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# ATTACHMENT 1

## Preliminary Estimate of Perchlorate, Chromium and Total Dissolved Solids Mass in Groundwater

### 1. Introduction

The Nevada Environmental Response Trust operates a groundwater extraction and treatment system (GWETS) at the Site to remove perchlorate and hexavalent chromium from shallow groundwater. The GWETS consists of three extraction well fields: (1) the on-site Interceptor Well Field (IWF) and barrier wall; (2) the Athens Road Well Field (AWF), which is situated approximately 8,200 feet north (downgradient) of the IWF; and (3) the Seep Well Field (SWF) situated approximately 4,500 feet north of the AWF near the Las Vegas Wash.

The IWF coupled with the barrier wall provides capture of the highest concentrations of perchlorate and chromium in downgradient groundwater. Although the AWF captures lower concentrations of both perchlorate and chromium, it contributes significantly to the overall contaminant mass removal from the groundwater and mitigates its impact in downgradient groundwater. The SWF, which is in close proximity to the Las Vegas Wash, contributes the highest flows to the GWETS, but captures significantly lower concentrations of perchlorate than the other two well fields. Chromium concentrations are not of significant concern at the SWF. The performance and monitoring of the GWETS are discussed in detail in remedial performance monitoring reports submitted to the Nevada Division of Environmental Protection (NDEP) on a semi-annual basis.

The purpose of this study is to estimate the total mass of perchlorate, total chromium and total dissolved solids (TDS) in groundwater on-site, between the Site and the AWF, and between the AWF and Las Vegas Wash. The estimates are based on the chemical sampling data collected in 2002, 2006 and 2012. This report provides the details of the data used, list of assumptions and the methods used to carry out these estimations. The mass estimates are also compared to the mass removal rates presented in Appendix E of the 2012 Annual Performance Report (ENVIRON, 2012).

## **2. Data Compilation**

### **2.1 Mass Estimate Boundaries**

The mass estimates were performed within the boundaries defined in Figure 1. These boundaries divide the contaminant plumes into three areas: 1) on-site, 2) between the northern Site boundary and the AWF, and 3) between the AWF and Las Vegas Wash. The vertical extent of the mass estimation volume extends from the water table surface to the approximate depth of contamination in the Upper Muddy Creek Formation (UMCf). To account for differences in the porosity between aquifer materials in the alluvium and UMCf, the contaminant masses in these units were calculated separately.

The saturated thickness of alluvium was determined by comparing the groundwater elevations to the elevation of the alluvium/UMCf contact. The interpolated contact surface elevation between the alluvium and UMCf was extracted from the NDEP-approved groundwater model of the Site developed by Northgate (Northgate, 2010a). Site-wide historical hydrographs were examined over a period between 2002 through 2012 to determine whether there were significant changes in groundwater elevations during that period. The groundwater elevations have been relatively stable in the area over the last decade, and therefore the groundwater elevations from 2012 were used to determine the saturated thickness of the alluvium for all years.

The vertical extent of contamination in UMCf was estimated based on the cross-sectional maps at the three well fields presented in the 2012 Annual Performance Report (ENVIRON, 2012) as follows:

- At the IWF (Plate 3, ENVIRON, 2012), the deeper wells, M-134, M-136, M-164 and M-133, have perchlorate concentrations above the Environmental Protection Agency (EPA) defined maximum contaminate level (MCL) for Nevada. These wells are screened approximately 20 to 50 feet below the alluvium/UMCf contact. Based on this information, the contaminated saturated thickness of the UMCf was set to 50 feet in the on-site area.
- At the AWF (Plate 4, ENVIRON, 2012), the deeper wells, PC-134A and PC-148, have perchlorate concentrations above the MCL. These wells are screened approximately 5 to 15 feet below the alluvium/UMCf contact. The contaminated saturated thickness of the UMCf was set to 15 feet in the area extending from the site boundary to the AWF.
- At the SWF (Plate 5, ENVIRON, 2012), all well screens with measured concentrations are in the shallow alluvium. Hence, it was assumed that there is no contaminant mass in the UMCf north of the AWF.

### **2.2 Historical Chemical Concentration Data**

The perchlorate, total chromium, and TDS groundwater sampling data for the years 2002, 2006, and 2012 were compiled from the NERT database. The data were sorted by the second quarter for each year to match the data presented in the Annual Performance Report of each year. There is limited total chromium and TDS data available for the year 2002 and these results were

not presented in the 2002 Annual Performance Report. As a result, no mass estimates were calculated for chromium and TDS in 2002. The location of wells with available sampling data for each year is presented on Figure 2. The contaminant iso-concentration contour lines presented in the Annual Reports for 2002, 2006, and 2012 were also incorporated into the interpolation process described in Section 4.3 below. All of the data used for this study are presented in a series of figures in Appendix A (available electronically).

### **2.3 Total Porosity**

The total porosity values for the alluvium and UMCf used in the mass estimates were selected based on a review of historical Site documents. The data reviewed included the following:

- As part of a screening-level indoor air health risk assessment conducted for Tronox Parcels A/B, a total porosity of 0.366 was assumed for the shallow alluvium (Northgate, 2010b).
- To calculate leaching-based site-specific soil screening levels near the Beta Ditch, TIMET assumed an average porosity of 0.46 for shallow soil and 0.54 for the Muddy Creek Formation (TIMET, 2013).
- Based on the general soil types of alluvium (sand and gravel) and UMCf (sandy/silty clay), the total porosities for alluvium and UMCf are assumed as 0.25 and 0.4 respectively in the Site wide groundwater model developed by University of Las Vegas (UNLV, 2003).

For the mass estimates, porosity values of 0.366 for alluvium and 0.54 for the UMCf were used.

### **2.4 Data Preparation and Interpolation**

Concentration data were interpolated onto a 40-foot grid using three different methods: kriging, spline, and contour interpolation. The data from individual wells was interpolated using kriging and spline methods. Kriging is a standard interpolation method, but it is not able to incorporate the abrupt change in concentration levels that occurs at the IWF barrier wall. To incorporate this effect, log-normalized concentrations were also interpolated using a spline method with a barrier function. In addition to the interpolations of point data, the hand drawn concentration contours presented in the 2002, 2006, and 2012 Annual Reports were used to generate concentration data grids. These hand-drawn contour lines incorporate hydrogeological features (such as the presence of paleochannels) or other trends that are more difficult to capture using automated interpolation procedures.

To perform the interpolations of point data, the following assumptions were made:

- 1) For non-detects, the concentration was set to half of the detection limit.
- 2) In lieu of TDS data for few locations in 2006, the laboratory conductivity values were multiplied by 0.67 to convert to TDS concentrations (McPherson, 1995).
- 3) The concentrations were log normalized prior to interpolation to reduce the skewness of the data.

- 4) The resulting concentration distributions were assumed to be representative of both the alluvium and UMCf.

The kriging interpolations were performed with KT3D\_H2O using ordinary kriging on the log-normalized data values using a spherical variogram. The kriging results are presented in Appendix A, Figures 1-1a to 1-7b. The spline interpolations were performed in ArcGIS Spatial Analyst using the spline method with a barrier function. The results are presented in Appendix A, Figures 2-1a to 2-7b. Interpolation from the contour lines was performed using the Topo to Raster function within ArcGIS Spatial Analyst. These results are presented in Appendix A, Figures 3-1a to 3-7b.

## **3. Mass Estimates**

### **3.1 Mass Estimate Calculations**

For each aquifer, the dissolved mass within each grid cell was calculated by multiplying the concentration by the area of grid (1,600 square feet), the saturated thickness of aquifer, and the porosity of the aquifer material. The masses were then summed within the boundaries shown in Figure 1 for each aquifer.

Tables 1 to 3 present the mass estimates for perchlorate, total chromium and TDS based on the three interpolation methods. The mass estimates for the three methods are generally in agreement. The results demonstrate decreasing concentrations of perchlorate and chromium for both on-site and off-site areas of the plume over the course of the study period. The TDS concentration levels remain unchanged. A bar chart showing the different estimates is shown in Figure 3.

### **3.2 Validation of Interpolated Values**

Two validation statistics were used to assess how well each interpolation fits the measured values. The validation results are presented in Table 4. The root mean squared error (RMSE) provides a measure of the accuracy of each interpolation by comparing the interpolated and measured values at each measurement location. By comparing RMSE values for individual chemicals, we observe that the lowest RMSE values are produced using the spline procedure, which is expected since the spline function produces a surface that passes through the data points. The RMSE values for kriging are about half those from contour interpolation.

The average percent difference (APD) was used to evaluate the relative bias of each interpolation. The APD for each interpolation was determined by dividing the average difference between the interpolated and measured values by the average measured value. The APD results ranged from -20 to 8.6 percent, with negative numbers indicating that the interpolated values are biased low relative to measured values. The APD values for the contour-based interpolations varied more significantly than the other interpolation methods. The interpolated values for perchlorate and chromium determined by kriging and spline were slightly biased low (< 3%) compared to measured values.

### **3.3 Historical Mass Removal Rates**

For the purposes of verifying the mass estimate results, a summary of historical mass removed by the three extraction well fields was compiled from the results presented in Appendix E of the 2012 Annual Performance Report (ENVIRON, 2012). These annual mass removal rates were calculated using historical flow and concentration data from each extraction well. Table 5 compares the total contaminant mass removed by the extraction systems for the 2002-2006 and 2006-2012 time periods with the difference in total mass derived from the mass estimates. These values are in close agreement, providing evidence that the estimated parameters used to calculate the mass estimate (i.e. porosity, depth of contamination) are reasonable.

## 4. References

- ENSR. 2007. Semi-Annual Performance Report for Chromium and Perchlorate, Tronox LLC, Henderson, Nevada, July – December 2006. February 26, 2007.
- ENVIRON International Corporation (ENVIRON). 2012. Annual Remedial Performance Report for Chromium and Perchlorate, Nevada Environmental Response Trust Site, Henderson, Nevada July 2011 – June 2012. August 31.
- Kerr-McGee Corporation. 2002. Quarterly Performance Report for Chromium and Perchlorate, Kerr-McGee Corporation, Henderson, Nevada, Second Quarter 2002. August 1. Revised October 14, 2002.
- McPherson, Lori, 1995. Correlating Conductivity to PPM of Total Dissolved Solids. Reprinted from Water Engineering and Management. August.
- Northgate Environmental Management, Inc. (Northgate). 2010a. Capture Zone Evaluation Report. December 10.
- Northgate Environmental Management, Inc. (Northgate). 2010b. Revised Technical memorandum: Screening-Level Indoor Air Health Risk Assessment for 2008 Tronox Parcels A/B, Henderson, Nevada, November 12.
- TIMET. 2013. Calculation of leaching-based Site-specific levels BMI Beta Ditch/Northwestern ditches located on the Titanium Metals Corporation Plant Site, BMI Common Areas, Clark County, Nevada, February 26
- UNLV. 2003. Fate and Transport of Perchlorate in a Contaminated Site in the Las Vegas Valley prepared for USEPA

## Tables



**TABLE 1: PERCHLORATE MASS ESTIMATES**  
**Nevada Environmental Response Trust Site**  
**Henderson, Nevada**

	On-site		Off-site to AWF		AWF to Wash		Entire Area
	Alluvium	UMCF	Alluvium	UMCF	Alluvium	UMCF	
<b>Kriging</b>							
2002	16	3,339	617	1,455	86	0	5,514
2006	11	2,106	488	1,110	10	0	3,724
2012	9	1,564	348	741	12	0	2,674
<b>Spline</b>							
2002	15	3,986	864	1,924	105	0	6,893
2006	11	2,246	605	1,321	15	0	4,199
2012	10	1,774	418	846	14	0	3,061
<b>Contour</b>							
2002	22	3,905	865	1,789	162	0	6,743
2006	11	2,181	523	1,111	17	0	3,843
2012	16	2,296	453	947	16	0	3,728

**Notes:**

Mass values are presented in metric tons.

AWF = Athens Road Well Field

UMCF = Upper Muddy Creek Formation

**TABLE 2: CHROMIUM MASS ESTIMATES**  
**Nevada Environmental Response Trust Site**  
**Henderson, Nevada**

	On-site		Off-site to AWF		AWF to Wash		Entire Area
	Alluvium	UMCF	Alluvium	UMCF	Alluvium	UMCF	
<b>Kriging</b>							
2006	0.06	28.79	1.62	4.18	0.10	0.00	34.76
2012	0.04	18.28	1.08	2.73	0.03	0.00	22.17
<b>Spline</b>							
2006	0.06	31.00	1.87	4.76	0.12	0.00	37.80
2012	0.04	20.04	1.19	2.89	0.05	0.00	24.22
<b>Contour</b>							
2006	0.05	33.60	1.44	3.43	0.52	0.00	39.04
2012	0.05	19.32	1.32	3.26	0.09	0.00	24.04

**Notes:**

Mass values are presented in metric tons.

AWF = Athens Road Well Field

UMCF = Upper Muddy Creek Formation

**TABLE 3: TOTAL DISSOLVED SOLIDS MASS ESTIMATES**  
**Nevada Environmental Response Trust Site**  
**Henderson, Nevada**

	On-site		Off-site to AWF		AWF to Wash		Entire Area
	Alluvium	UMCF	Alluvium	UMCF	Alluvium	UMCF	
<b>Kriging</b>							
2006	1,966	66,940	26,874	50,576	14,598	7	160,961
2012	2,079	67,787	26,700	50,381	13,801	0	160,748
<b>Spline</b>							
2006	1,999	66,300	27,970	53,701	14,218	0	164,187
2012	2,203	70,826	27,728	52,779	13,639	0	167,174
<b>Contour</b>							
2006	1,921	82,967	31,623	60,064	19,095	63	195,732
2012	2,075	84,082	29,051	55,267	19,264	53	189,792

**Notes:**

Mass values are presented in metric tons.

AWF = Athens Road Well Field

UMCF = Upper Muddy Creek Formation

**TABLE 4: VALIDATION STATISTICS FOR INTERPOLATIONS**  
**Nevada Environmental Response Trust Site**  
**Henderson, Nevada**

Analyte	Year	Root Mean Square (RMS) Error [a]			Average Percent Difference [b]		
		Kriging	Spline	Contour	Kriging	Spline	Contour
Perchlorate	2002	106.46	55.20	354.46	-2.14	-0.21	2.59
	2006	111.28	62.57	348.97	-0.85	-0.17	-20.09
	2012	69.28	20.71	113.07	-2.79	-0.51	-5.90
Chromium	2006	0.79	0.01	1.48	-2.15	-0.01	5.77
	2012	0.76	0.60	1.57	-2.81	-1.91	-12.21
TDS	2006	946.84	1,014.31	2,250.31	8.00	7.38	8.61
	2012	408.13	180.50	2,224.00	-0.79	0.06	4.03

**Notes:**

[a] Calculated as follows for all measurements used in an interpolation:

$$\sqrt{\frac{\text{sum}(\text{measured} - \text{interpolated})^2}{\text{number of samples}}}$$

[b] Calculated as the average difference between the interpolated and measured values, divided by the average measured value. A negative value indicates the average interpolated value is biased low relative to the measured value.

**TABLE 5: COMPARISON OF MASS REMOVAL ESTIMATES**  
**Nevada Environmental Response Trust Site**  
**Henderson, Nevada**

	Plume Mass Reduction [a]			Mass Removed by Pumping [b]
	Kriging	Spline	Contour	
<b>Perchlorate</b>				
2002 - 2006	1,790	2,693	2,900	1,305
2006 - 2012	1,050	1,138	115	1,489
<b>Chromium</b>				
2006 - 2012	13	14	15	10

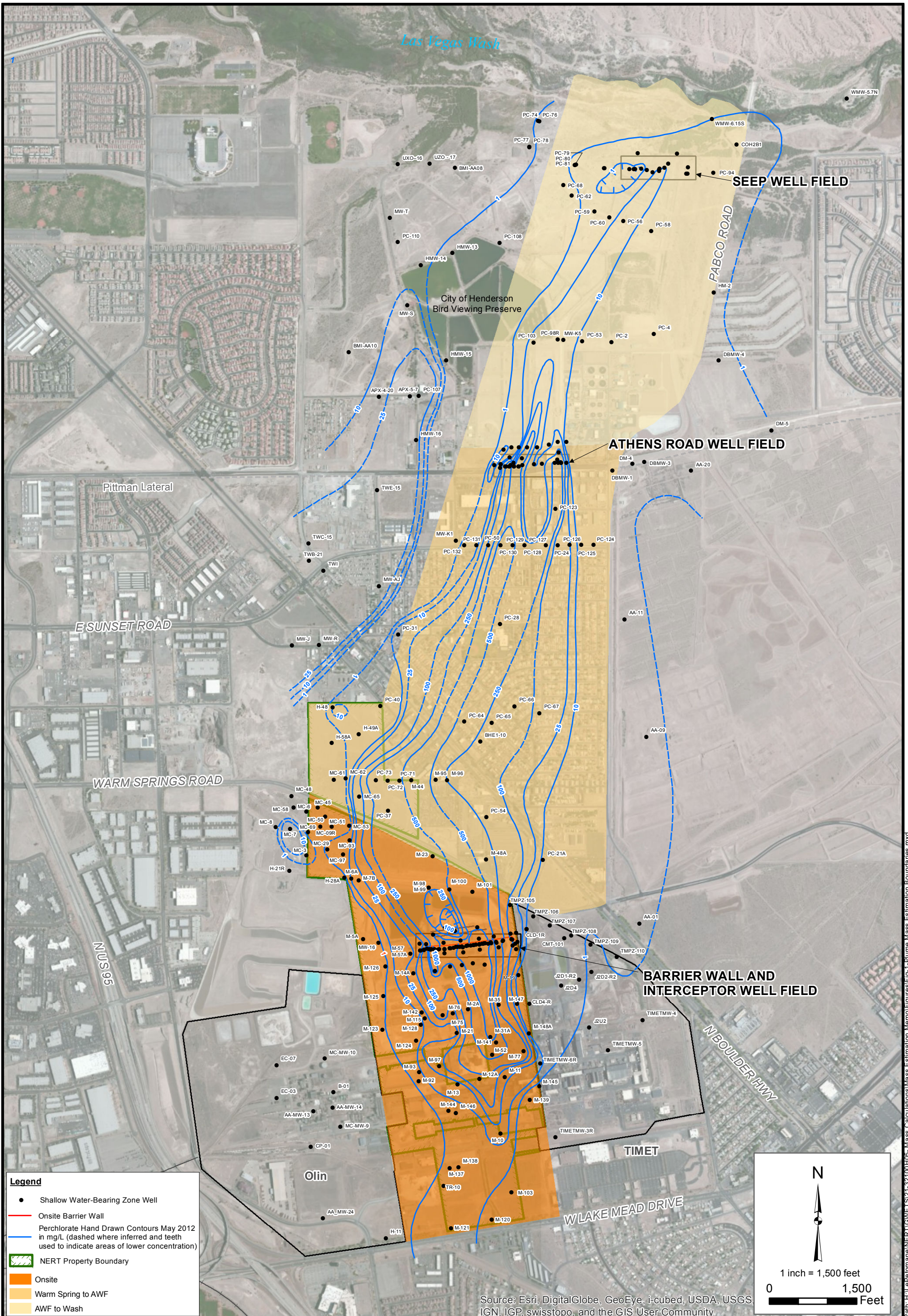
**Notes:**

Data presented in metric tons.

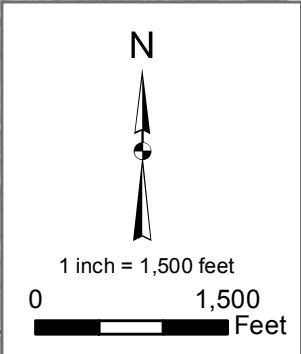
[a] Estimated reduction in mass derived from contaminant plume mass estimates - see Tables 1-3.

[b] Mass removed by pumping derived from measured flow rates and concentration at extraction wells.

## Figures

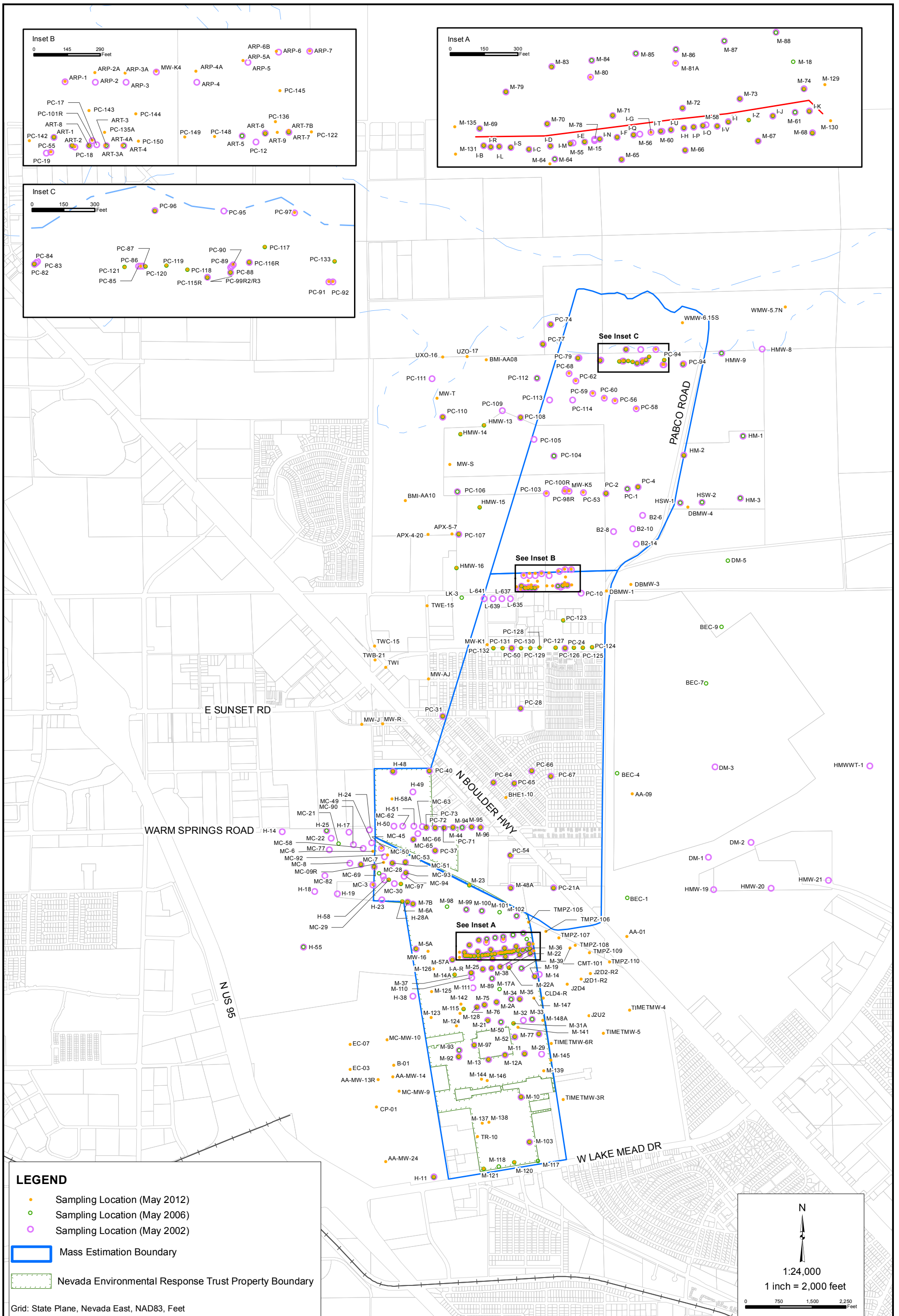


- Legend**
- Shallow Water-Bearing Zone Well
  - Onsite Barrier Wall
  - Perchlorate Hand Drawn Contours May 2012 in mg/L (dashed where inferred and teeth used to indicate areas of lower concentration)
  - ▭ NERT Property Boundary
  - ▭ Onsite
  - ▭ Warm Spring to AWF
  - ▭ AWF to Wash



Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, IGN, IGP, swisstopo, and the GIS User Community

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Historical Groundwater Chemical Sampling Location  
 Nevada Environmental Response Trust Site, Henderson, Nevada

Drafter: AS      Date: 8/30/2013      Contract Number: 21-32100H      Approved by: CS      Revised: AS

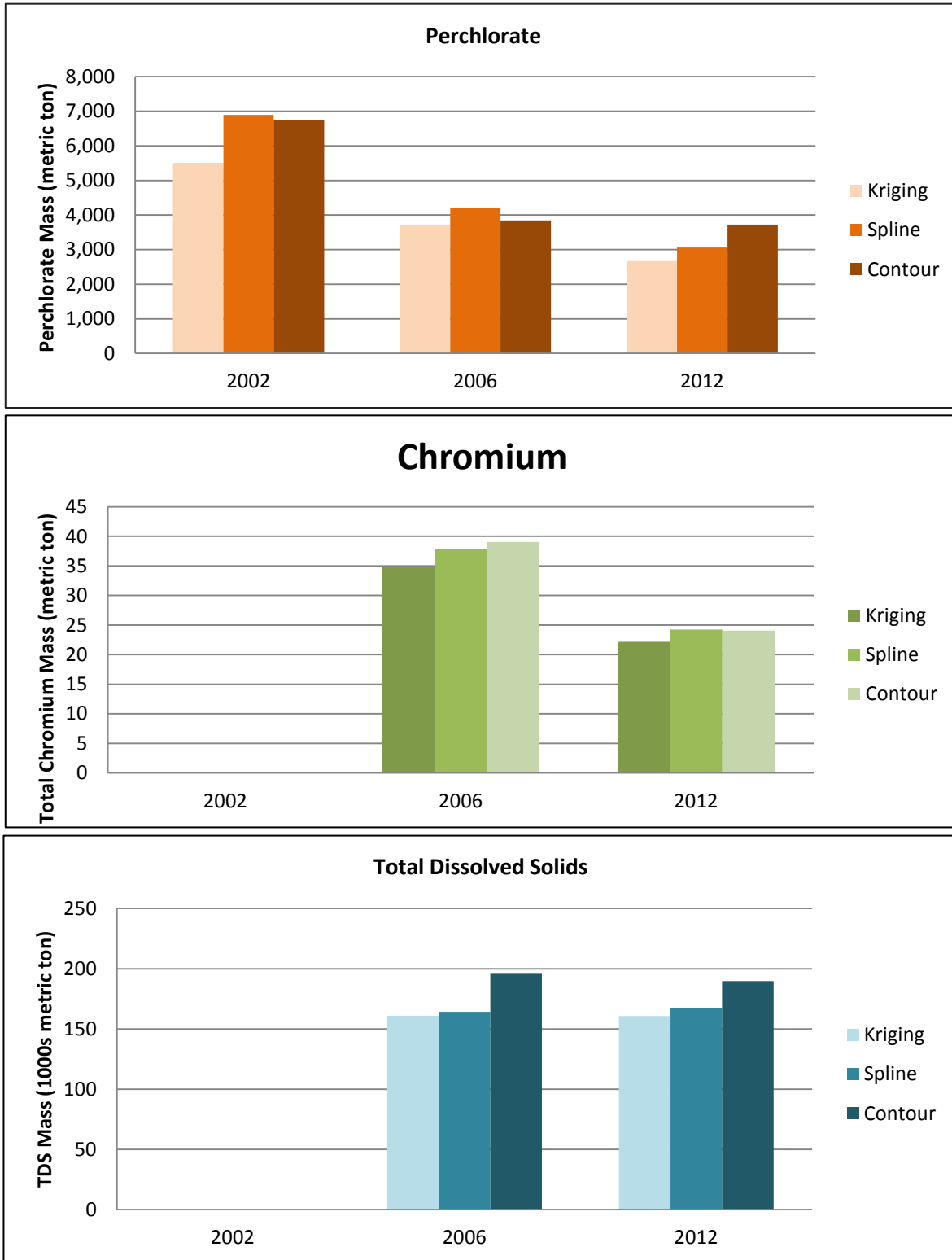
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### FIGURE 3: COMPARISON OF MASS ESTIMATE

Nevada Environmental Response Trust  
Henderson, Nevada



**Appendix A**  
**Iso-Concentration Maps for Perchlorate, Total Chromium and TDS**  
**(available in electronic format)**

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