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# Factor Analysis Reveals Effects of Reducing Conditions on the Fate and Transport of RDX in Groundwater

## **Cover Page Footnote**

The authors wish to thank the Army Environmental Center Impact Area Groundwater Study Group, Camp Edwards, Massachusetts; and the U.S. Army Corps of Engineers, New England District, Concord, Massachusetts, for access to the data collected in the L Range studies and for their comments on the manuscript. These agencies provide the technical expertise and funding for the past and continuing L Range groundwater monitoring program.

# FACTOR ANALYSIS REVEALS EFFECTS OF REDUCING CONDITIONS ON THE FATE AND TRANSPORT OF RDX IN GROUNDWATER

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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 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.

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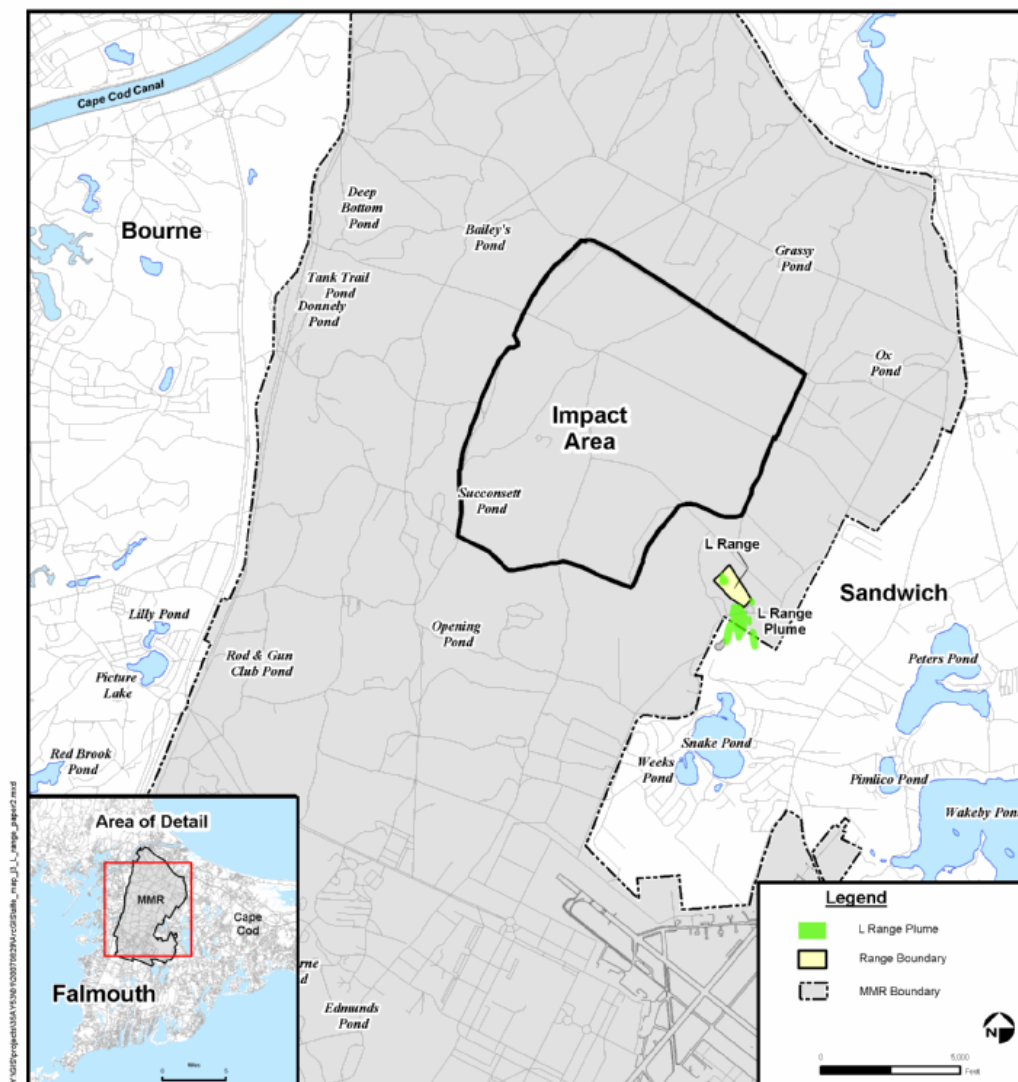


Figure 1. Location of L Range and L Range Plumes on the Massachusetts Military Reservation.

Both the MMR and nearby areas outside the reservation are replete with groundwater monitoring wells that were installed to characterize the nature and extent of MMR-related contaminants in groundwater. The subject of this investigation consists of a series of contaminant plumes emanating from a military test range (e.g. the L 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 for these plumes was designed to capture the variability of these three contaminants in the aquifer, it is reasonable to ask if only the variability in the three contaminants is actually what is shown within the groundwater data set. It is possible that variability in other groundwater components is captured as well. The purpose of this investigation is to explore what variability is actually characterized and what factors are responsible for this variability.

## 2. 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 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 aquifer that occupies a series of glacial deposits primarily consisting of outwash as thick as 400 feet over bedrock. The Sagamore Lens is 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 used historically as a troop infiltration practice 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. 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 military activities conducted at this site 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 plumes that are detached and attenuating, consistent with a depleted source. The varying transport distance and depth of the contamination lobes of the two primary contaminants relative to the L Range footprint suggest that there were: (1) multiple source areas, (2) multiple release events, or (3) differences in the chemical-specific subsurface migration and attenuation rates. 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).

The development of the Fuel Spill-12 (FS-12) plume has complicated attempts to identify the processes that have affected the nature and extent of the explosives plumes emanating from the L Range. The FS-12 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 (particularly under aerobic conditions) 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). Because  $K_d$  values are variable under variable soil organic matter contents, the lower  $K_d$  values for RDX and HMX would be more applicable to characterizing the thin, low organic, sandy soils of the MMR. 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 et al., 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).

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 2. 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. Once in the saturated zone, RDX, HMX, and perchlorate migrate under the influence of the flow patterns, which are generally south to southeast.

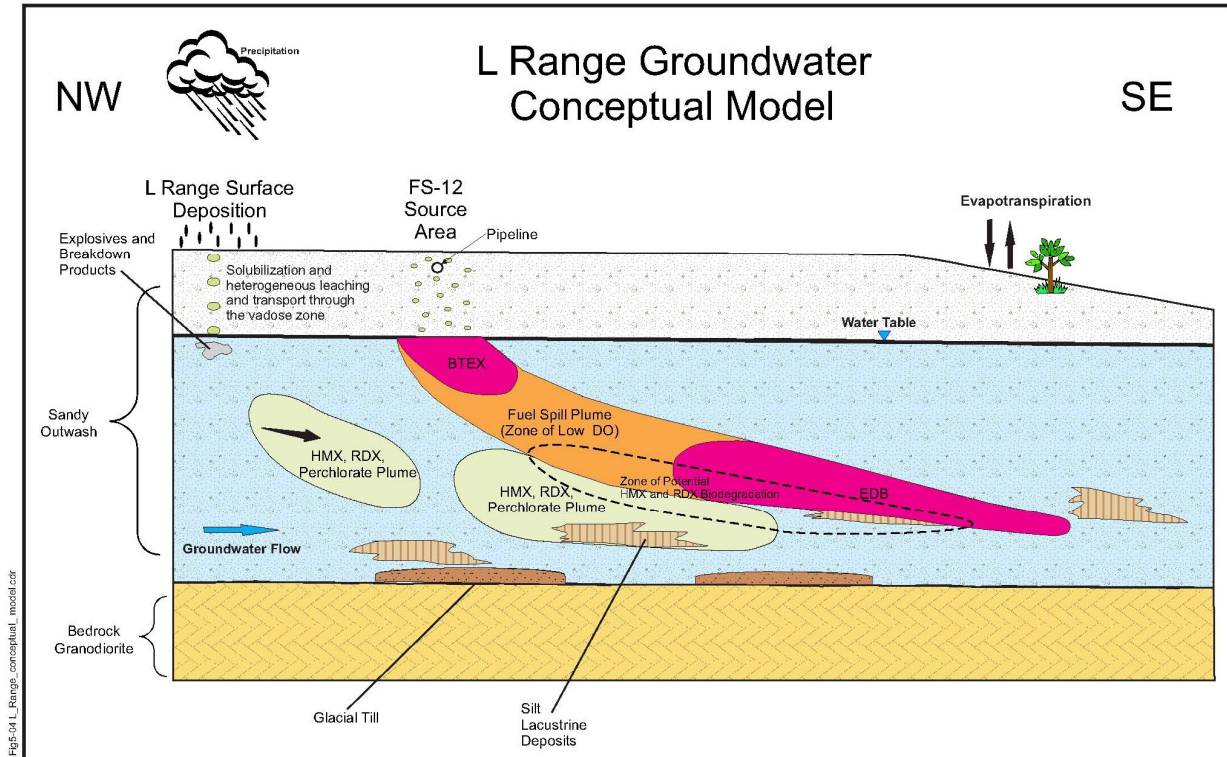


Figure 2. L Range Site Groundwater Conceptual Model (Source: ECC, 2005).

### 3. BACKGROUND

Samples from the L Range groundwater study area were initially evaluated using a correlation matrix and an integrated multivariate factor analysis (FA) was used to provide an overall picture of contaminant trends in the L Range plumes. FA is an exploratory multivariate method that can be used to explain the relationships among several variables. In the simplest sense, the FA method arranges the sites and environmental variables in multidimensional space. FA 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. FA calculations result in clustering of sites (e.g. 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. FA 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 FA method extracts “principal components,” also known as “factors” that explain variation in the data. These are derived by determining the eigenvectors of a given data matrix, where the eigenvector is the linear transform that produces a non-zero vector. In FA, the eigenvectors of a covariance or correlation matrix correspond to factors, and eigenvalues to the variance explained by these factors. These eigenvectors are arranged in multidimensional space such that they are orthogonal to each other. The first eigenvector explains the greatest amount of variance (i.e., has the highest eigenvalue). The second eigenvector captures the second most

important amount of variance orthogonal to the first axis. The third eigenvector is orthogonal to the first two axes, and it captures the next most important component of the remaining variance. FA deviates from principal components analysis (PCA) 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. This usually involves applying a correction factor to the provisional factor loadings that produces new factors that are each highly correlated with only a few of the original variables. The goal is to cluster the variables into groups and each group can be interpreted as a factor. The final stage of the analysis is the calculation of factor scores that are applied to each observation. These observations can then be plotted in multidimensional space to interpret relationships between these observations. If desired, FA 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 been used to provide insight into the mechanisms or processes that control the distribution of analytes within a defined aquifer or groundwater location of concern. Many of these studies demonstrate the utility of basic geochemical parameters in groundwater and understanding contaminant distribution. One particular example is a groundwater FA that 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 over pumping of groundwater led to subsidence, which caused introduction of more saline seawater into the water supply, thus possibly causing complicating health problems. Other studies have shown that geochemical variability due to seawater-groundwater interaction (Voudouris et al., 1997; Olobaniyi and Owoyemi, 2006) or surface water-groundwater interaction (Reghunath et al., 2002) can be effectively illustrated using FA. Chemical changes in groundwater due to transport through variable geologic formations have also been characterized using FA (Invernizzi and Barros de Oliveira, 2004). Chemical variability due to human impact has been characterized using FA (Muñoz-Carpena et al., 2005; Gonçalves et al., 2007) and variability due to mixtures of varying geology and variable human impact was also characterized with FA (Pujari and Deshpande, 2005). In many of these studies, the importance of field geochemical parameters is paramount in understanding the distribution of contaminants in groundwater.

#### **4. 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 work plans (AMEC, 2004) and were analyzed for explosives by U.S. Environmental Protection Agency (EPA) Method SW846/8330 (EPA, 1998) and for perchlorate by EPA Method E314.0 (EPA, 1999). Metals analyses were conducted using EPA Method SW846/60108/7470A (EPA, 1998), 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 effort and are presented on Figure 3. 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 are 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

Note: detection limits are 0.25 µg/L for RDX and HMX, 0.35 µg/L for perchlorate, 14.5 µg/L for iron and 0.9 µg/L for manganese

ND = below method detection limits

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 using Walsh's test (EPA, 2000), however, no outliers were determined and no data were removed from the dataset. After these treatments, the data were subjected to Correlation Analysis and FA.

A correlation matrix was generated to evaluate relationships among specific parameters (Table 2). 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 nonparametric Spearman ranked correlation procedure was used for this analysis. 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. A value of  $\alpha = 0.05$  was chosen as the significance level for this analysis.

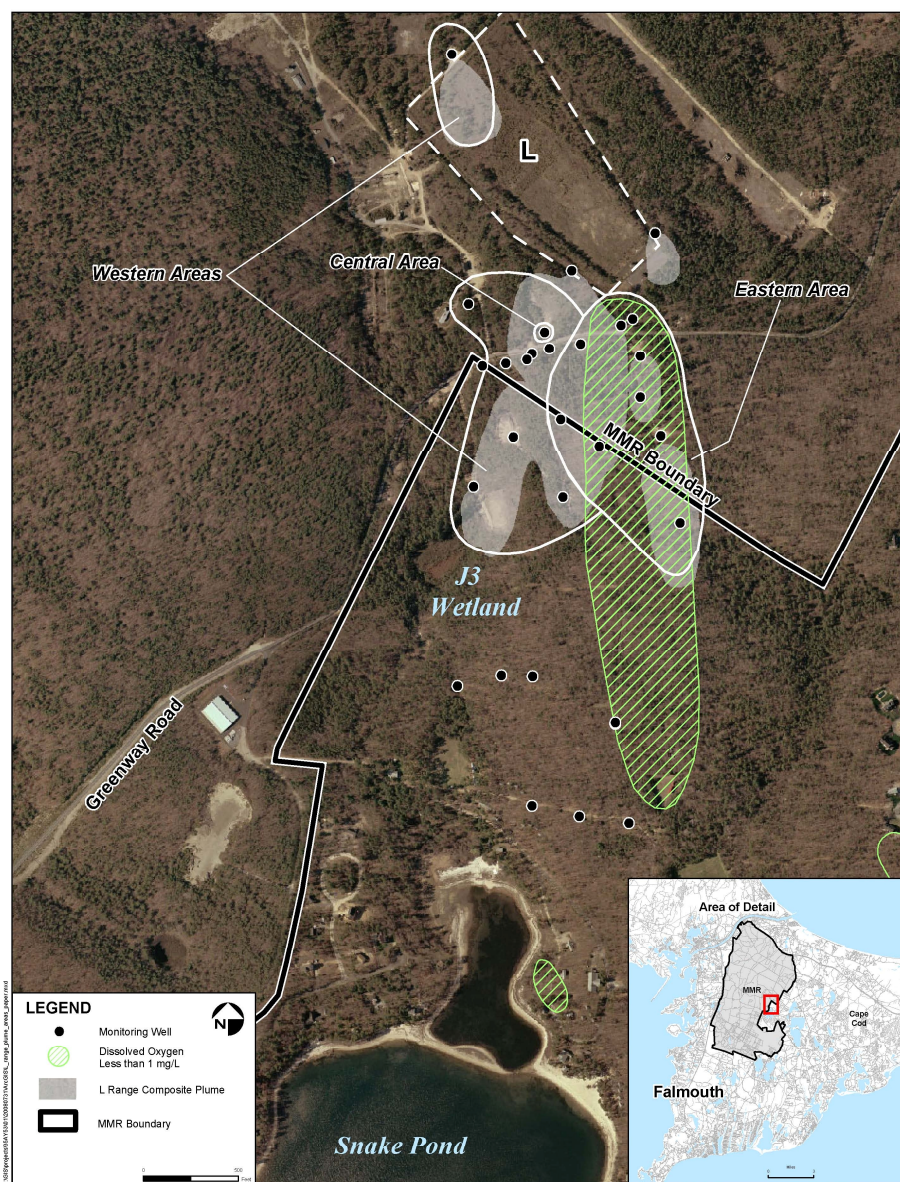


Figure 3. Location of L Range Groundwater Study Area, Factor Analysis Groundwater Zones, and anoxic zone.

The FA procedure for this investigation used the following variables: perchlorate, RDX, HMX, pH, temperature, dissolved oxygen (DO), oxidation-reduction potential (ORP), specific conductivity (SpC), turbidity, northing, easting, and elevation. These variables were selected because they either conveyed contaminant concentration, general geochemistry of the aquifer, or location of the sample in three-dimensional space. The FA 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 with sufficient data completeness were retained for the FA.

## 5. RESULTS

The statistical analyses performed for groundwater samples from the L Range indicated that the geochemistry of the aquifer was important in explaining the variability of other components in the aquifer such as contaminants. 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 was significantly positively correlated with RDX ( $r = 0.167$ ), temperature ( $r = 0.183$ ), and DO ( $r = 0.126$ ) (Table 2). The relationship between perchlorate and RDX suggests 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 these constituents in the plumes. The significant correlation with increasing temperature likely reflects the shallow nature of the perchlorate contamination and the fact that the groundwater temperature in the aquifer decreases with depth. The significant correlation with DO indicates that the perchlorate contamination, found mainly in the western portion of the L Range plumes (Figure 3) 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 ( $r = 0.635$ ), indicating that these two explosive compounds are likely from a similar 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 tendency of the explosives to be more highly concentrated in the more oxic portions of the aquifer where lower SpC values likely reflect lower concentrations of redox-sensitive metals. 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 expected (Table 2).

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 3). 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

**Table 2.** Correlation Matrix for L Range Groundwater

	Perc	RDX	HMX	Fe	Mn	pH	Temp	DO	ORP	SpC	Turb	North	East	Elev
Perc	<b>1.000</b>													
RDX	<b>0.167</b>	<b>1.000</b>												
HMX	-0.018	<b>0.635</b>	<b>1.000</b>											
Fe	-0.313	-0.393	-0.379	<b>1.000</b>										
Mn	<b>-0.567</b>	-0.050	-0.359	<b>0.756</b>	<b>1.000</b>									
pH	-0.101	-0.088	-0.051	<b>0.620</b>	<b>0.736</b>	<b>1.000</b>								
Temp	<b>0.183</b>	<b>-0.133</b>	<b>-0.209</b>	0.111	0.430	<b>-0.187</b>	<b>1.000</b>							
DO	<b>0.126</b>	<b>0.157</b>	0.039	<b>-0.681</b>	<b>-0.893</b>	<b>-0.465</b>	-0.030	<b>1.000</b>						
ORP	0.077	<b>0.233</b>	0.079	-0.453	-0.445	<b>-0.440</b>	-0.013	<b>0.676</b>	<b>1.000</b>					
SpC	-0.086	<b>-0.186</b>	<b>-0.128</b>	<b>0.775</b>	<b>0.552</b>	<b>0.329</b>	-0.011	<b>-0.643</b>	<b>-0.640</b>	<b>1.000</b>				
Turb	-0.115	-0.025	0.077	<b>0.912</b>	<b>0.750</b>	<b>0.266</b>	-0.033	<b>-0.241</b>	-0.131	<b>0.181</b>	<b>1.000</b>			
North	0.094	0.072	0.022	<b>0.491</b>	<b>0.511</b>	-0.026	0.001	<b>0.228</b>	<b>0.300</b>	<b>-0.240</b>	-0.020	<b>1.000</b>		
East	-0.007	<b>-0.116</b>	<b>-0.110</b>	<b>0.628</b>	<b>0.861</b>	<b>0.240</b>	0.068	<b>-0.540</b>	<b>-0.363</b>	<b>0.439</b>	<b>0.209</b>	0.031	<b>1.000</b>	
Elev	-0.095	<b>-0.322</b>	-0.103	<b>0.660</b>	0.373	-0.054	0.034	<b>-0.146</b>	<b>-0.299</b>	<b>0.381</b>	-0.097	<b>0.232</b>	<b>0.187</b>	<b>1.000</b>

Notes:

Coefficients in **BOLD** are considered significant at  $\alpha = 0.05$ .

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, such as an increase in dead cells and soluble metals. 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 correlation analysis was used to compare two variables and interpret the correlation in terms of cause and effect. However, that cause and effect can only be based on the coefficient for each two-variable comparison. The FA represents a multivariate approach where all of the variables are analyzed simultaneously and interpretations are made based on how these observations are partitioned into multidimensional space. The FA also showed the importance of the aquifer's geochemistry in determining 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. Based on the factor loadings for each eigenvector, these 5 factors have been identified as: Factor 1—oxic/anoxic water quality; Factor 2—biological activity; Factor 3—perchlorate; Factor 4—RDX; and Factor 5—location.

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 FA. Factor 1 is 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. Denitrification can also cause a pH increase in oxygen depleted groundwater zones as nitrate is consumed and bicarbonate and hydroxyl groups are produced. The presence of these bacteria and by-products can lead to 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	44.20	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	-0.224360	-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
Dissolved Oxygen	<b>0.713282</b>	-0.144288	0.012391	-0.241942	-0.350318
Oxidation Reduction Potential	0.232568	-0.156122	-0.200806	-0.249305	-0.344063
Specific Conductivity	<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

Note: **Bold** indicates factor scores greater than |0.4|

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 4). The wells were organized according to their location (east, central, or 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 3). Figure 4 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 3. 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.

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 5) 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.

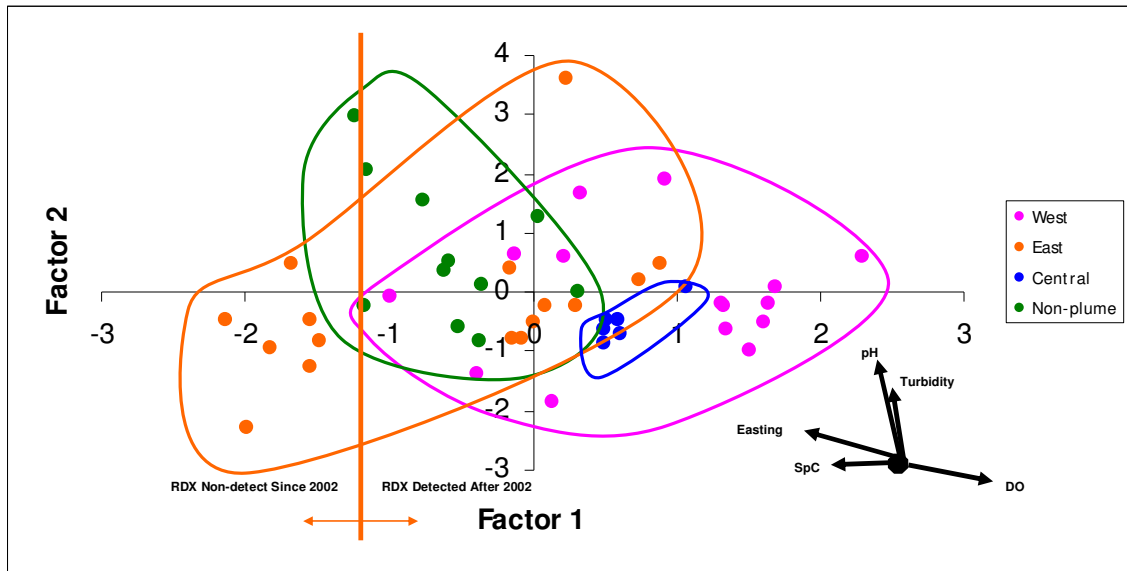


Figure 4. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 2

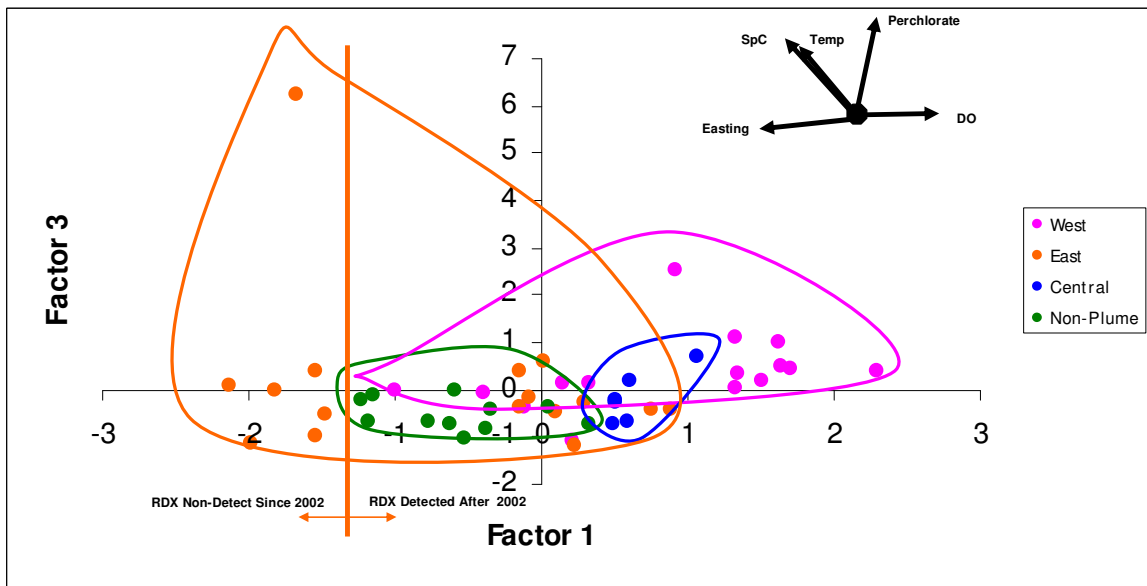


Figure 5. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 3

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 6 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.

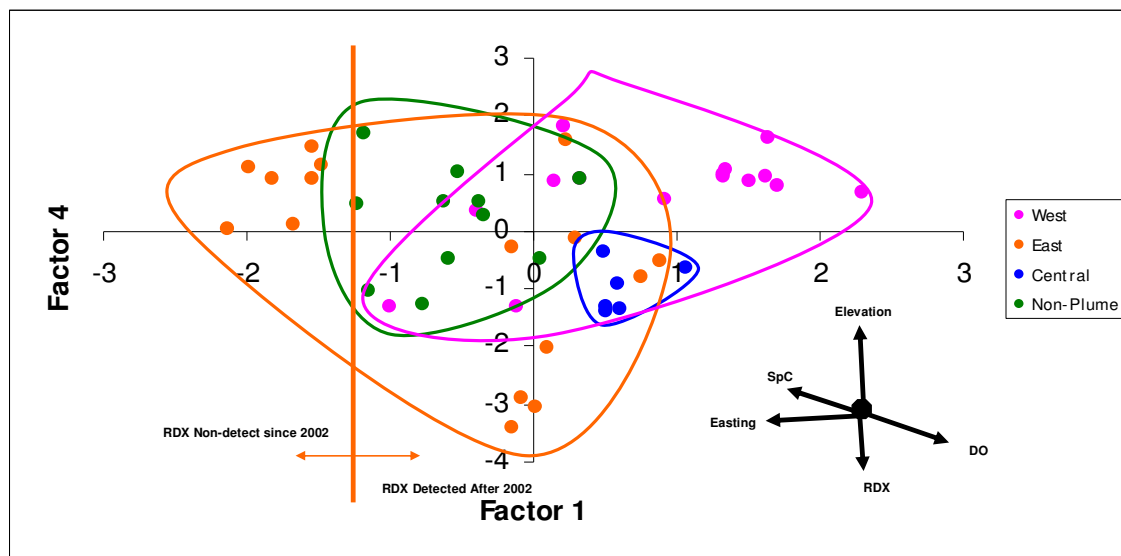


Figure 6. L Range Groundwater Factor Analysis, Factor 1 vs. Factor 4

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.

## 6. DISCUSSION

The results of the correlation analysis and FA indicate that knowing geochemical parameters (e.g., DO, ORP, and SpC) is critical to understanding the structure of these contaminant plumes (i.e., perchlorate, RDX, and HMX) in the aquifer. Significant correlations between RDX and the parameters related to the redox conditions in the aquifer show the influence of a former fuel spill in controlling the distribution of the contaminants. The biological interaction with the fuels from



the FS-12 plume has created an oxygen-depleted, chemically reducing area in the aquifer. In turn, these reducing conditions are conducive to the reductive dissolution of iron and manganese oxyhydroxides in the aquifer matrix resulting in elevated dissolved concentrations of these metals in the groundwater. Under oxygen-depleted conditions, dissolved iron and manganese complexes tend to remain in solution rather than re-precipitate as solid phases. The resulting elevated levels of dissolved constituents increase the electrical conductivity of the water downgradient from the fuel spill. The relationship between the concentrations of perchlorate, RDX, and HMX and reducing 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 in the immediate vicinity of the FS-12 plume) 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 abiotic reduction of nitroaromatic compounds (such as RDX and HMX) to primary amines by an oxidation-reduction reaction with metals where the reduced metals in solution are oxidized and the nitro-compounds are reduced. A third explanation for lower RDX and HMX concentrations in the vicinity of the FS-12 plume could be the dispersion of the dissolved explosives plume as it migrates away from the source area. Based on the results of the correlation analysis and FA, it seems most likely that the biodegradation of the fuels in the vicinity of the L Range is the most likely explanation for the distribution and/or degradation of contaminants in the aquifer. The FA identified an oxic/anoxic and a biological activity factor that explained over 44 percent of the variation in the multivariate data set. Therefore, biodegradation is the best explanation for decreasing levels of RDX and HMX near the fuel spill.

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 FA 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. The third and fourth factors are perchlorate and RDX factors and explain more than 30 percent of the variation and are an indicator of anthropogenic impact on the aquifer. Although they are of lesser importance, their contribution to variability is significant based on the FA. 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 important in defining the distribution of all parameters within the aquifer.

## 7. 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 indicate that the primary factors regarding variability of parameters in groundwater are related to the geochemical nature of the aquifer. 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 positive correlation between RDX and with DO and ORP and a negative correlation with SpC. These correlations are consistent with the fact 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 probable that RDX is subject to more rapid degradation when this contaminant migrates into the portion of the aquifer where reducing conditions prevail. A multivariate FA showed that the first two derived factors were related to (1) the reducing conditions in the aquifer and (2) the biological activity associated with these reduced zones. The distribution of perchlorate and RDX in the aquifer were captured in the following two factors. Therefore, knowing the geochemical patterns in the aquifer is critical to understanding 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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