended to normalize non-normal data sets.

An integrated multivariate investigation was used to provide an overall picture of contaminant trends in the L Range plumes. Unlike a series of independent comparisons involved in constructing a correlation matrix, a multivariate investigation compares several variables in a single analysis with the goal of isolating trends in complex environmental data sets. This is accomplished with a multivariate factor analysis.

Factor Analysis, like the statistically similar Principal Components Analysis, is an exploratory multivariate method that can be used to explain the relationships among several variables. In the simplest sense, the Factor Analysis method arranges the sites and environmental variables in multidimensional space. Factor Analysis captures variability through the use of eigenvectors, which define linear factors that capture the maximum variability (i.e., environmental gradients) in a multivariate data set. Factor Analysis calculations result in clustering of sites (wells) based on their environmental similarity. In such an analysis, samples that occur close together have similar environmental characteristics, and samples that plot far apart are environmentally different. Likewise, environmental variables that lie near a specific variable tend to be “high” in that variable, and lower in others. Factor Analysis is particularly useful because it can provide a visual assessment of a large matrix of complex data by displaying relationships among variables and sites.

The Factor Analysis method extracts “principal components,” also known as “factors” that explain variation in the data. The first axis explains the greatest amount of variance (i.e., has the highest eigenvalue). The second axis captures the second most important amount of variance orthogonal to the first axis. The third axis is orthogonal to the first two axes, and it captures the next most important component of the remaining variance. Factor Analysis deviates from Principle Components Analysis in that after the eigenvectors are defined, the factors are “rotated” to optimize the capture of the variability in the data set. This is accomplished through a varimax rotation that maintains the same orthogonal relationship as the original eigenvectors. If desired, Factor Analysis calculations may continue until only random variation remains, but in most environmental data sets, four or fewer factors often explain most, if not all, of the nonrandom variation. In turn, the factor scores can be calculated for each data point (well), and predicted factor scores can be calculated for each well and plotted in multiple dimensions. Generally, eigenvalues that are greater than one are retained, and factors that explain a cumulative variation between 80 and 90 percent are considered important (Manly, 1991).

Statistical analyses of groundwater have long provided insight into the distribution of analytes within a defined aquifer or groundwater location of concern. Gonçalves et al. (2007) used a factor analyses to determine the effect of agricultural practices on distribution of pesticides and their impacts on water quality in Portugal. They found that five principal components were attributed to environmental and agrochemical managing factors. The distribution of pesticides detected in groundwater was related to the character of local agricultural practices. Chen et al. (2006) examined 17 trace elements in groundwater samples from Shenzhen, China. Their principal components analysis found that the oxidizing and reducing conditions in the aquifer were primarily responsible for the distribution of metals in the aquifer and that the seasonality of the groundwater sampling was of lesser importance in defining

this variability. A Factor Analysis study of groundwater at a landfill site in Nagpur, India (Pujari and Deshpande, 2005) showed that five factors (including geological setting, leaching from host rock, leachate of heavy metals from the landfill, and bacterial contamination from the landfill) were responsible for the variability in this aquifer. A Factor Analysis conducted on groundwater in the Everglades National Park (Muñoz-Carpena et al., 2005) examined the variability of nitrate, phosphate, fluoride, and chloride anions. They found that nitrate and phosphate compounds were affected by water table depth, enriched topsoil, and occurrence of a leaching rainfall event. The Factor Analysis indicated that leaching by rainfall was the main mechanism explaining concentration peaks in groundwater. A groundwater Factor Analysis was applied to 13 hydrochemical parameters in Taiwan to determine the causes of variability in a blackfoot disease area (Liu et al., 2003). The study isolated two factors (seawater salinization and arsenic pollutant) that explained almost 78 percent of the variability. This study found that overpumping of groundwater led to subsidence, which caused introduction of more saline seawater into the water supply, thus possibly causing complicating health problems. A study by Reghunath et al. (2002) of groundwater in Karnataka, India showed that variability, defined by a Factor Analysis, could be attributed to various degrees of mixing between river and groundwater. A study in northwest Peloponnesus, Greece used Factor Analysis to explain the variability in a Plio-Pleistocene aquifer (Voudouris, et al., 1997). This study found that seawater intrusion and possible groundwater-halite interaction was responsible for the variability of analytes in the aquifer. A study of groundwater in Western Nigeria (Olobaniyi and Owoyemi, 2006) used factor analysis to understand the variability in the deltaic plain sands aquifer, and study isolated three factors: the first factor was interpreted to reflect the signature of saline water incursion resulting from seepages into the aquifer from the tide-influenced River Warri. The second factor was attributed to the processes of natural rainwater recharge and water-soil/rock interaction. The third factor was related to the dissolution of sulfides from interstratified peat within the geological formation. A Factor Analysis study in the Mogi-Pardo watershed in Brazil (Invernizzi and Barros de Oliveira, 2004) found that two factors explained the variability in the groundwater dataset. The first factor represented the flushing of evaporate minerals, and the second factor represented the progressive interaction between the water and the Botucatu Formation along the flow gradient from the recharge zone to the zone confined by basalt lavas. It is interesting to note that the theme among all of these studies is that geochemical variability in the aquifer is often the most important factor in defining the variability, particularly among contaminants in groundwater.

## 2. METHODS AND MATERIALS

Data for the multivariate investigation were collected from monitoring wells and groundwater screening borings in the vicinity of the L Range. Groundwater samples were collected in accordance with approved workplans (AMEC, 2004) and were analyzed for explosives by U.S. Environmental Protection Agency (EPA) Method SW846/8330 and for perchlorate by EPA Method E314.0. Metals analyses were conducted using EPA Method SW846/60108/7470A, and field parameters were collected using a Yellow Springs Instrument water analyzer with a flow through cell. Wells used in the study were installed as part of the L Range characterization and are presented on Figure 2. All monitoring well locations were surveyed, and horizontal position was referenced to the North American Datum of 1983,

Universal Transverse Mercator Zone 19 North in meters. The vertical datum was referenced with an accuracy of 0.005 ft vertical/horizontal control to the North American Datum of 1927 in feet. Summary statistics for L Range groundwater is presented in Table 1.

Table 1. L Range Groundwater Summary Statistics

Parameter	n	Mean	Median	Range
<b>RDX (µg/L)</b>	354	0.58	ND	ND to 9.2
<b>HMX (µg/L)</b>	352	ND	ND	ND to 0.8
<b>Perchlorate (µg/L)</b>	315	ND	ND	ND to 2.8
<b>Total Fe (µg/L)</b>	20	23,800	74.25	ND to 99,400
<b>Total Mn (µg/L)</b>	20	475	60.8	ND to 2,260
<b>Temperature (°C)</b>	335	11.37	11.10	4.5 to 18.7
<b>pH</b>	344	5.77	5.78	4.06 to 7.17
<b>DO (mg/L)</b>	362	6.98	8.66	0.08 to 15.97
<b>ORP (mV)</b>	99	192	213	-238 to 507
<b>SpC (µS/cm)</b>	343	105	74	38 to 554
<b>Turbidity (ntu)</b>	289	3.08	1.22	0 to 65.9
<b>Elevation (ft msl)</b>	423	3.80	8.74	-127.84 to 70.04
<b>Northing (m)</b>	423	-	-	484
<b>Easting (m)</b>	423	-	-	1230

Data from 425 groundwater samples collected from 42 well locations (many of which contain multiple screens) between January 1998 and May 2007 were used in this investigation. For the statistical analyses, the non-detect data were transformed to one-half the detection limit. The data were screened for outliers; however, none were removed from the dataset. After these treatments, the data were subjected to Correlation Analysis and Factor Analysis.

Intervariable comparisons were made for analyte pairs (e.g., RDX vs. perchlorate, or HMX vs dissolved oxygen [DO]) measured in the L Range study area. A correlation matrix was generated to address information about relationships among specific parameters. These parameters included RDX, HMX, perchlorate, total iron, total manganese, DO, oxidation-



reduction potential (ORP), pH, temperature, specific conductivity (SpC), turbidity, easting coordinate, northing coordinate, and elevation. Because not all locations were analyzed for all parameters, there were a number of null data points in the measured data set, so the number of pairwise comparisons in correlation calculations ranged from 423 (northing vs easting) to 13 (manganese vs. ORP). The Spearman Ranked Correlation procedure was used for this analysis. This is a nonparametric procedure used when data distributions express nonlinearity that would affect parametric tests. This procedure was used because many of the data points for perchlorate, RDX, and HMX were below the detection limits, assuring a non-normal distribution of values. In general, a greater number of pairwise comparisons increases the statistical strength of the correlation analysis. A value of 0.0 indicates no correlation between variables. A value of  $\alpha = 0.05$  was chosen as the significance level for this analysis.



Figure 2. Location of L Range Groundwater Study Area, Factor Analysis Groundwater Zones, and anoxic zone.

The Factor Analysis procedure for this investigation used the following variables: perchlorate, RDX, HMX, pH, temperature, DO, ORP, SpC, turbidity, northing, easting, and elevation. The Factor Analysis procedure required that all cells be filled for each row; therefore, a missed analyte removed that sampling point data from the analysis. Because sampling of explosives and perchlorate were sometimes on different schedules, a large number of observations were removed from the analysis because perchlorate was frequently sampled on a different date than explosives. A total of 48 observations were retained for the Factor Analysis due to their data completeness.

### **3. RESULTS**

The statistical analyses performed for groundwater samples from L Range indicated that the chemistry of the aquifer was the primary factor affecting the variability that is observed within the aquifer. The distribution of contaminants (perchlorate, RDX, HMX) is not only a result of anthropogenic deposition, but also the result of post-depositional processes that govern the nature of these groundwater plumes.

The correlation analysis for perchlorate indicated that this analyte had a significant relationship to a few other parameters (Table 2). Perchlorate was significantly positively correlated with RDX ( $r = 0.167$ ), temperature ( $r = 0.183$ ), and DO ( $r = 0.126$ ). This relationship reveals that there is some co-location of perchlorate (a propellant) with RDX (an explosive) and indicates either similar depositional processes or extensive co-mingling of the plume. The high correlation with temperature is primarily a result of the shallow nature of the perchlorate contamination because the temperature in the aquifer decreases with depth. The high correlation with DO indicates that the perchlorate contamination, found mainly in the western portion of the L Range plumes (Figure 2) is located in an area not affected by the reducing conditions caused by the FS-12 Plume farther east.

The correlation analysis shows that RDX and HMX are significantly positively correlated with each other ( $r = 0.635$ ), indicating that these two explosive compounds are likely from the same source(s) (Table 2). RDX and HMX are significantly negatively correlated with SpC ( $r = -0.186$  and  $-0.128$ , respectively) and temperature ( $r = -0.133$  and  $-0.209$ , respectively). The negative correlation between SpC and each of these explosives is likely due to the contaminants' preference for the more oxic portions of the aquifer and, therefore, lower concentrations of soluble metals and lower SpC values. The negative correlation with temperature could be an indication of the location of these compounds in the deeper portions of the aquifer where temperatures are cooler. This is also observed in the negative correlation between RDX and elevation ( $r = -0.322$ ), confirming the higher occurrence of RDX in the deeper portions of the aquifer. This could be the result of RDX source areas farther upgradient and thus occupying the lower portions of the aquifer with increasing distance from the source. In addition, RDX has high positive correlations with DO and ORP ( $r = 0.157$  and  $0.233$ , respectively). Because RDX is likely to decompose under reducing conditions, this correlation is reasonable (Table 2)

Table 2. Correlation Matrix for L Range Groundwater

	P erc	R DX	H MX	F e	M n	p H	T emp	D O	O RP	S pC	T urb	N orth	E ast	E lev
P erc	1. 000													
R DX	0. 167	1. 000												
H MX	- 0.018	0. 635	1. 000											
F e	- 0.313	- 0.393	- 0.379	1. 000										
M n	- 0.567	- 0.050	- 0.359	0. 756	1. 000									
p H	- 0.101	- 0.088	- 0.051	0. 620	0. 736	1. 000								
T emp	0. 183	- 0.133	- 0.209	0. 111	0. 430	- 0.187	1. 000							
D O	0. 126	0. 157	0. 039	- 0.681	- 0.893	- 0.465	- 0.030	1. 000						
O RP	0. 077	0. 233	0. 079	- 0.453	- 0.445	- 0.440	- 0.013	0. 676	1. 000					
S pC	- 0.086	- 0.186	- 0.128	0. 775	0. 552	0. 329	- 0.011	- 0.643	- 0.640	1. 000				
T urb	- 0.115	- 0.025	0. 077	0. 912	0. 750	0. 266	- 0.033	- 0.241	- 0.131	0. 181	1. 000			
N orth	0. 094	0. 072	0. 022	0. 491	0. 511	- 0.026	0. 001	0. 228	0. 300	- 0.240	- 0.020	1. 000		
E ast	- 0.007	- 0.116	- 0.110	0. 628	0. 861	0. 240	0. 068	- 0.540	- 0.363	0. 439	0. 209	0. 031	1. 000	
E lev	- 0.095	- 0.322	- 0.103	0. 660	0. 373	- 0.054	0. 034	- 0.146	- 0.299	0. 381	- 0.097	0. 232	0. 187	1. 000

Notes: Coefficients in **BOLD** are considered significant at alpha = 0.0

Total iron and manganese concentrations were included in the correlation analysis because these metals are sensitive to reducing conditions and are generally more common in anoxic portions of an aquifer. The development of the FS-12 plume, located downgradient from the L Range, provided a carbon source for bacteria; from its benzene, toluene, ethylbenzene, and xylenes (AFCEE, 2001). This fuel spill created an anoxic to suboxic zone in the aquifer (Figure 2). As expected, total iron and manganese are significantly positively correlated with SpC and each other, and are significantly negatively correlated with ORP and DO (Table 2). There is also a significant positive correlation with both pH (which is interpreted as an indicator of biological activity) and turbidity. The turbidity could be related to fines in the aquifer that bear these metals, but it could also be attributed to by-products of biological degradation. The correlation coefficients for these two metals are much higher than the correlation coefficients for the explosives and perchlorate. This is partially due to a lower number of samples, which makes higher correlation coefficients necessary to meet the level of significance. It is also important to note that there is only one significant correlation between total manganese and perchlorate. In fact all of the correlations between these metals and the explosives are negative but insignificant, indicating that these analytes do not necessarily occupy the same portions of the aquifer. This analysis confirms that there is an active anoxic zone in the aquifer located downgradient from the L Range that has a significant effect on the aquifer's geochemistry.

The Factor Analysis also showed that the aquifer's geochemistry is the primary factor dictating the distribution of contaminants in the aquifer (Table 3). A total of five factors were identified that explained more than 87 percent of the variability in the data set. The first factor explains approximately 25 percent of the total variability, and this factor is loaded on two geochemical parameters. Factor 1 is mostly influenced by the easting of the well with contributions from both DO and SpC (Table 3). The negative easting and SpC and the positive DO factor loadings demonstrate that increasing DO is negatively associated with easting and SpC which shows that the areas of the aquifer with low SpC and high DO occupy the more western portion of the site. This indicates that the presence (or absence) of reducing conditions in the aquifer is primarily responsible for the variability of the parameters used in this Factor Analysis. One of the unique qualities of a Factor Analysis is that the varimax rotation strengthens the factor loadings, and these combinations of variables can be interpreted and named (Manly, 1991). In this case, Factor 1 would be the oxic/anoxic water quality factor.

Factor 2, which explains almost 20 percent of the variation in the dataset, has factor loadings on the pH and turbidity parameters (Table 3). The pH in this aquifer has two major sources of variability. First, there is a low to high pH gradient with depth that has been noted in other MMR studies (ECC, 2006). This gradient has been attributed to recharge by acid rain and the influx of organic acids released by the predominantly acid-soil tolerant vegetation on the MMR. Higher pH values are also noted in other areas of the MMR exhibiting elevated biological activity, such as near fuel spills and sewage discharge areas (AFCEE, 2001; 2002b). Factor 2 is determined to be biological because the combined higher pH and turbidity are associated with biological activity in the reducing zone (i.e., the remnants of the former fuel spill). The pH in the reducing zone can be raised by iron bacteria, which form ammonia by metabolizing certain protein or protein derived materials and synthesize alkali hydroxyl groups by consuming the salts of organic acids. The presence of these bacteria and by-products can lead to occlusion and increased turbidity.

Table 3. Eigenvalues and Factor Loadings for L Range Groundwater

Factor	1	2	3	4	5
Eigenvalue	1.90593	1.51169	1.36542	1.02061	0.89083
Variability Explained (%)	24.65	19.55	17.66	13.20	11.52
Cumulative Variability (%)	24.65	44.2	61.86	75.06	86.58
Factor Loadings After Varimax Rotation					
Perchlorate	0.162871	-0.045954	<b>0.775064</b>	0.063321	-0.063346
RDX	0.034555	-0.165173	0.027123	<b>-0.528309</b>	-0.138301
HMX	0.186822	-0.115209	-0.22436	-0.201112	-0.144153
pH	-0.211025	<b>0.859164</b>	-0.011842	-0.053552	-0.056475
Temperature	-0.377075	-0.293366	<b>0.457436</b>	0.017534	-0.251397
DO	<b>0.713282</b>	-0.144288	0.012391	-0.241942	-0.350318
ORP	0.232568	-0.156122	-0.200806	-0.249305	-0.344063
SpC	<b>-0.594435</b>	-0.017736	<b>0.663904</b>	0.186991	0.234547
Turbidity	-0.105161	<b>0.662933</b>	-0.096222	0.143898	-0.123877
Northing	0.115200	0.234282	0.057466	-0.087637	<b>-0.676596</b>
Easting	<b>-0.845562</b>	0.248292	-0.091189	-0.038476	-0.018001
Elevation	-0.032654	-0.208017	0.227928	<b>0.712981</b>	-0.104661

A plot of factor scores between Factor 1 and Factor 2 shows how the wells in the eastern, central and western portions of the study area arrange themselves in two-dimensional space (Figure 3). The wells were organized according to their location (east, central, west) or whether they had measurable levels of contaminants (i.e plume vs. non-plume wells). In general, the eastern area contained the RDX plumes, the western area contained the perchlorate plumes, and the central area contained one location (two wells) that had measurable levels of HMX (as shown in Figure 2). Figure 3 shows how the eastern areas (i.e., the RDX plumes) plot to the left in the direction of higher SpC values and lower DO values, and the western areas (i.e., the perchlorate plumes) plot toward the lower right quadrant in the direction of higher DO and lower SpC values. A line divides the eastern portion into two sections on Figure 2. The left side of the line represents eastern portion wells where RDX has not been detected since 2002 and the right side of the line represents eastern portion wells that have had RDX detected after 2002. The eastern portion wells on the left had side of the dividing line are all located within the portion of the aquifer characterized by reducing conditions. This is the reason the eastern portion wells plot in the same direction as the non-plume wells because RDX is degrading over time. The Factor 2 axis is weighted with pH and turbidity, therefore, as expected, the western portion of the study area plots in the lower half of the graph and the eastern, perchlorate free zones plot in the upper half. The central portion plots as a subsection of the western portion and this part of the aquifer is likely related to the western portion based on Factors 1 and 2. The non-plume portion plots in the upper left quadrant, indicating that these wells are high primarily in pH and turbidity. It is important to note that there is a relationship between non-plume areas and the presence of biologically active reducing conditions.

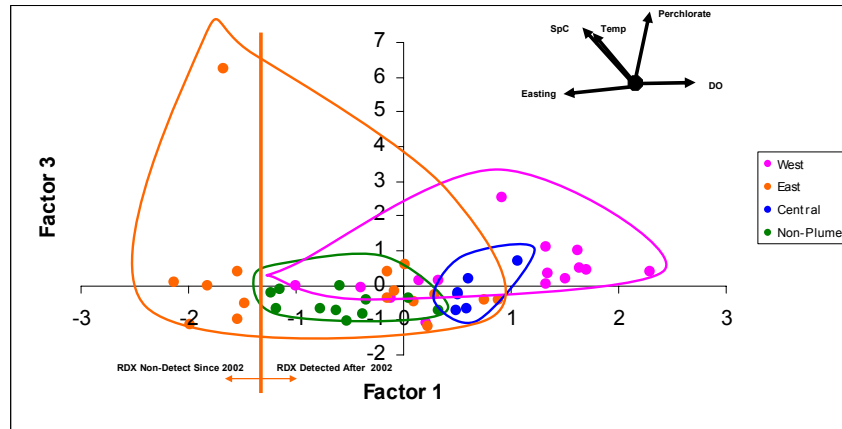


Figure 3. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 2

Factor 3 is weighted mostly on perchlorate concentrations, temperature, and SpC, making this the perchlorate factor (Table 3). This factor accounts for approximately 16 percent of the variability in the groundwater dataset; and indicates that portions of the aquifer with elevated perchlorate, groundwater temperatures, and SpC differentiate from lower perchlorate, lower temperature, and lower SpC portions of the aquifer. An examination of the plots of Factor 1 vs. Factor 3 (Figure 4) with Factor 1 on the x-axis and Factor 3 on the y-axis shows how Factor 3 helps define the groundwater areas. The central area, with measurable HMX concentrations, plots as a subset of the western area. The western portion of the study area plots to the upper right quadrant toward high perchlorate and high DO, while the eastern portion plots to the left toward low perchlorate and high SpC. The non-plume area plots as a subset of the eastern portion of the study area. This graph mainly shows the difference between areas with measurable levels of perchlorate and areas devoid of perchlorate.

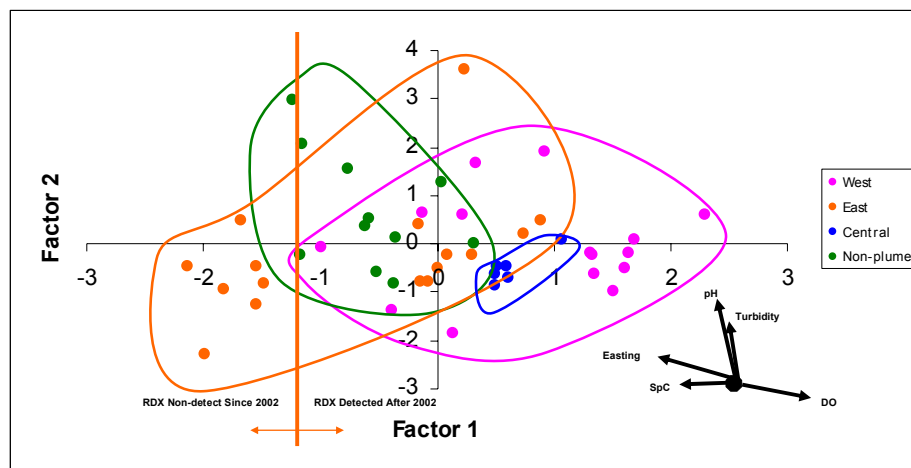


Figure 4. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 3

Factor 4 is negatively loaded on the RDX parameter and positively loaded on the elevation parameter (Table 3). Factor 4 is the RDX factor, and implies that there is a general increase in RDX values with depth. This factor explains almost 13 percent of the variability in the dataset.

Figure 5 shows a plot between Factor 1 and Factor 4. While much of the discrimination is along the x-axis (Factor 1), the eastern portion of the aquifer shows a tendency to plot in the direction of high RDX and increased depth. The western, central, and non-plume areas plot more in the direction of the upper half of the graph. It is interesting to note that the left hand side of the eastern portion dividing line shows that the wells where RDX was not detected after 2002 plots similarly to non-plume wells. Therefore, the variability explained by Factor 4 is primarily due to the increased presence of RDX with depth in the plume.

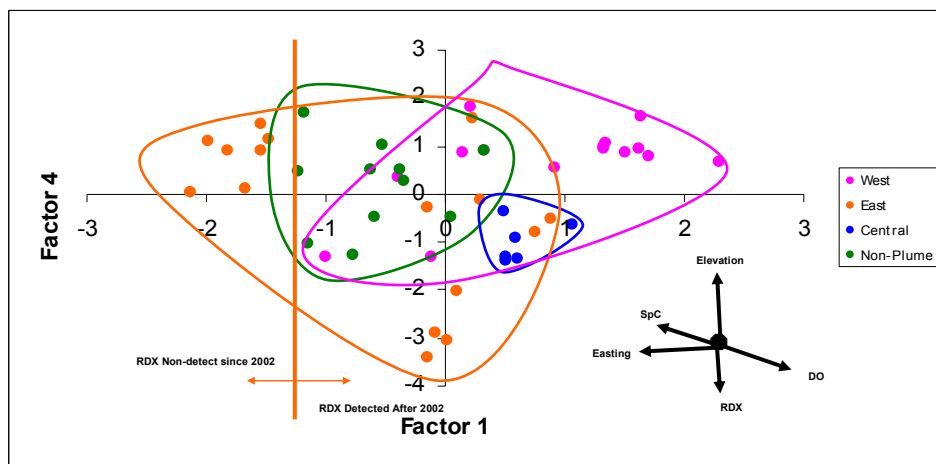


Figure 5. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 4

The remaining Factor 5 explains almost 12 percent of the variability and is weighted on a single variable, northing (Table 3). This factor is negatively weighted with all other factors based on a comparison to the contaminants and indicates that there is a relationship between the north to south well location and decreasing to increasing contaminant concentrations. The correlation analysis (Table 2) indicates that the DO, ORP, and SpC have the strongest relationship to the northing parameter with decreasing values of DO and ORP and increasing values of SpC from north to south.

#### 4. DISCUSSION

The results of the Correlation and Factor Analyses indicate that there is a relationship between the geochemistry of the aquifer and the distribution of contaminants in the aquifer downgradient from the L Range. The correlations between the contaminants (i.e., perchlorate, RDX, and HMX) and geochemical parameters (e.g., DO, ORP, and SpC) indicate that the geochemical parameters are of primary importance in determining the distribution of the contaminants in the aquifer. Significant correlations between RDX and the parameters related to oxidizing and reducing conditions in the aquifer show the importance of a former fuel spill in characterizing the distribution of the contaminants. The biological interaction with the fuels from the FS-12 plume has created a zone of water that, due to oxygen depletion by biological organisms, is a chemically reduced area in the aquifer. In turn, these reducing conditions create an environment conducive to reducible metal solubility. Under oxygen depleted conditions, easily reducible metals such as iron and manganese, tend to go into or remain in solution rather

than precipitate into the solid phase. This increases the electrical conductivity of the water downgradient from the fuel spill. The relationship between perchlorate, RDX, and HMX with these geochemical conditions has potential implication for the distribution of these contaminants in the aquifer. Generally, the concentrations of perchlorate, RDX, and HMX are lower inside and higher outside of the FS-12 source area. This relationship implies that RDX and HMX are degrading in the aquifer near the fuel spill. Perchlorate is absent in the area of the fuel spill mainly because it occupies a flow path that is west of the low DO area. Biodegradation is one explanation for the decreasing levels of RDX and HMX near the fuel spill. An alternative explanation is the reduction of nitroaromatic compounds to primary amines by an oxidation-reduction reaction with metals where the reduced metals act as a reducing agent and the nitro-compounds are reduced. A third explanation for higher RDX and HMX concentrations north of the FS-12 plume could be the attenuation of explosives through dispersion.

The primary source of contamination at the L Range area is probably from historical use of grenades and possibly mortars to produce localized discrete areas of contamination. A conceptual site model for the L Range is presented in Figure 6. During use, explosives would have detonated near targets and propellants would have accumulated near the firing points. The sources would have accumulated particulates on or near the ground surface. Groundwater modeling (ECC, 2005) suggests that rather than a widespread diffuse source, fewer small area sources of higher concentration may have dispersed particles or larger pieces, and infiltration would act to dissolve the constituent compounds and transport them to groundwater. The heterogeneous nature of the source deposition combined with the episodic pattern of infiltration would have resulted in a heterogeneous (in both space and time) contaminant source to groundwater. On the soil surface or in the aerobic vadose zone, little degradation of RDX, HMX or perchlorate would have occurred.

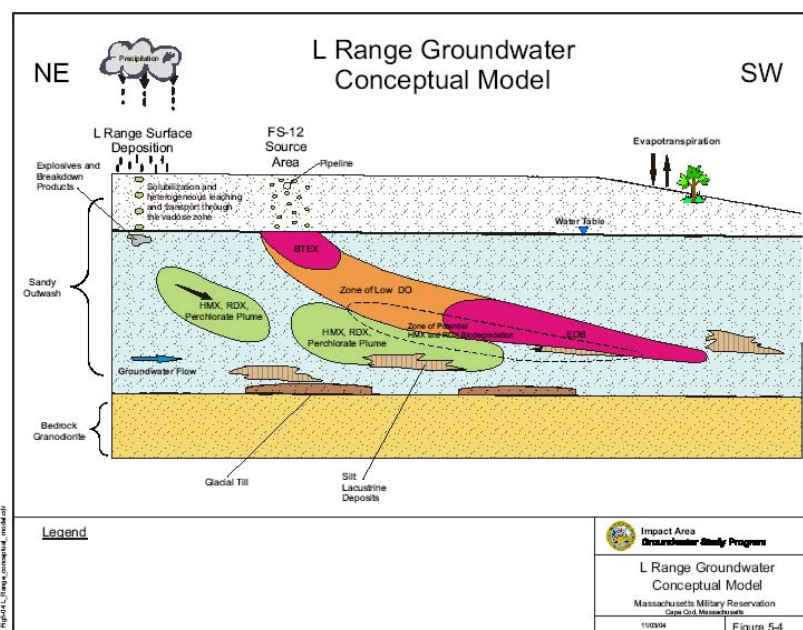


Figure 6. L Range Site Groundwater Conceptual Model (Source: ECC 2005).



Once in the saturated zone, RDX, HMX, and perchlorate migrate under the influence of the flow patterns, which are generally south to southeast. Because both RDX and HMX can be degraded under anaerobic conditions, any local anaerobic conditions due to the FS-12 plume may facilitate the degradation of the RDX and HMX, and hence contribute to the laterally and vertically discontinuous distribution of RDX and HMX in L Range groundwater. Statistical correlations between RDX and HMX with parameters such as DO and ORP (positive) and SpC (negative) indicate these compounds' preference for the more oxic portions of the aquifer. This may also indicate that the absence of these compounds in the anaerobic portions of the aquifer means the breakdown of these compounds. The results of the Factor Analysis show that Factor 1, the oxic/anoxic aquifer quality factor, is the primary factor that defines the variability of the parameters within the L Range aquifer. The second derived factor is a biological factor weighted on pH and turbidity. These geochemical properties explain more than 44 percent of the variation in the groundwater dataset. The third and fourth factors are perchlorate and RDX factors and explain more than 30 percent of the variation. Although they are of lesser importance, their contribution to variability is significant based on the Factor Analysis. Therefore, the sampling design for the L Range groundwater not only accomplished its goal of defining the distribution of contaminants in the aquifer, but also managed to show that the geochemical parameters are of the utmost importance in defining the distribution of all parameters within the aquifer.

## 5. CONCLUSIONS

Many of the investigations on the MMR, including those on the L Range, have emphasized the placement of groundwater wells in order to characterize the contamination emanating from the various source areas. It has been assumed that this monitoring design is biased toward capturing the variability of contaminants within each of the plumes. However, multivariate studies of groundwater indicate that the primary factors regarding variability of parameters in groundwater are related to the geochemical nature of the groundwater. This is important in L Range groundwater because a known area of the aquifer is characterized by low DO, low ORP, and high SpC downgradient from the L Range. A correlation analysis of groundwater parameters shows that there is a significant correlation between RDX and several geochemical parameters. In general, RDX is positively correlated with DO and ORP and negatively correlated with SpC. One of the implications is that RDX is preferentially found in the more oxic portions of the aquifer. Because the RDX plumes in the eastern portion of the study area co-mingle with the reducing conditions promulgated by a former fuel spill, it is possible that RDX is breaking down when this contaminant migrates into the portion of the aquifer where reducing conditions prevail. A multivariate factor analysis showed that the first two factors that explained 44 percent of the total variability were related to the reducing conditions in the aquifer and the biological activity associated with these reduced zones. The contaminants perchlorate and RDX were captured in the next two most important factors and accounted for approximately 30 percent of the variability in the data set. Therefore, the geochemical nature of the aquifer is the most important influence on the distribution of contaminants in the L Range plumes. While the monitoring well placement design functions well in defining the nature and extent of perchlorate, RDX, and HMX contamination downgradient from the L Range, the sampling design was instrumental in demonstrating how important the geochemistry of the aquifer is in defining the distribution of contaminants.

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