



Technical Memorandum

Statistical Trend Analysis of the Analytical Results of Sediment, Landfill Gas, and Ground-Water Samples from Site 09

Naval Construction Battalion Center (NCBC) Davisville North Kingstown, Rhode Island

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TECHNICAL MEMORANDUM

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SUBJECT: Statistical Trend Analysis of the Analytical Results of Sediment, Landfill Gas, and Ground-Water Samples from Site 09, Naval Construction Battalion Center (NCBC) Davisville, North Kingstown, Rhode Island

Introduction:

Sufficient sets of laboratory results were available for statistical trend analysis of samples collected from 3 media at Site 09 (ground-water collected from 18 monitoring wells, landfill gas from 5 gas vents, and sediment from 10 locations). Chemical data were available for samples collected for the Phase III Remedial Investigation (RI) (1995) and the Long-Term Monitoring Program (LTMP) (2001-2004) of ground-water from monitoring wells (MWs) at Site 09. Data were available for samples of landfill gas and sediment collected during the LTMP only. The location of the site and the samples are shown in Figures 1 and 2. The 10 sediment sample locations are immediately adjacent to each of the 10 piezometer locations shown on Figure 2. The LTMP data included are those from the first 10 quarterly monitoring events. The collection of the samples and validation of the laboratory results was completed in accordance with the general methodologies established in the Final LTM QAPP for Site 09. Because of difficulty collecting water samples from piezometers early in the LTMP, there were not at least 8 sets of data available for all the analytical categories from each of the 10 locations. Therefore, these data could not be included in this statistical trend analysis. The LTMP analytical program for the 3 media evaluated is as follows:

- Ground-water samples have been collected from 18 MWs and analyzed for Targeted Compound List (TCL) volatile organic compounds (VOC) by U.S. Environmental Protection Agency (EPA) Method 8260B, TCL semivolatile organic compounds (SVOC) by EPA Methods 8270C and 8151M, polycyclic aromatic hydrocarbons (PAH) by EPA Method 8310, TCL polychlorinated biphenyls (PCB) by EPA Method 8082 and TCL organochlorine pesticides by EPA Method 8081A, total and dissolved metals by EPA Methods 3005A/3020A/6010B/7000, and salinity by EPA Method 2520B.

- Sediment samples have been collected from 10 locations and analyzed for TCL VOC by EPA Method 8260B, TCL SVOC by EPA Methods 8270C and 8151M, PAH by EPA Method 8310, TCL PCB by EPA Method 8082, TCL organochlorine pesticides by EPA Method 8081A, total metals by EPA Methods 3005A/3020A/ 6010B/7000, and total organic carbon.
- Landfill gas samples have been collected from the 5 gas vents and analyzed for methane (gas chromatograph/flame ionization detector, American Society for Testing and Materials D-1945), total petroleum hydrocarbons as gasoline (TO-3), SVOC (TO-13), and VOC (TO-14).

Of these data for sediment and ground water, the contaminants of concern (COC), as identified in the Record of Decision for this site, have been examined to determine if there are statistically significant temporal trends in detected analyte concentrations. Statistically significant trends were observed in only some of these data, specifically:

- PAH in sediment sample SED09-01
- Chlorinated ethenes (trichloroethene and vinyl chloride) in selected wells
- Metals in selected wells
- Unique VOC in MW09-11S.

COC were not established in the Record of Decision for landfill gas because the gas vents were constructed as part of the selected remedy for the site. Therefore, for this assessment, the VOC and SVOC COC for ground water were used as a surrogate, plus methane. None of these landfill gas data exhibited statistically significant trends.

Methodology:

Statistical methods were used to evaluate temporal trends following the methodology used in the Revised Conceptual Site Model and Monitoring Optimization Report for Site 07 (Battelle 2004).

For each of these contaminants, trend analyses were performed for individual wells at the site if: 1) the well had been sampled three or more times (i.e., during three sampling events); and 2) the contaminant was detected in the well in at least one sampling event.

Three separate analyses were conducted to evaluate trends in individual wells, including linear regression analysis, the Mann-Kendall test, and the Sen test. Linear regression analysis involved fitting a linear regression of the form

$$\ln(C_t) = \alpha + \beta t$$

to the data from each well to test for the presence of a linear trend over time as proposed by Buscheck and Alcantar (1995). In this model, C_t represents contaminant concentration at time t , α represents the concentration at $t = 0$, and β is the average change in the logarithm of the contaminant per unit of time. A nonparametric approach

suggested by Mann and Kendall (Mann 1945; Kendall 1938) was also used to test for a temporal trend at each well. Although the Mann-Kendall test can detect the presence of a trend, it gives no estimate of its magnitude. Sen (1968) proposed a nonparametric method for estimating a trend that is used here in conjunction with the Mann-Kendall result.

Because concentration data frequently follow a log-normal distribution and normally distributed errors are an assumption of the parametric approach (linear regression), the logarithms of the data were used in the analysis (i.e., data were transformed by taking the logarithm of the concentration). Also, non-detects were represented by a value equal to one-half of the detection limit, and as stated previously, wells with less than three measurements and those wells with three or more measurements where contamination was never detected were not included in the analysis because in such cases the regression model parameters cannot be estimated.

Results of the Mann-Kendall tests were used to identify COC with discernible trends at the 95% significance level for which the trends could not be attributed to analytical artifact such as varying detection limits. The COC that exhibited significant temporal trends are discussed below. The tabular results of this statistical trend analysis are appended for reference (Appendix 1 – Sediment, Appendix 2 – Landfill Gas, and Appendix 3 – Ground Water). Appendix 4 includes a copy of the database file (Site_09_trend_data.mdb) and trend statistical program file (Davisville_Trend_Analysis.sas) used for this assessment. The SAS-based program was developed by EA to read the time monitoring results data from the database, compute trend statistics, and export the results back to the database. The various queries in the database then operate on the results table to display the results of the trend analysis.

Results and Discussion:

As stated in the introduction, four basic types of temporal trends were observed from this exercise. Those observations are as follows:

PAH in sediment sample SED09-01

Figures 3 and 4 show the significant decrease in the detected concentrations of benzo(b)fluoranthene and benzo(a)pyrene, respectively, from late 2001 to 2004. These samples are located at approximately 2-3 ft below the sediment surface; consequently, the decrease cannot be accounted for by cleaner sediment depositing on top of more contaminated sediment. These concentrations have decreased from between 300 and 400 $\mu\text{g}/\text{kg}$ in December 2001 to single digit concentrations in 2004. Other detected PAH did not show significant decreases or increases in concentrations.

Chlorinated ethenes (trichloroethene and vinyl chloride) in monitoring wells

The chlorinated ethenes undergo a reductive dechlorination process, with trichloroethene higher in the reduction chain. Ground-water samples from two monitoring wells

(MW09-08S and MW09-21D) showed clear decreasing trends of trichloroethene concentrations (Figures 5 and 6). Vinyl chloride is further dechlorinated. Ground-water samples from MW09-09S showed significantly increasing concentrations of vinyl chloride (Figure 7), while ground-water samples from MW09-08S showed significantly decreasing vinyl chloride concentrations (Figure 8).

Metals in monitoring wells

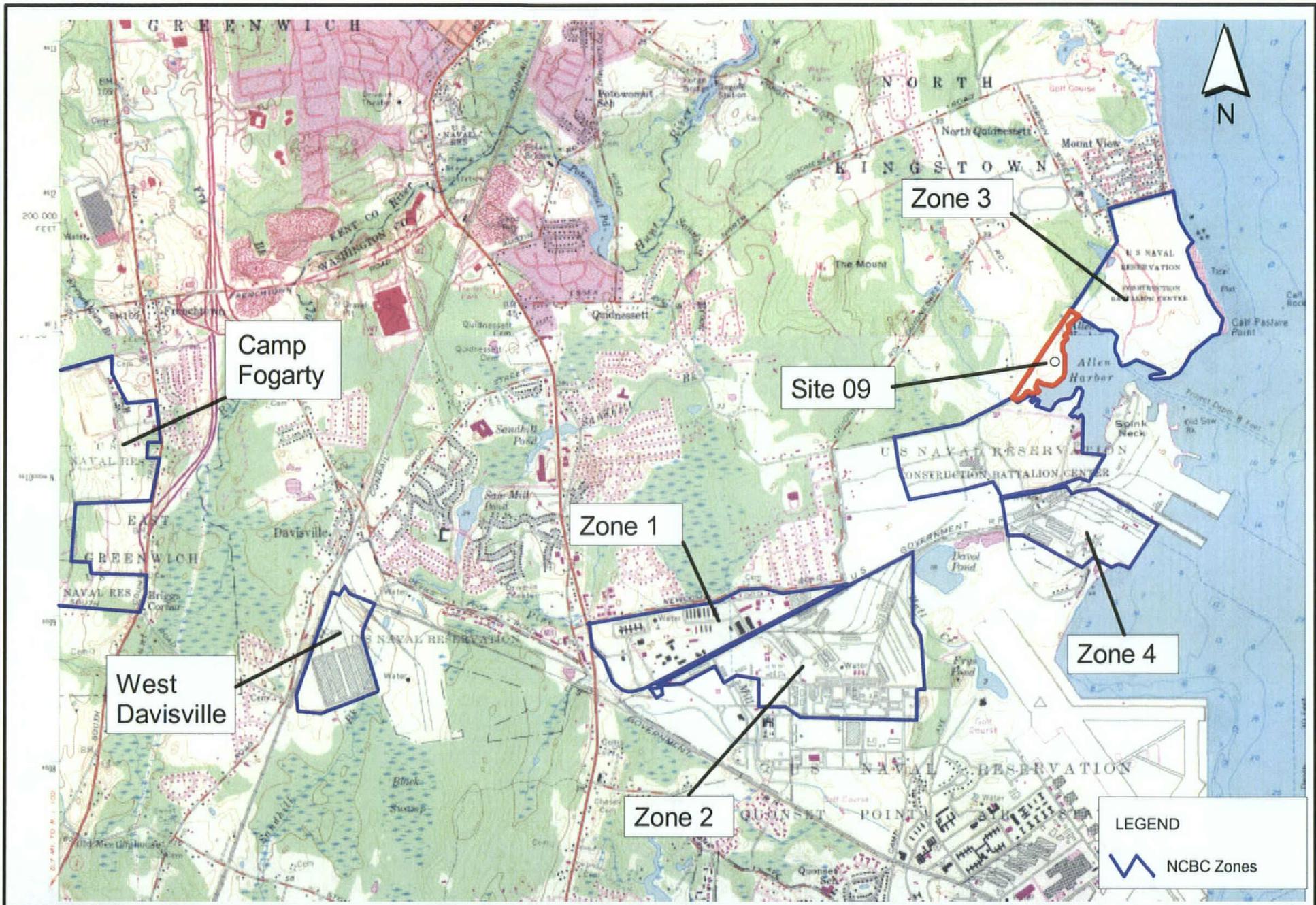
The detected concentrations of dissolved arsenic were found to be significantly increasing in ground-water samples from five monitoring wells (MW09-08S, Figure 9; MW09-14D, Figure 10; MW09-20I, Figure 11; MW09-21S, Figure 12; and MW09-24S, Figure 13). Alternatively, detected dissolved manganese was found to be significantly decreasing in ground-water samples from MW09-09S (Figure 14) and MW09-21S (Figure 15). Finally, detected total chromium concentrations were found to be significantly decreasing in samples from MW09-09S (Figure 16). Because these monitoring wells are located in a landfill, it could not be determined what processes accounted for the increase of dissolved arsenic concentrations or the decrease observed for dissolved manganese and total chromium concentration.

Unique VOC in MW09-11S

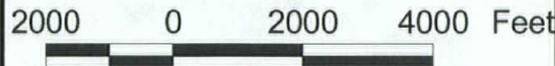
Three generally unique VOC were detected in ground-water samples from monitoring well MW09-11S, and the concentration of each of these VOC has been significantly decreasing over time. These VOC were 1,4-dichlorobenzene (Figure 17), benzene (Figure 18), and chlorobenzene (Figure 19). As with the other temporal trends discussed above, the specific process(s) accounting for the decrease in detected concentrations is not known.

References:

- Battelle. 2004. Revised Conceptual Site Model and Monitoring Optimization Report for Site 07, Calf Pasture Point. Naval Construction Battalion Center (NCBC) Davisville, Rhode Island. August.
- Buscheck, T.E., and Alcantar, C.M. 1995. "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In *Proceedings of the 1995 Battelle International Conference on In Situ and On-Site Bioreclamation*.
- Kendall, M.G. 1938. "A New Measure of Rank Correlation," *Biometrika* 30: 81-93.
- Mann, H.B. 1945. "Nonparametric Tests Against Trend," *Econometrica* 13: 245-259.
- Sen, P.K. 1968. "Estimates of the Regression Coefficient Based on Kendall's Tau," *J. American Statistical Association*, 63: 1379-1389.



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EFANE
LONG TERM MONITORING PROGRAM
SITE 09, NCBC DAVISVILLE
NORTH KINGSTOWN, RHODE ISLAND

SITE LOCUS MAP

FIGURE 1

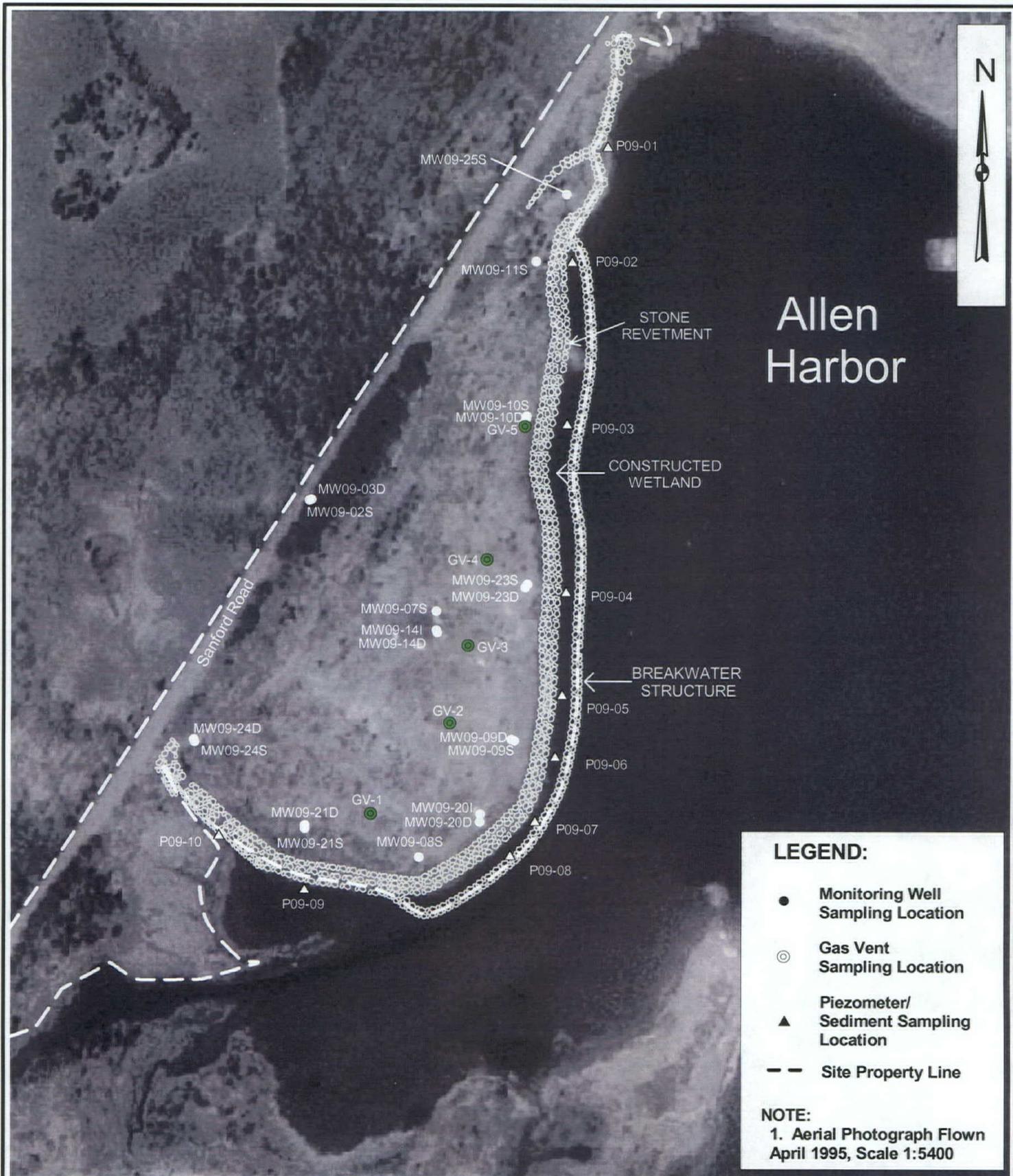


Figure 3 Concentration Trend Plot for Benzo(b)fluoranthene in Sediment at Location SED09-01

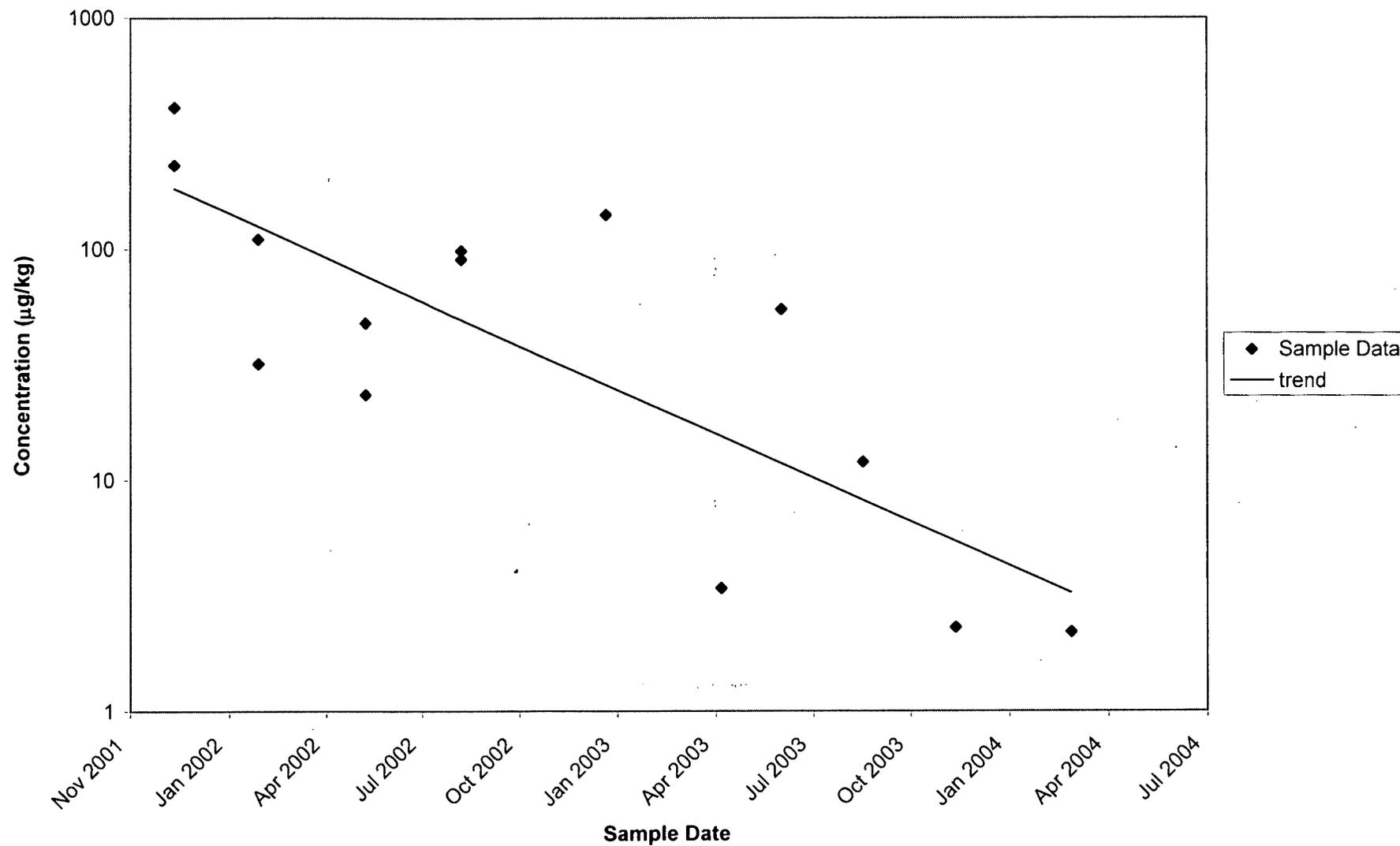


Figure 4 Concentration Trend Plot for Benzo(a)pyrene in Sediment at Location SED09-01

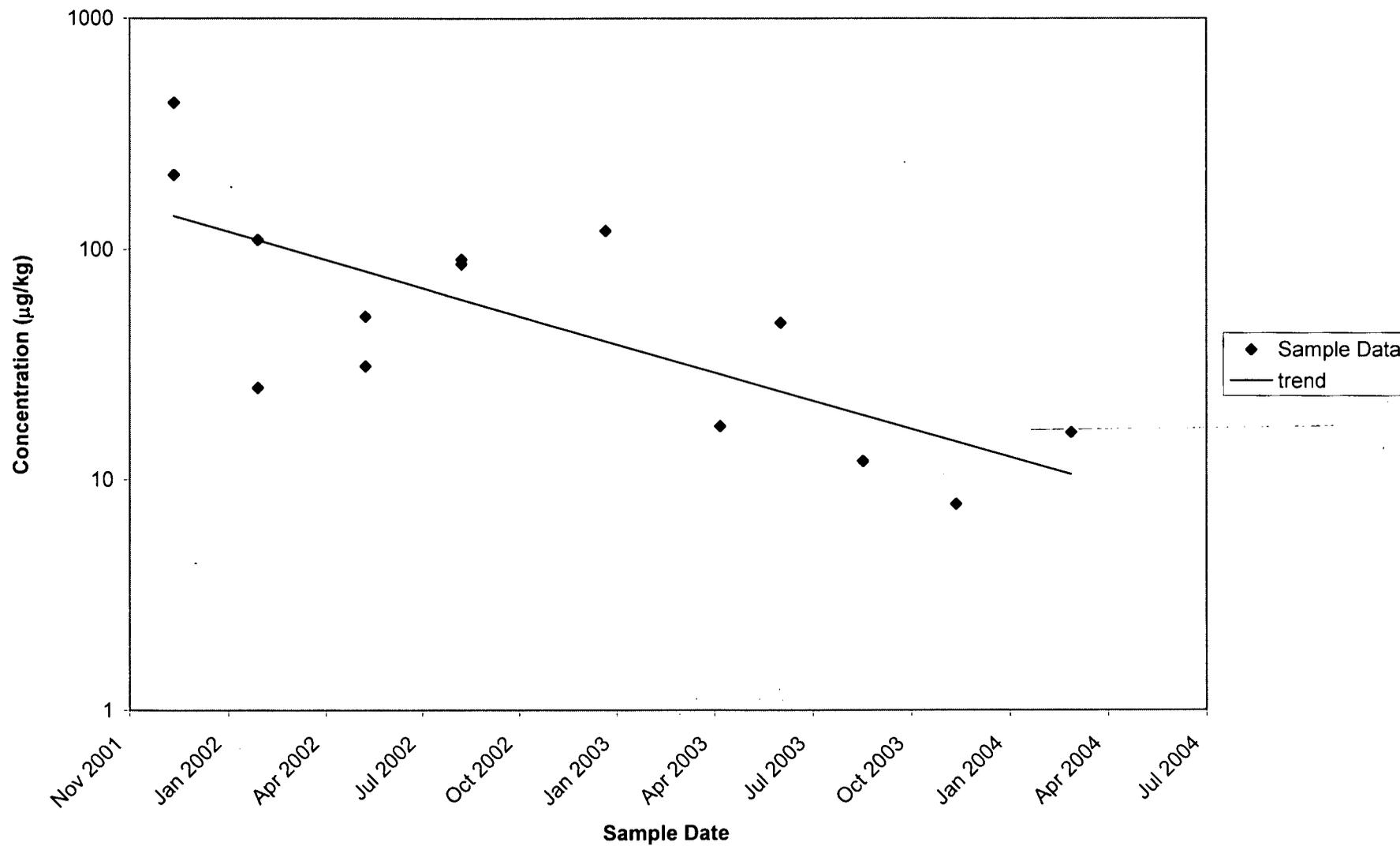


Figure 5 Concentration Trend Plot for Trichloroethene in Ground Water Monitoring Well MW09-08S

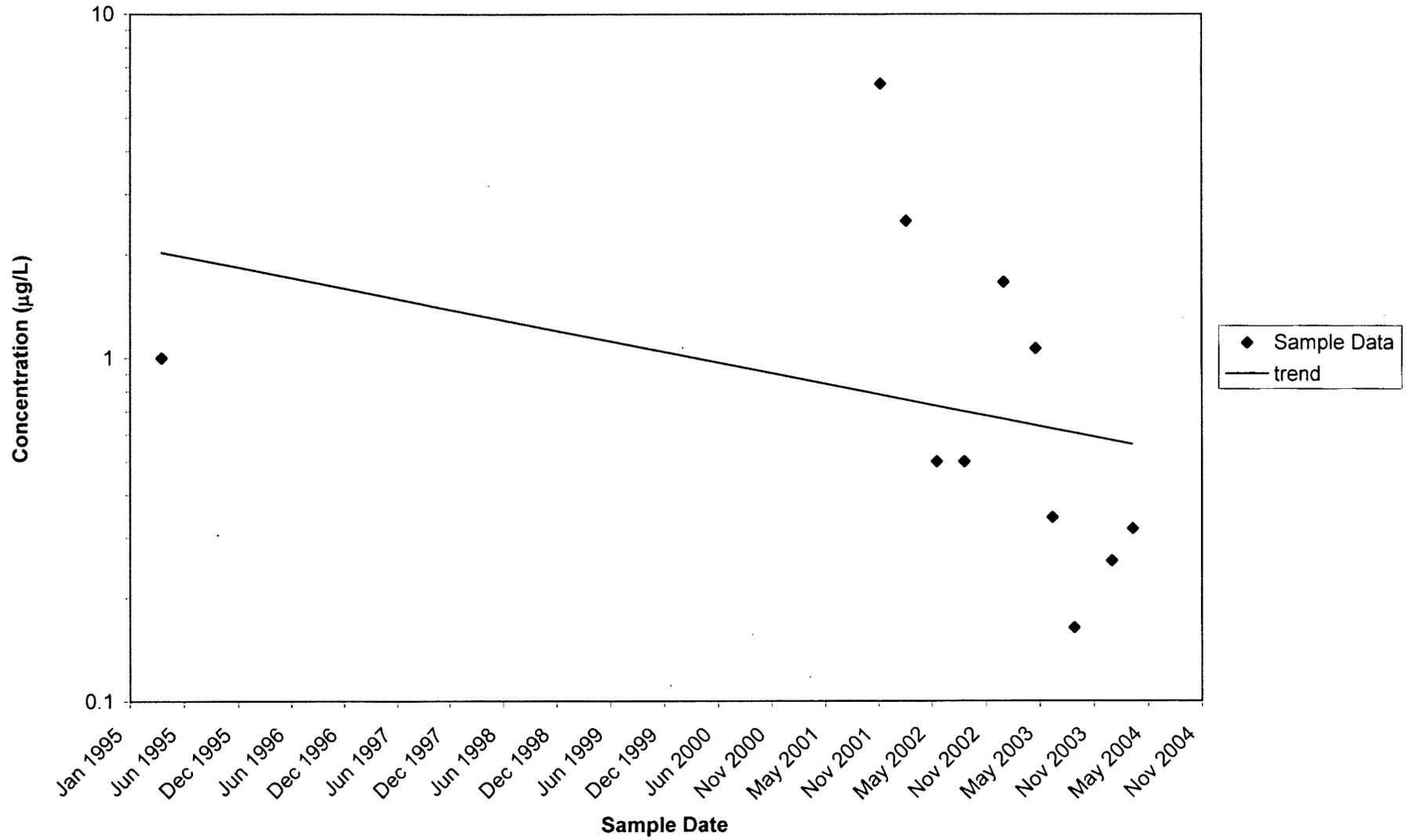


Figure 6 Concentration Trend Plot for Trichloroethene in Ground Water Monitoring Well MW09-21D

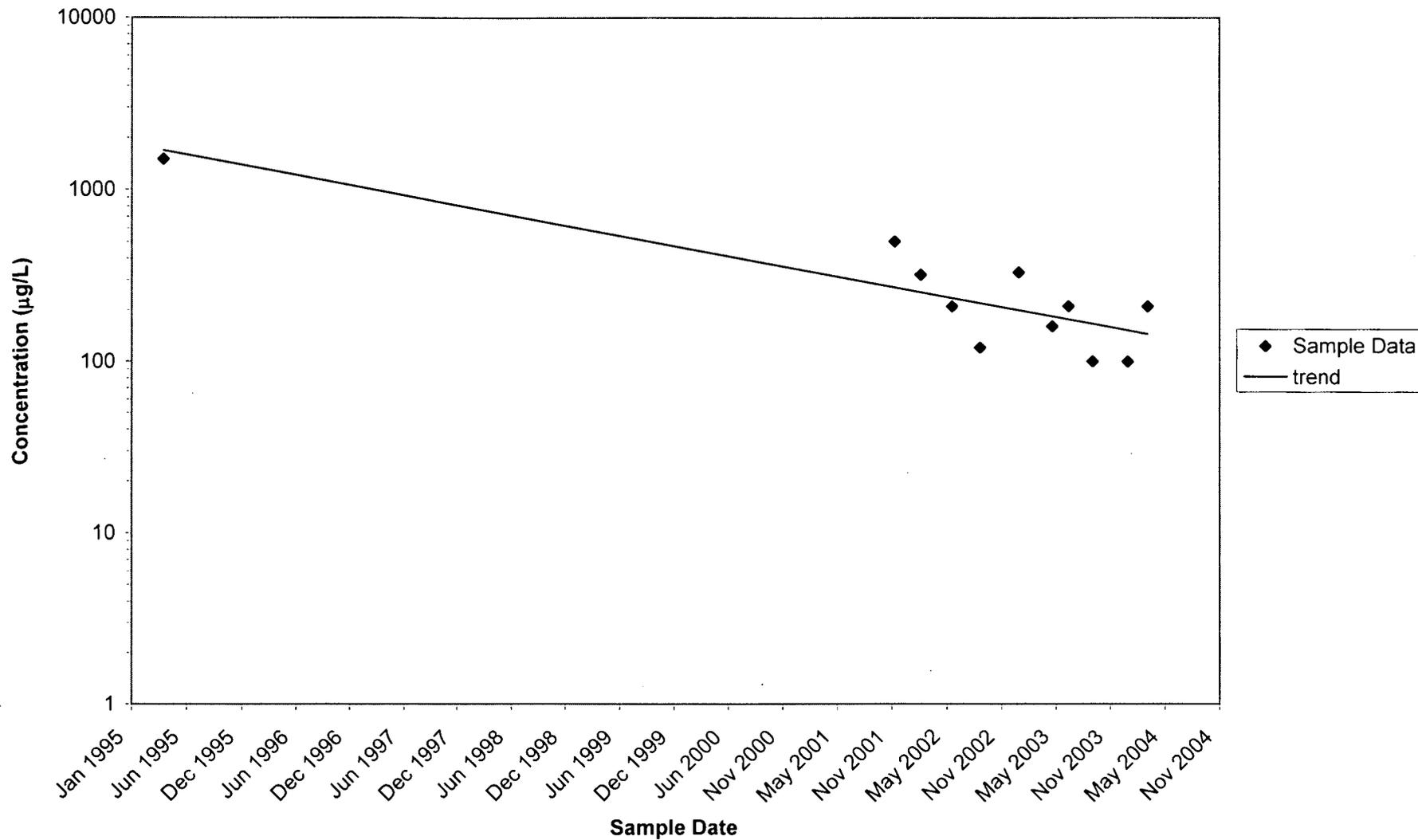


Figure 7 Concentration Trend Plot for Vinyl Chloride in Ground Water Monitoring Well MW09-09S

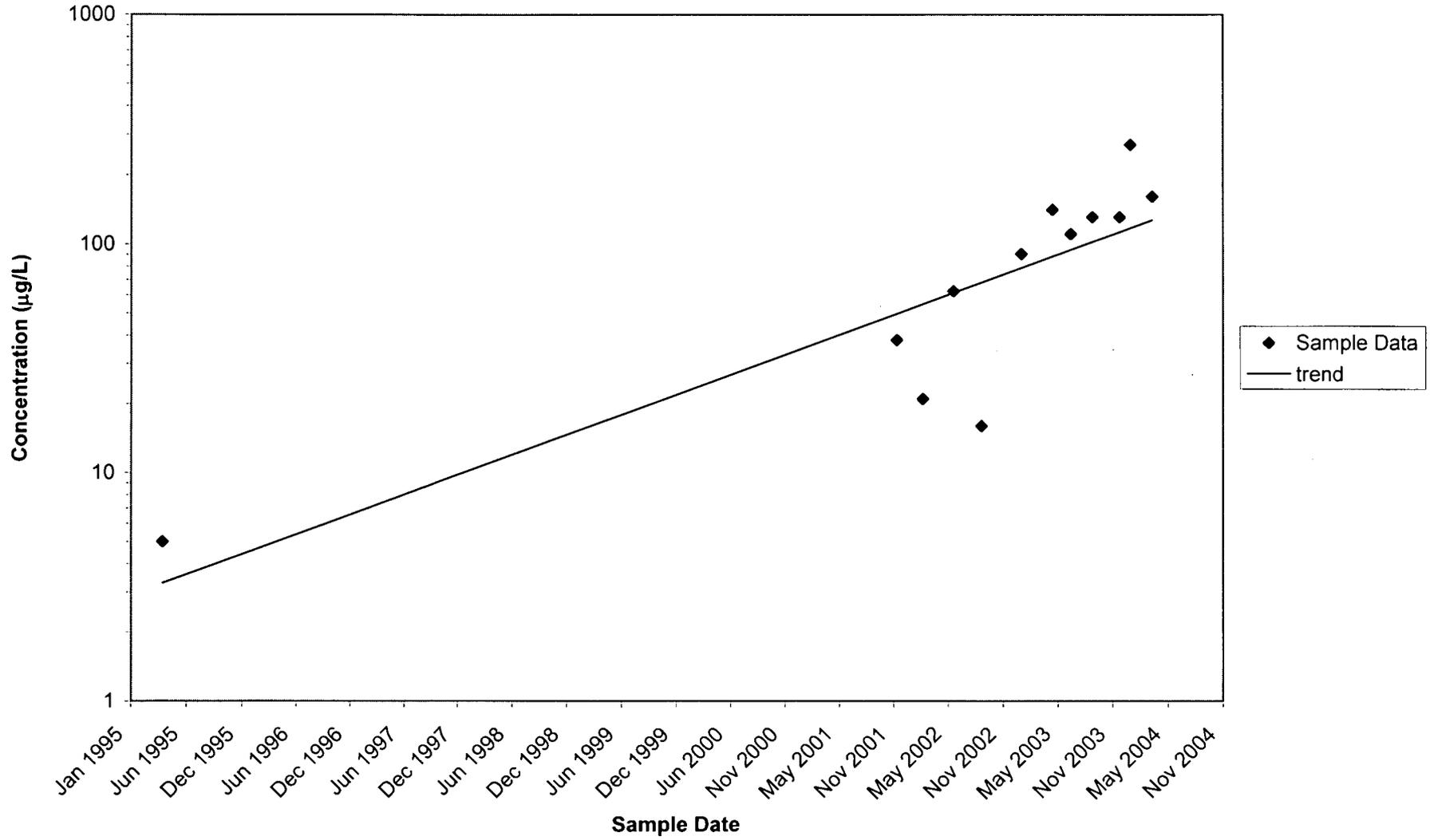


Figure 8 Concentration Trend Plot for Vinyl Chloride in Ground Water Monitoring Well MW09-10S

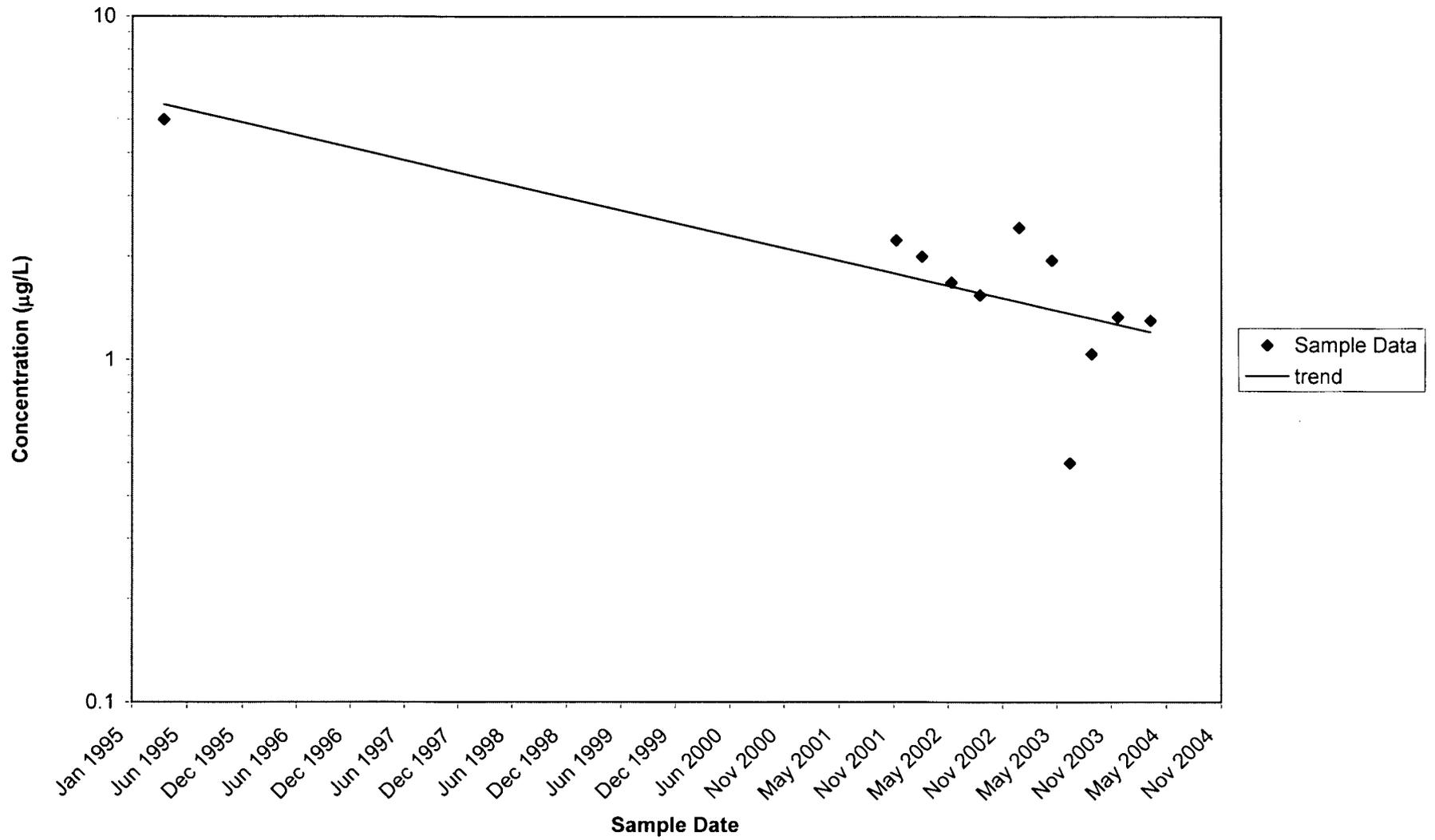


Figure 9 Concentration Trend Plot for Dissolved Arsenic in Ground Water Monitoring Well MW09-08S

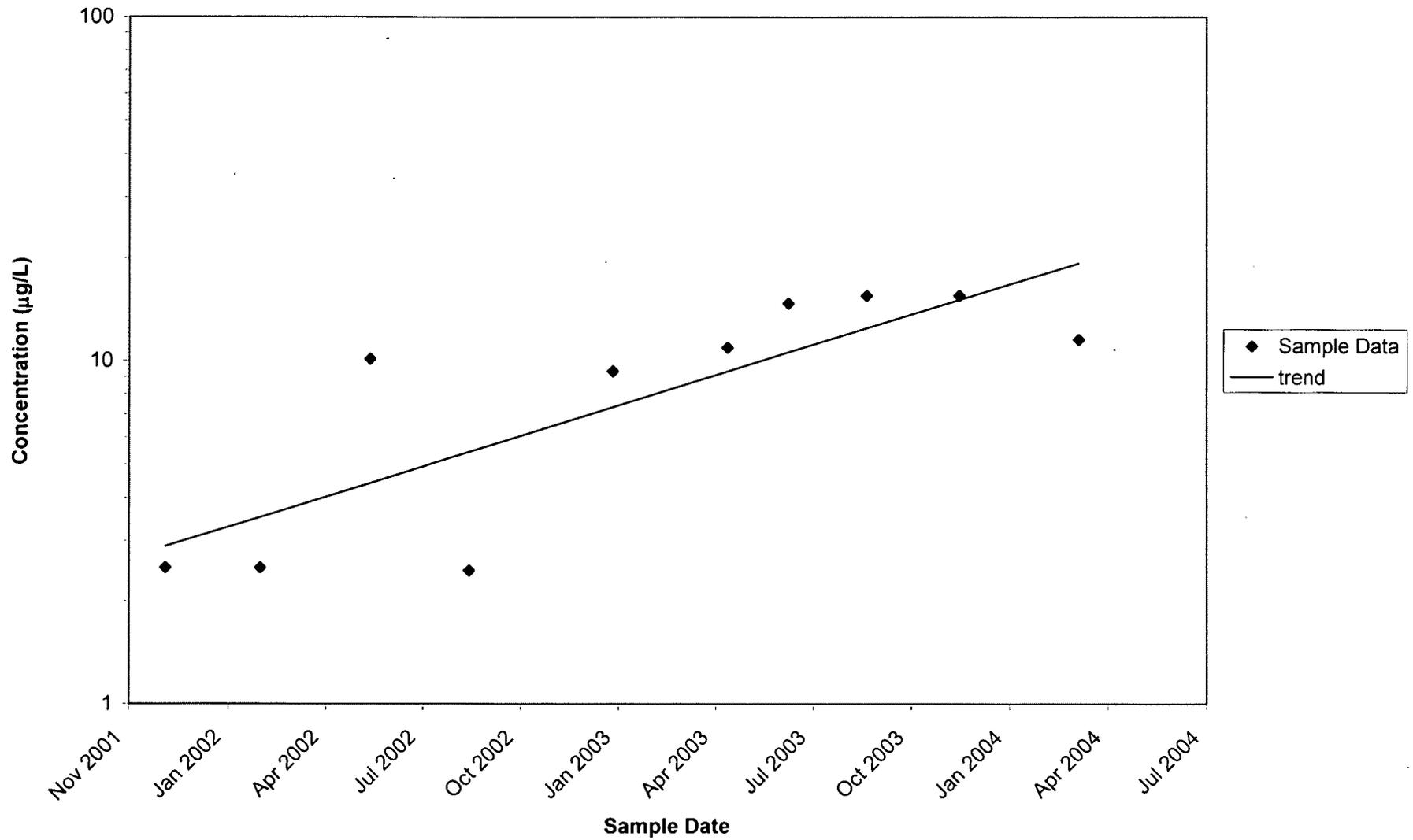


Figure 10 Concentration Trend Plot for Dissolved Arsenic in Ground Water Monitoring Well MW09-14D

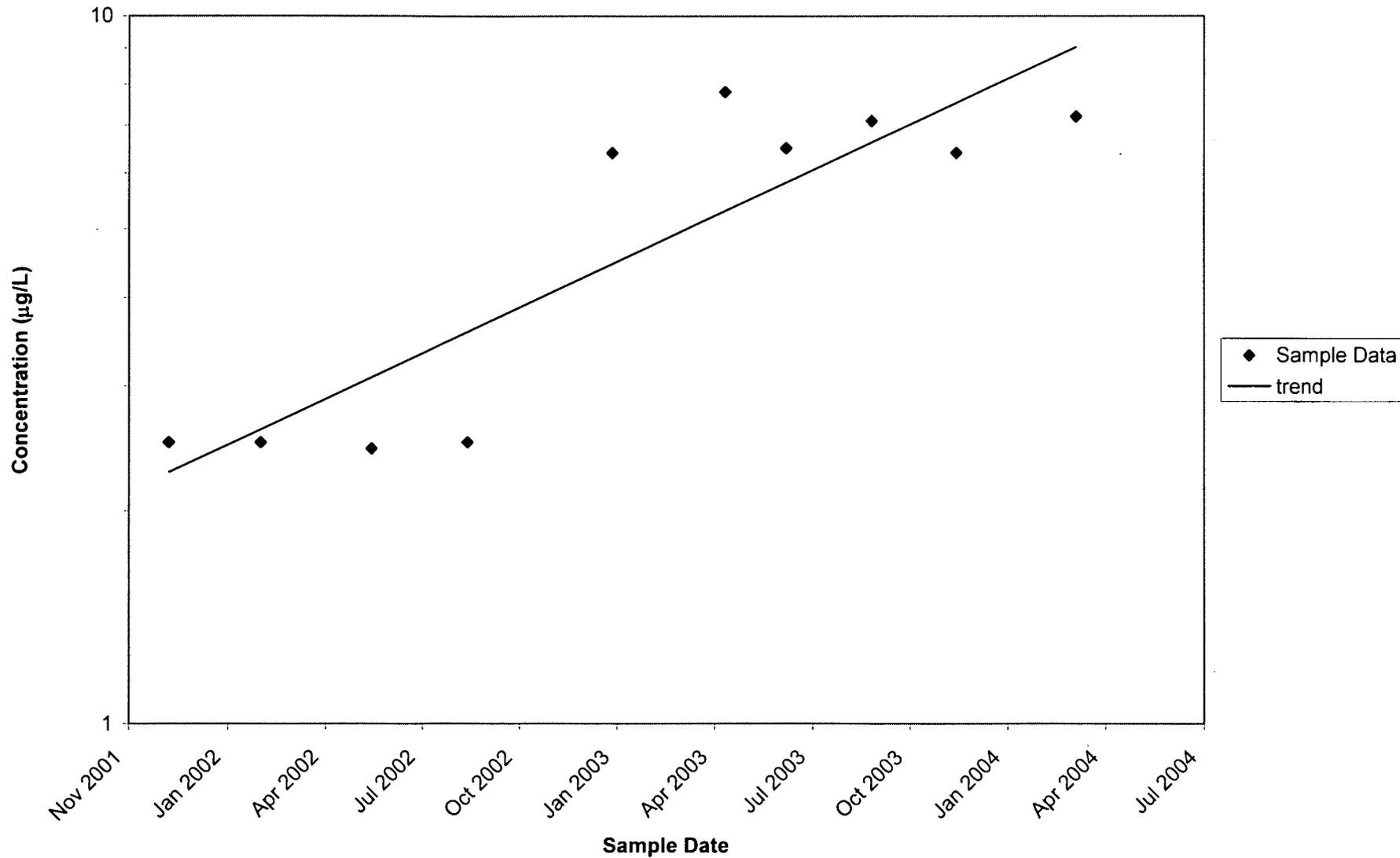


Figure 11 Concentration Trend Plot for Dissolved Arsenic in Ground Water Monitoring Well MW09-20I

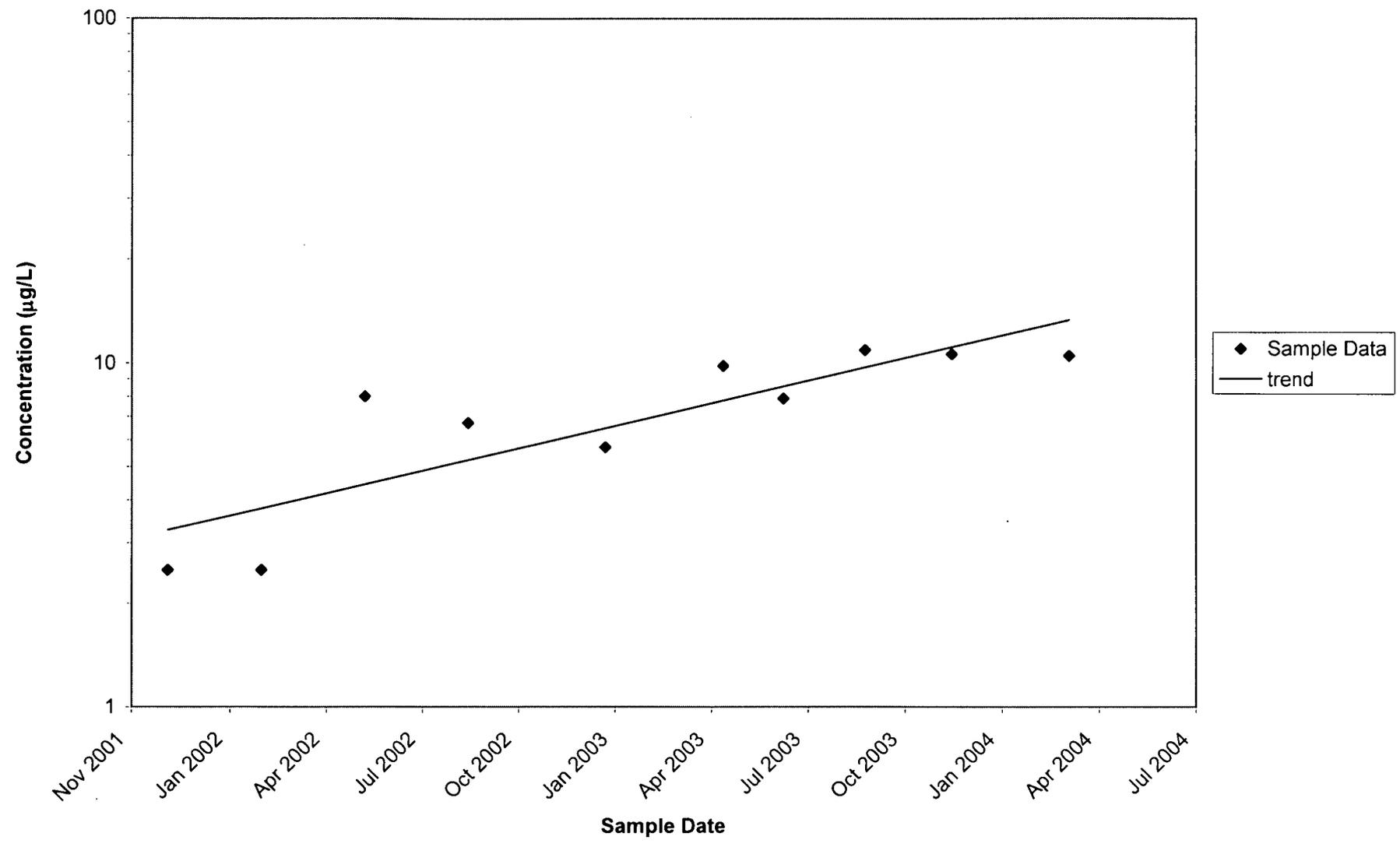


Figure 12 Concentration Trend Plot for Dissolved Arsenic in Ground Water Monitoring Well MW09-21S

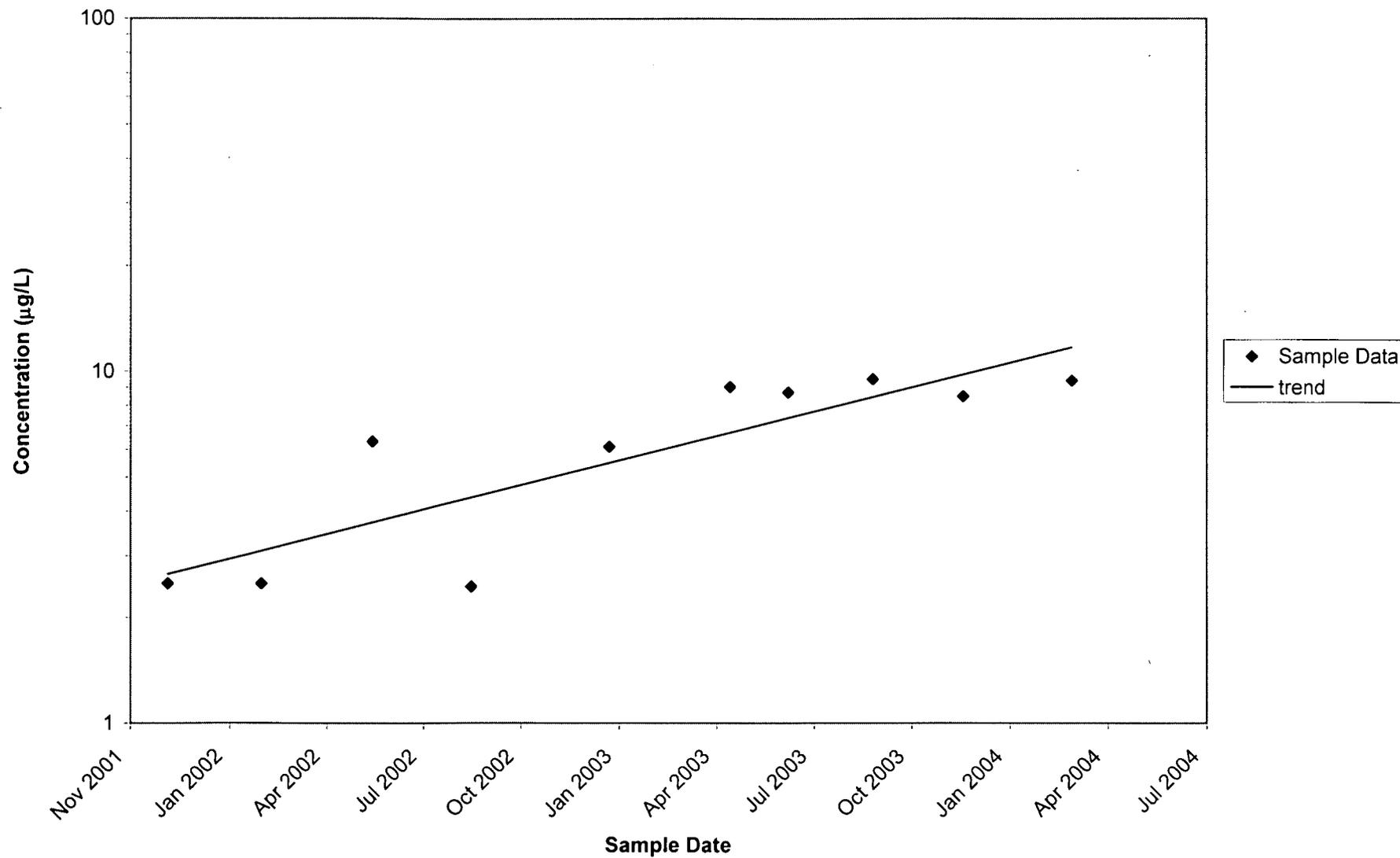


Figure 13 Concentration Trend Plot for Dissolved Arsenic in Ground Water Monitoring Well MW09-24S

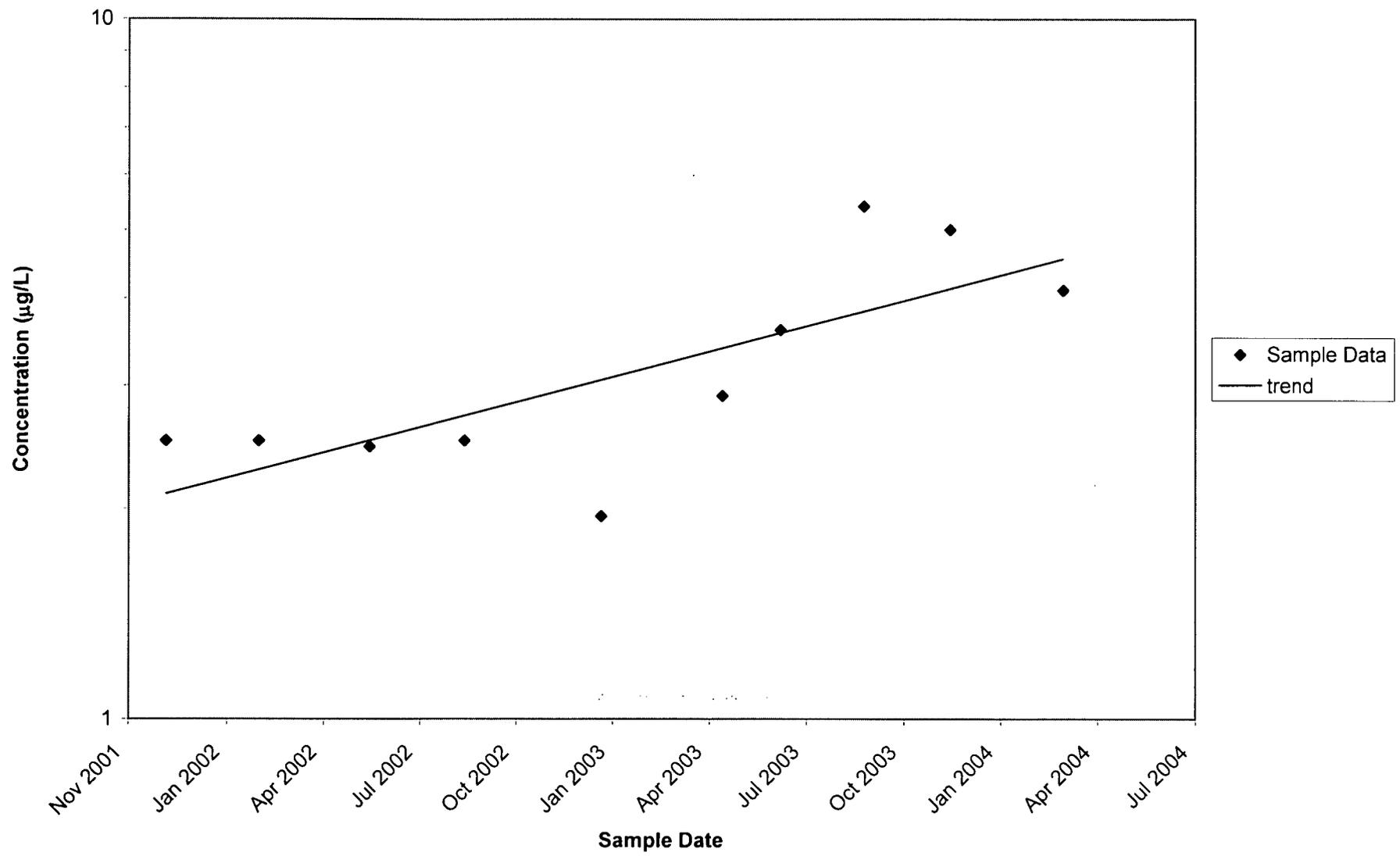


Figure 14 Concentration Trend Plot for Dissolved Manganese in Ground Water Monitoring Well MW09-09S

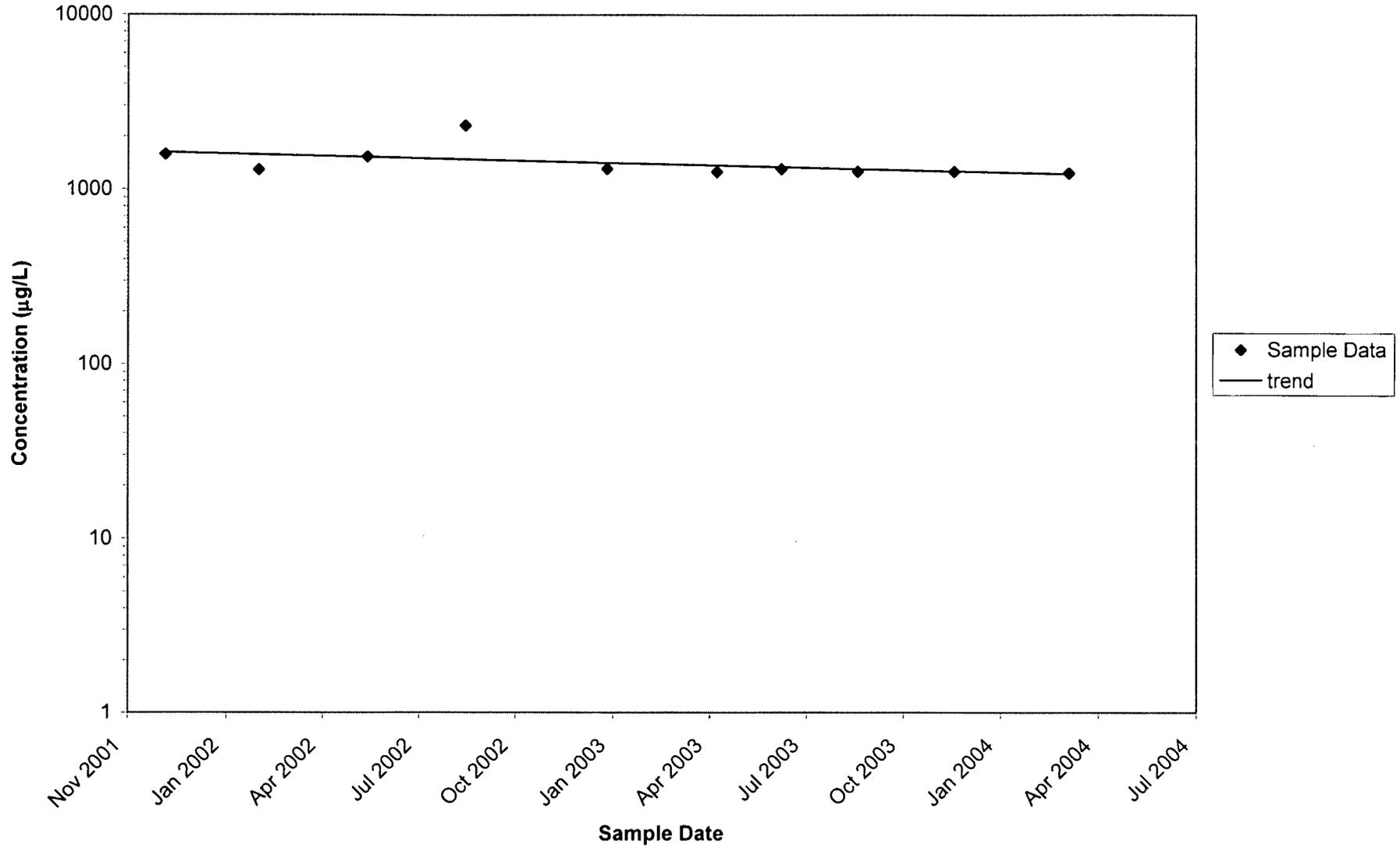


Figure 15 Concentration Trend Plot for Dissolved Manganese in Ground Water Monitoring Well MW09-21S

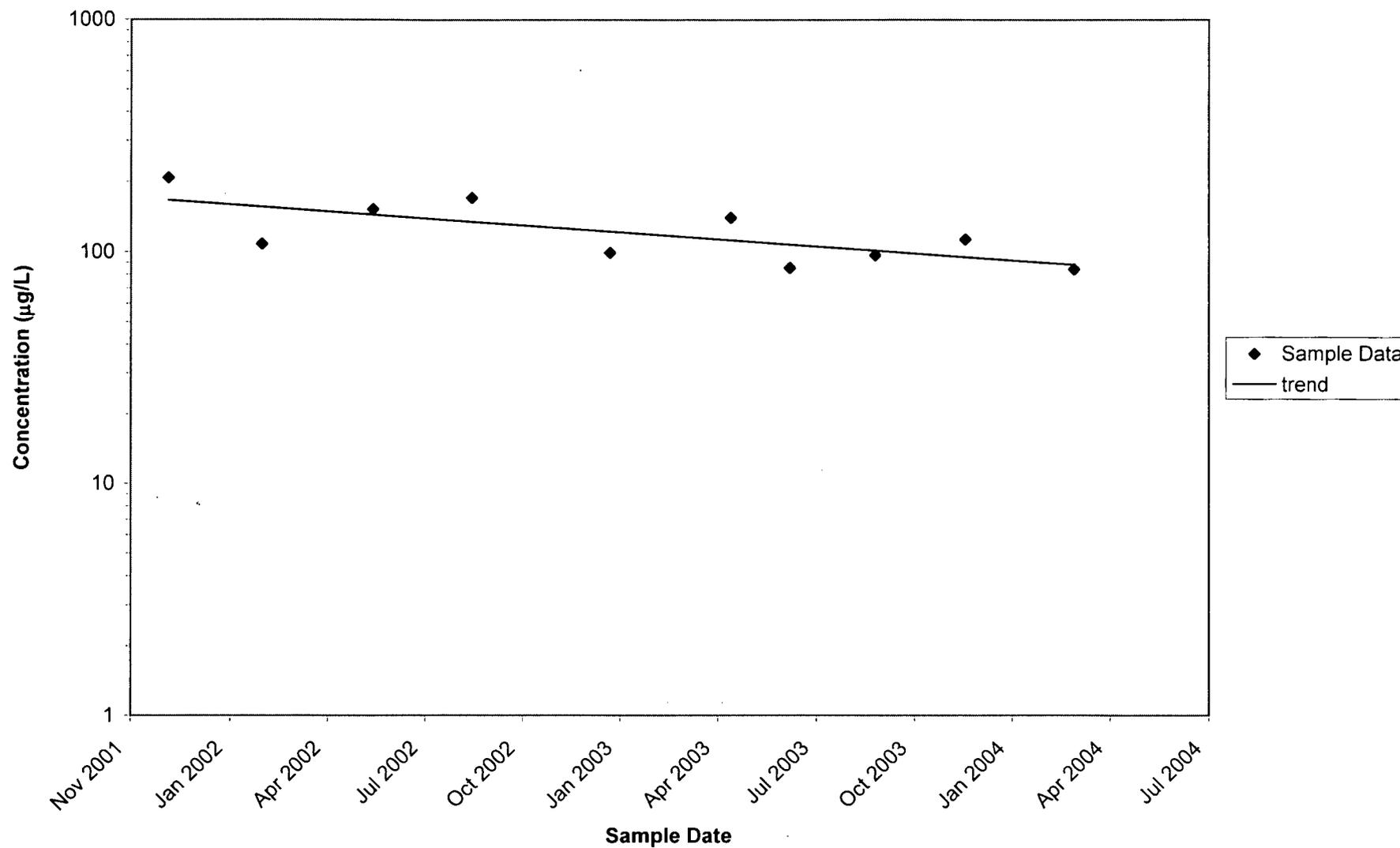


Figure 16 Concentration Trend Plot for Total Chromium in Ground Water Monitoring Well MW09-09S

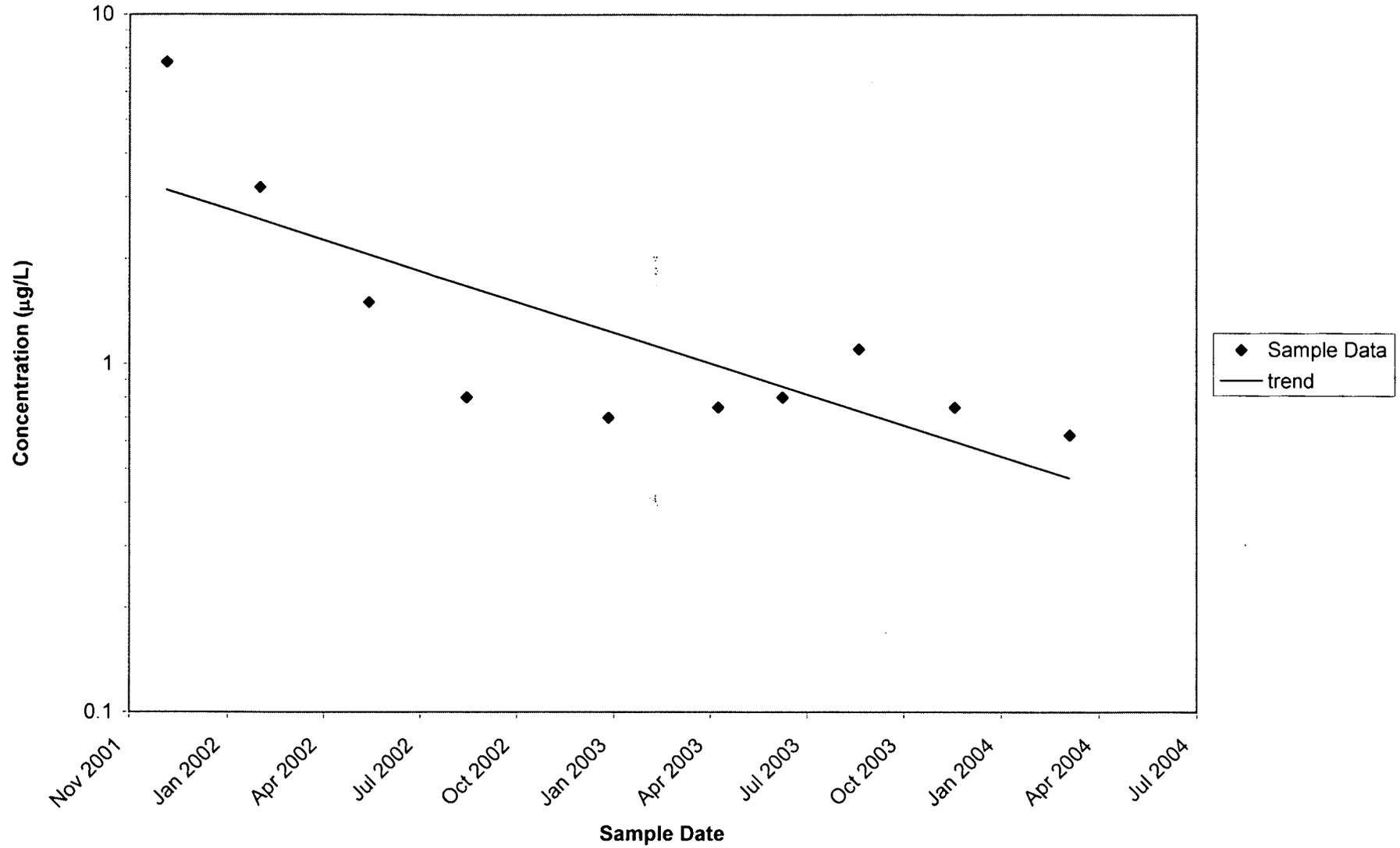


Figure 17 Concentration Trend Plot for 1,4-Dichlorobenzene in Ground Water Monitoring Well MW09-11S

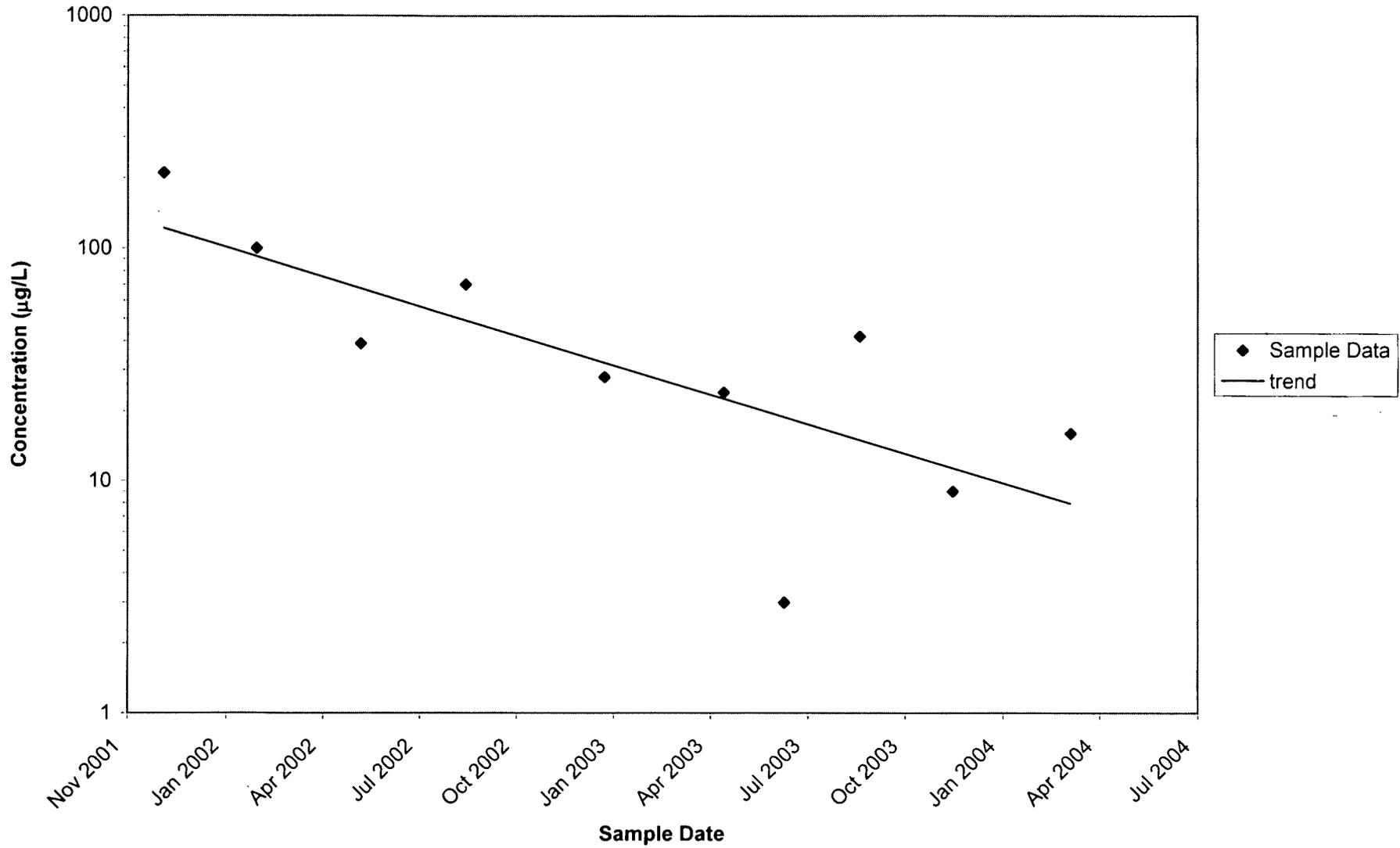


Figure 18 Concentration Trend Plot for Benzene in Ground Water Monitoring Well MW09-11S

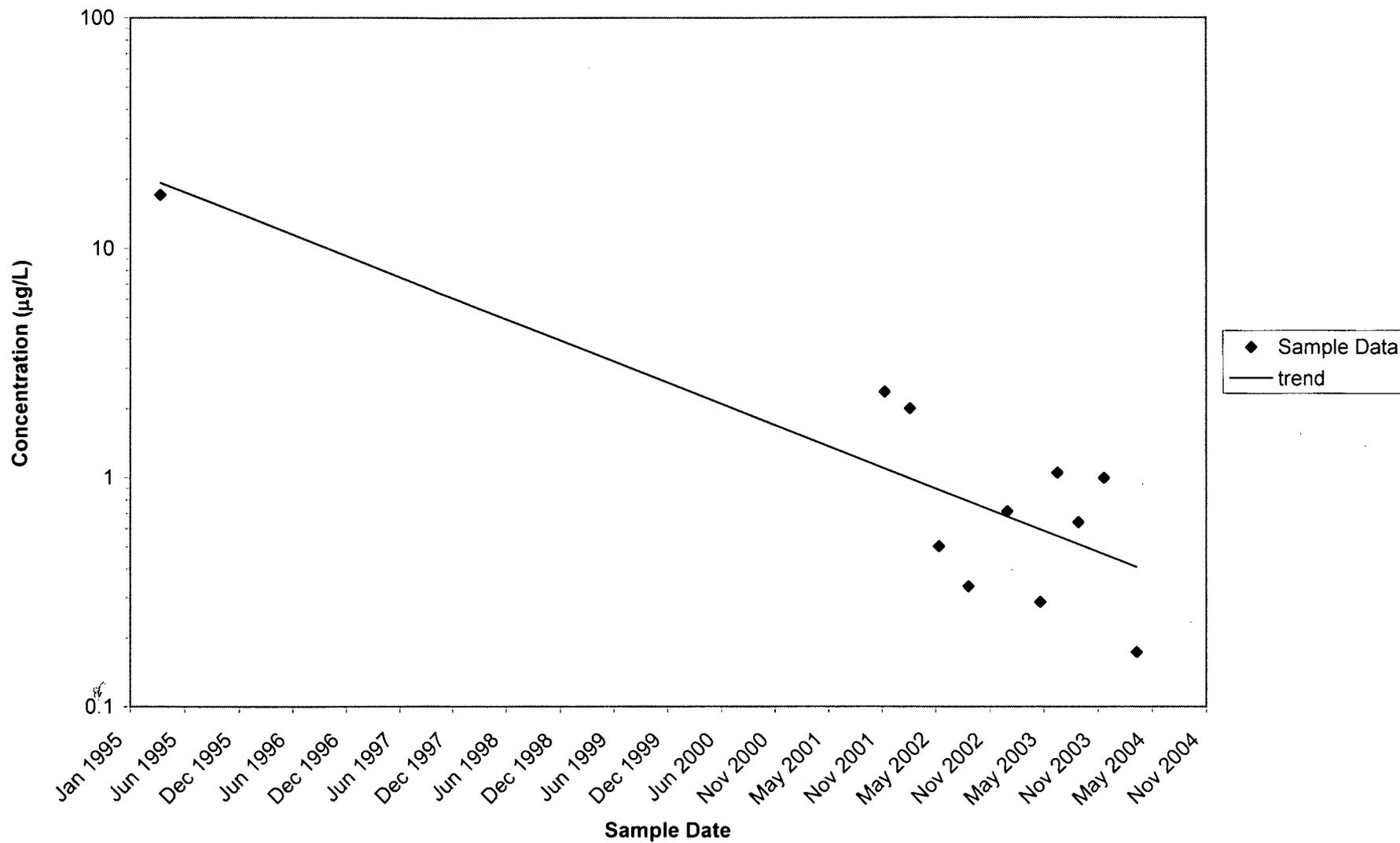
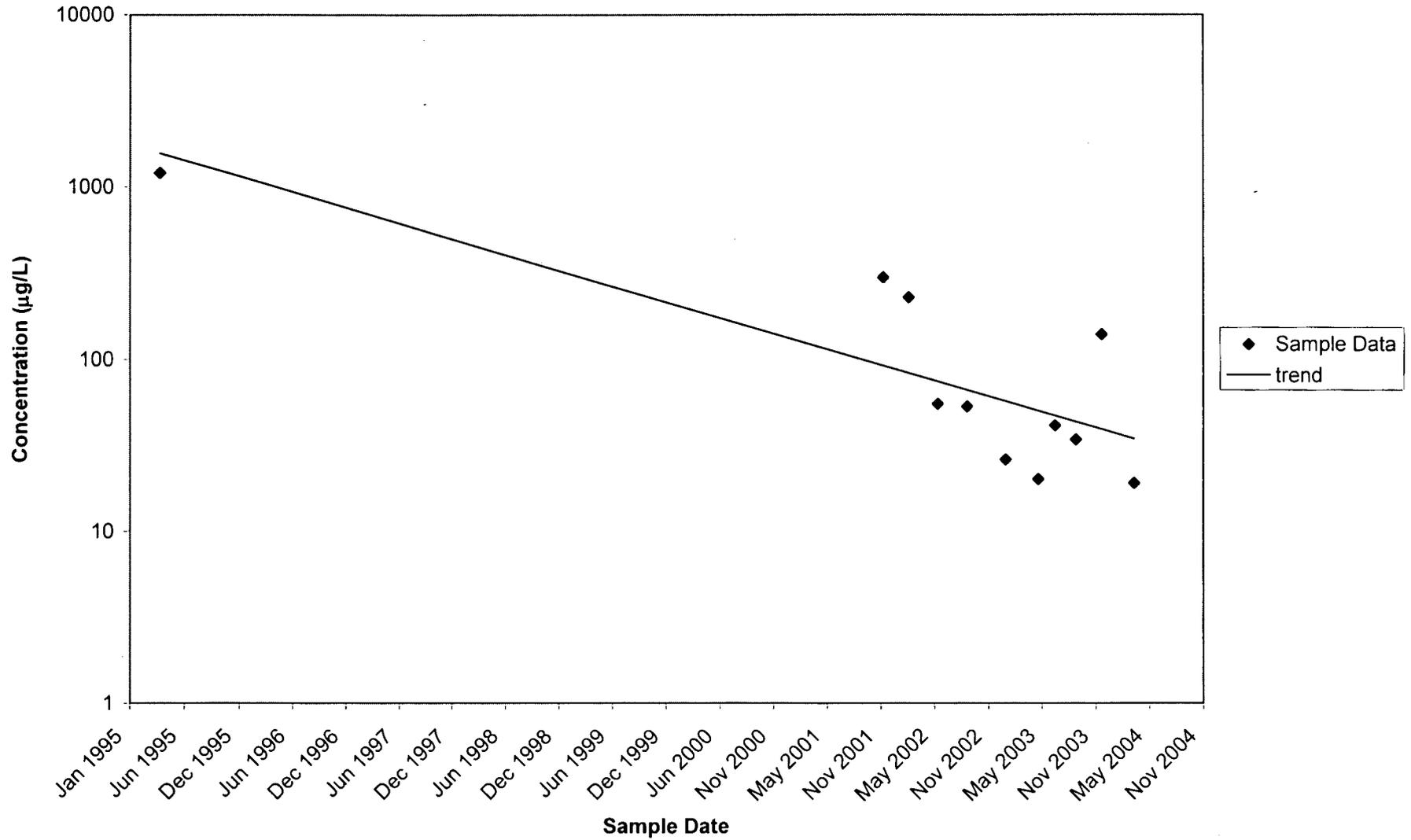


Figure 19 Concentration Trend Plot for Chlorobenzene in Ground Water Monitoring Well MW09-11S



Appendix A
Tabular Results for Sediment

Appendix B
Tabular Results for Landfill Gas

Appendix C
Tabular Results for Ground Water

Appendix D
Database File and
Trend Statistical Program File