

**ATTACHMENT 2N  
GROUNDWATER COPC TRENDING ANALYSIS  
USDOE/NNSA PANTEX PLANT  
AMARILLO, TEXAS**

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## 2N.0 GROUNDWATER COPC TRENDING ANALYSIS

This appendix details the trending analysis conducted on the groundwater dataset for the perched groundwater at Pantex Plant. A detailed table of results of the trending analysis and EPC calculation for each monitoring and extraction well and COPC pair for just the wells used in the evaluation of offsite risk and all perched wells sitewide are presented in Table 2N-1 and 2N-2 of this attachment, respectively.

### 2N.1 INTRODUCTION

Trending analysis has been done on groundwater data to refine the definition of the source term for risk calculations. The reason for using trend evaluations is that constituents having significant trends are not best represented in risk calculations by the normal upper confidence limit calculations used to derive EPCs. A better exposure point concentration for wells exhibiting statistically significant trends is the last measured value. This is because, with significant trends, the last value represents the best estimate of either the lower limit of concentration (for upward trending constituents) or the best estimate of the upper limit of concentration (for downward trending constituents). Trending analysis was conducted on each well and COPC pair identified in the Human Health Risk Assessment dataset as described in Appendix I.

Trends are also useful in determining the original source term for modeling of future groundwater concentrations.

### 2N.2 METHODOLOGY

Two different methodologies were used for trend analysis. Both a statistical technique call Mann-Kendall and the visual graphing of data were used.

The Mann-Kendall analysis is a non-parametric evaluation of trend. It depends only on the direction of changes in data and not on the magnitude. No evaluation of distribution is needed. It can be considered a non-parametric test for zero slope of the linear regression of time-ordered data versus time (Gilbert 1987). The Mann-Kendall statistic only considers the direction of changes and not at the magnitude of the changes, so a large decline in concentration can be offset by even a very small increase. This can cause a discrepancy between the visual plots of concentration and the Mann Kendall evaluation.

The groundwater data considered for this evaluation is the data collected since the beginning of 1999 because that point represents the beginning of low flow, dedicated sampling for all wells in the dataset. Groundwater sampling conducted at Pantex Plant since First Quarter 1999 has been conducted using low flow sampling methodology. Prior to this time, groundwater samples were collected under various methodologies and do not provide for a reliable statistical comparison to the post 1998 dataset. At least 4 detections and greater than 50% frequency of detection is required to evaluate the trend for a COPC/well pair. It is assumed that the data is independent, and there is no correlation among data due to the groundwater not moving a sufficient distance from the sampling points among sampling events. This condition is normally met if sampling is no more frequently than quarterly. If groundwater velocities are high, then independence may be maintained with more frequent sampling.

The analytical data may also be inspected visually for trends. Analytical data for a well over time appears as a hydrograph, but plots concentration rather than water elevation. All the graphs of COPC/well pairs that had sufficient data for trending are shown at the end of this attachment

### 2N.3 EPC CALCULATION METHODOLOGY

As a first step to determine EPCs, groundwater trending analyses were performed for monitoring well and extraction well COPC/well pairs using an expanded dataset acquired from 1999 to present. Trending included filtered and unfiltered data for metals and unfiltered data for organic parameters; however, for metals, only EPCs derived from unfiltered data are incorporated in the risk assessment. Chromium, manganese, molybdenum, and nickel perched groundwater data have been excluded from the evaluation of monitoring wells with stainless steel casings/screens due to corrosion issues presented in the *Groundwater RFIR* (Stoller, 2004). A more detailed assessment of the well corrosion issues is presented in Section I.3.1.1. Results of the analyses determine whether an increasing or decreasing trend is evident for each COPC/well pair. For trends determined to be statistically significant for a given COPC/well pair, the most recently measured concentration was designated the EPC for determining current offsite risks.

When no significant trend existed or if a trend could not be determined due to an insufficient amount of data (i.e., less than 4 samples or 50% frequency of detection), with the latter being the case for filtered metals data, then additional steps were taken to determine if the EPC should be a 95% UCL, as defined by data distribution, or the maximum detected concentration. The methods used for calculating UCLs are consistent with those approved by TCEQ for the ERA. This methodology was presented in a letter from USDOE/NNSA to TCEQ on November 26, 2003 (“Transmittal of Approach to Calculating the Exposure Point Concentration for the Ecological Risk Assessment”) and approved by TCEQ in a letter to USDOE/NNSA dated January 12, 2004 (“Conditional Approval: Approach to Calculating the Exposure Point Concentration for the Ecological Risk Assessment, Dated November 26, 2003”).

Prior to calculating 95% UCLs for each COPC/well pair, the data distribution of each COPC/well pair was determined as being normal, lognormal, or undefined. This was done using the Shapiro-Wilk statistic assuming a 0.05 significance level. Once the distribution was identified, normal 95% UCLs were calculated for normally distributed and undefined data using the t-statistic; lognormal 95% UCLs were calculated using the Land Statistic to correct for bias in the normal calculation of transformed data. Individual COPC/well pair datasets in which less than 50% of the data are detected concentrations are assumed to be non-parametric.

The 95% UCL calculations included both detected and non-detected concentrations. To account for the uncertainty inherent in a reported non-detect value, a proxy value equal to one-half the reported detection limit was used in the 95% UCL calculation.

The maximum detected concentration was used as the EPC for datasets containing less than ten samples. For all datasets for which a 95% UCL was calculated, the lesser of the 95% UCL and maximum detection was used as the EPC.

### 2N.4 RESULTS OF TRENDING ANALYSIS AND CURRENT EPC CALCULATION

Based on the perched groundwater well-specific COPC evaluation, there are 546 COPC/well pairs that were evaluated. Of those, 426 had sufficient data to evaluate trends. Sixty-four of the pairs had upward trends and 136 had downward trends. Data trends for all other COPC/well pairs could not be reliably determined (neither a significant decreasing nor increasing trend). Tables 2N-3 and 2N-4 present the list of COPC/well pairs with significant increasing and decreasing trends, respectively. As noted above, trends for filtered metals were not assessed due to small sample size (typically 4 or less); the EPCs are presented in Table 2N-2. The remainder of the discussion of perched groundwater trends will pertain to unfiltered data results

### 2N.4.1 RDX

Concentrations of RDX were trended at a total of 84 monitoring and extraction well locations. A total of 26 perched well locations showed significant decreasing trends, 11 showed significant increasing trends, while the remaining 47 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-1 depicts the results of the trending analysis for the RDX/well pairs. Significant decreasing trends were observed primarily east/southeast of Zone 12. Significant increasing trends are noted south/southeast of Zone 12, at a single location northwest of Playa 1, and south of Zone 11. Current RDX EPCs among perched monitoring and extraction wells ranged between 0.0005 mg/L (PTX06-EW-10) and 7.5 mg/L (PTX06-EW-44). Results for trending and EPC calculation for all RDX/well pairs are presented in Attachment 2N-2.

### 2N.4.2 HMX

Concentrations of HMX were trended at a total of 21 monitoring and extraction well locations. A total of 3 perched well locations showed significant decreasing trends, 2 showed significant increasing trends, while the remaining 16 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-2 depicts the results of the trending analysis for the HMX/well pairs. Significant decreasing and increasing trends were observed southeast of Zone 12. Current HMX EPCs among perched monitoring and extraction wells ranged between 0.0036 mg/L (PTX06-EW-42A) and 0.91 mg/L (PTX06-EW-44). Results for trending and EPC calculation for all HMX/well pairs are presented in Attachment 2N-2.

### 2N.4.3 TNT and TNT Degradation Products

As a result of the well-specific COPC evaluation, TNT results were trended at a total of 33 monitoring and extraction well locations. In addition, several monitoring and extraction well locations were trended for TNT degradation products; 2-Amino-4,6-Dinitrotoluene (DNT2A; 56 well locations) and 4-Amino-2,6-Dinitrotoluene (DNT4A; 73 well locations). Significant decreasing trends were observed at 13 TNT/well pairs, 26 DNT2A/well pairs and 22 DNT4A/well pairs. Significant increasing trends were observed at 4 TNT/well pairs, 2 DNT2A/well pairs and 22 DNT4A/well pairs. Apparent from a review of figures 2N-3, 2N-4, and 2N-5, that depict the results of the trending of TNT, DNT2A, and DNT4A, respectively, that the observed significant decreasing and increasing trends among the parent/daughter products appear to be spatially correlated. Significant decreasing trends are generally clustered in areas that historically have the highest TNT concentrations while significant increasing trends are observed on the leading edge of the TNT plume. Current EPCs among perched monitoring and extraction wells ranged between 0.00024 mg/L (PTX06-1038) and 0.24 mg/L (PTX06-EW-41) for TNT, 0.00039 mg/L (PTX06-EW-20) and 0.062 mg/L (PTX06-EW-44) for DNT2A, and 0.00042 mg/L (PTX06-EW-20) and 0.047 mg/L (PTX06-EW-44) for DNT4A. Results for trending and EPC calculation for all COPC/well pairs are presented in Attachment 2N-2.

### 2N.4.4 2,4-Dinitrotoluene

Concentrations of 2,4-Dinitrotoluene (by-product of TNT production) were trended at a total of 54 monitoring and extraction well locations. A total of 17 perched well locations showed significant decreasing trends, 7 showed significant increasing trends, while the remaining 30 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-6 depicts the results of the trending analysis for the 2,4-Dinitrotoluene /well pairs. Significant decreasing trends were observed in the vicinity of well locations with decreasing TNT trends. Significant increasing trends were observed onsite along the eastern/southeastern plant boundary. Current 2,4-Dinitrotoluene EPCs among perched monitoring and extraction wells ranged between 0.00015 mg/L (PTX06-EW-47) and 0.10 mg/L

(PTX06-EW-44). Results for trending and EPC calculation for all 2,4-Dinitrotoluene/well pairs are presented in Attachment 2N-2.

#### **2N.4.5 2,6-Dinitrotoluene**

Concentrations of 2,6-Dinitrotoluene (by-product of TNT production) were trended at a total of 15 monitoring and extraction well locations. Due to a low frequency of detection, 14 well locations did not have enough data to assess a trend over time. The remaining well location did not have a significant trend. Figure 2N-7 depicts the results of the trending analysis for the 2,6-Dinitrotoluene/well pairs. Current 2,6-Dinitrotoluene EPCs among perched monitoring and extraction wells ranged between 0.00024 mg/L (PTX07-1006) and 0.0063 mg/L (PTX06-1005). Results for trending and EPC calculation for all 2,6-Dinitrotoluene/well pairs are presented in Attachment 2N-2.

#### **2N.4.6 1,3-Dinitrobenzene**

Concentrations of 1,3-Dinitrobenzene were trended at a total of 13 monitoring and extraction well locations. Due to a low frequency of detection, 12 well locations did not have enough data to assess a trend over time. The remaining well location did not have a significant trend. Figure 2N-8 depicts the results of the trending analysis for the 1,3-Dinitrobenzene/well pairs. Current 1,3-Dinitrobenzene EPCs among perched monitoring and extraction wells ranged between 0.00032 mg/L (PTX06-EW-2) and 0.0036 mg/L (PTX06-1005). Results for trending and EPC calculation for all 1,3-Dinitrobenzene/well pairs are presented in Attachment 2N-2.

#### **2N.4.7 1,3,5-Trinitrobenzene**

Concentrations of 1,3,5-Trinitrobenzene were trended at a total of 12 monitoring and extraction well locations. A total of 5 perched well locations showed significant increasing trends while the remaining 7 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-9 depicts the results of the trending analysis for the 1,3,5-Trinitrobenzene/well pairs. Significant increasing trends were observed onsite southeast of Zone 12. Current 1,3,5-Trinitrobenzene EPCs among perched monitoring and extraction wells ranged between 0.092 mg/L (PTX06-EW-21) and 1.3 mg/L (PTX06-EW-1). Results for trending and EPC calculation for all 1,3,5-Trinitrobenzene/well pairs are presented in Attachment 2N-2.

#### **2N.4.8 Boron**

Unfiltered boron concentrations were trended at a total of 73 monitoring and extraction well locations. A total of 19 perched well locations showed significant decreasing trends, 18 showed significant increasing trends, while the remaining 36 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-10 depicts the results of the trending analysis for the boron/well pairs. Significant decreasing trends were generally observed onsite southeast of Zone 12 in the vicinity of the current extraction well network. Significant increasing trends were observed onsite along the eastern Plant boundary, offsite southeast of Zone 12, and north of Playa 1. Current boron EPCs among perched monitoring and extraction wells ranged between 0.21 mg/L (PTX06-EW-24) and 1.8 mg/L (PTX06-1050). Results for trending and EPC calculation for all boron/well pairs are presented in Attachment 2N-2.

#### **2N.4.9 Total Chromium and Hexavalent Chromium**

As a result of the well-specific COPC evaluation, unfiltered total chromium results were trended at a total of 25 monitoring and extraction well locations. In addition, unfiltered hexavalent chromium was trended

at 16 monitoring and extraction well locations. Significant decreasing trends were observed at 2 total chromium/well pairs and one hexavalent chromium/well pair. Significant increasing trends were observed at 1 total chromium/well pair and 4 hexavalent chromium/well pairs. Figures 2N-11 and 2N-12 depict the results of the trending of total chromium and hexavalent chromium, respectively. Significant decreasing trends are generally clustered along the fence line south of Zone 12. Significant increasing trends are observed both onsite and offsite southeast of Zone 12, consistent with the areas of higher concentration within the total chromium and hexavalent chromium plumes. Current EPCs among perched monitoring and extraction wells ranged between 0.023 mg/L (PTX06-EW-46) and 16 mg/L (PTX08-1008) for total chromium and 0.040 mg/L (PTX06-EW-39) and 14 mg/L (PTX08-1008) for hexavalent chromium. Results for trending and EPC calculation for all COPC/well pairs are presented in Attachment 2N-2.

#### **2N.4.10 Selenium and Nitrate**

A single perched well location was evaluated for Pantex Lake (PTX06-1083). A total of two COPCs (selenium and nitrate) exceeded evaluation criteria (i.e., background and  $RBSV_{GW}$ ) at this well location. Trending could not be conducted for selenium due to small sample size and trending of nitrate resulted in an insignificant trend. Figures 2N-13 and 2N-14 depict the results of the trending of selenium and nitrate, respectively. Current EPCs for these COPCs were 0.059 mg/L and 48 mg/L for selenium and nitrate, respectively. Selenium and nitrate are only COPCs at this well location.

#### **2N.4.11 Perchlorate**

Concentrations of perchlorate were trended at a total of 15 monitoring and extraction well locations. A single perched well location showed significant decreasing trends while the remaining 14 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-15 depicts the results of the trending analysis for the perchlorate/well pairs. The significant decreasing trend was observed onsite south of Zone 11. Current perchlorate EPCs among perched monitoring and extraction wells ranged between 0.0045 mg/L (OW-WR-19) and 0.41 mg/L (PTX08-1006). Results for trending and EPC calculation for all perchlorate/well pairs are presented in Attachment 2N-2.

#### **2N.4.12 1,2-Dichloroethane**

Concentrations of 1,2-Dichloroethane were trended at a total of 9 monitoring and extraction well locations. A total of two perched well locations showed significant decreasing trends while the remaining 7 well locations had insignificant trends over time. Figure 2N-16 depicts the results of the trending analysis for the 1,2-Dichloroethane/well pairs. The significant decreasing trend was observed onsite southeast of Zone 12 along the fence line. Current 1,2-Dichloroethane EPCs among perched monitoring and extraction wells ranged between 0.0018 mg/L (PTX06-EW-5) and 0.018 mg/L (PTX08-1005). Results for trending and EPC calculation for all 1,2-Dichloroethane/well pairs are presented in Attachment 2N-2.

#### **2N.4.13 Chloroform**

Concentrations of chloroform were trended at a single monitoring well location (PTX08-1005). Based on the trending result, there was no significant trend. Figure 2N-17 depicts the results of the trending analysis for the chloroform/well pair. The current chloroform EPC at this monitoring well location was 0.082 mg/L. Results for trending and EPC calculation for this chloroform/well pair are presented in Attachment 2N-2.

**2N.4.14 Tetrachloroethylene**

Concentrations of tetrachloroethylene were trended at a single monitoring well location (PTX08-1006). Based on the trending result, there was no significant trend. Figure 2N-18 depicts the results of the trending analysis for the tetrachloroethylene /well pair. The current tetrachloroethylene EPC at this monitoring well location was 0.015 mg/L. Results for trending and EPC calculation for this tetrachloroethylene /well pair are presented in Attachment 2N-2.

**2N.4.15 Trichloroethene**

TCE concentrations were trended at a total of 29 monitoring and extraction well locations. A total of 4 perched well locations showed significant decreasing trends, 6 showed significant increasing trends, while the remaining 19 well locations had either insignificant trends or not enough data to assess a trend over time. Figure 2N-19 depicts the results of the trending analysis for the TCE/well pairs. Significant decreasing trends were generally observed onsite and offsite southeast of Zone 12 near the southern fence line. Significant increasing trends were observed onsite and offsite southeast of Zone 12 and south of Zone 11. Current TCE EPCs among perched monitoring and extraction wells ranged between 0.0031 mg/L (PTX06-EW-1) and 0.22 mg/L (PTX06-1088). Results for trending and EPC calculation for all TCE/well pairs are presented in Attachment 2N-2.

**2N.5 SUMMARY**

The results of the trending analysis on groundwater data from onsite and select offsite perched monitoring and extraction wells are used to refine the definition of the source term for risk calculations and determining the original source term for modeling of future groundwater concentrations. The observed trends among the groundwater COPCs were consistent with the current understanding of the nature and extent of groundwater contamination detected in the perched aquifer at Pantex..