DRAFT

Environmental Resources Management

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From: ERM Project Team

Date: 18 August 2005

Subject: Northern Area Steady State Analyses

INTRODUCTION

At this time, the horizontal, downgradient extent of the Northern Area plume is not delineated within the wetland and/or Sudbury River. The downgradient extent and temporal character of the plume (i.e. transient vs. steady state) is of interest to all project stakeholders due to the location of the plume within a GW-1 area. An extensive Waterloo Profiler program has provided reassurance that the plume has not migrated from the Sudbury River area to the east/northeast, beneath Conservation Commission land, toward the Baldwin Pond wellfield. An analysis of the temporal character of the plume at current sampling locations was conducted to evaluate whether the plume dynamics are transient or steady state.

METHODS

A literature review was conducted to support the selection of published statistical methods for evaluating temporal data trends of chemical concentrations in groundwater systems. A summary of literature references and key quotes supporting applicable statistical analyses of temporal groundwater concentration data has been compiled and is provided in Attachment A. Literature supported the use of T-test, Chi-squared, and Mann-Kendall analyses for this evaluation.

The following data plots and interpretations were generated for the analysis of plume temporal character:

- ternary diagrams used to graphically present the ratios of parent vs. daughter products for samples collected from Northern Area wells (Attachment B);

- Mann-Kendall analyses of time-series trends for individual constituents at individual wells, presented graphically in plan view maps of the Northern Area (Attachment C);

- a molar trend plot and Mann-Kendall analysis (acceptable 80% confidence level) for MW-268M (Attachment D);

- a total-plume-mass molar trend plot and Mann-Kendall analysis (acceptable 80% confidence level) using plume-centerline wells (Attachment D); and

- a graphical presentation of multiple statistical analyses, including the t-test, Chi-squared, and Mann-Kendall (90% confidence level) of concentration trends (Attachment E).

RESULTS

Ternary diagrams were produced for key wells within the Northern Area plume. The diagrams are presented individually and also compiled in a plan view map. Both types of output are provided in Attachment B. All ternary diagrams present dominant chemical signatures between TCE and cDCE, with only minor components of VC. The highest components of VC, however, are located relatively close to the source, at monitoring well locations MW-265M and MW-264M. The percentage of VC may generally be expected to increase in the downgradient plume direction. This is not apparent in this plume.

The results of Mann-Kendall analyses performed on concentration trends at individual monitoring wells for individual constituents are presented graphically in Attachment C. The majority of constituents at individual wells present stable or declining concentration trends. Although, increases, determined at the 80% confidence level for this analysis, were interpreted for 5 of the 28 Mann-Kendall analyses.

An evaluation of summed molar concentration of CVOCs over time was performed for downgradient monitoring well MW-268M. The molar concentrations of CVOCs were summed for each monitoring event, and then plotted over time (i.e., each subsequent sampling event). The molar trend chart is presented in Attachment D. A visual decline in concentration is apparent, and a Mann-Kendall analysis (also attached) confirmed this trend to an acceptable 80% confidence level. This determination is important for the determination of potential future impacts to receptors located downgradient of MW-268M. It may be predicted from this analysis that impacts to receptors located downgradient of MW-268M will remain stable or decline given no changes in source-area concentrations.

An evaluation of total molar plume concentration over time was performed. Monitoring wells that were sampled during every Northern Area sampling event were selected for this analysis (i.e., plume centerline wells). The molar concentrations from this subset of wells was summed for each monitoring event, and then plotted over time (i.e., each subsequent sampling event). The total molar trend chart is presented in Attachment D. A visual decline in concentration is apparent, and a Mann-Kendall analysis (also attached) confirmed this trend to an acceptable 80% confidence level. This analysis may be interpreted to show that the overall CVOC contaminant mass within the plume is declining due to natural attenuation processes.

The manual application of three statistical analyses to groundwater analytical data for the Northern Area wells was performed. Results are presented graphically in Attachment E. T-test and Mann-Kendall analyses are used to evaluate increasing, decreasing, or stable trends, while the Chi-squared analysis determines whether or not the data are normally distributed. The analyses presented stable or decreasing CVOC trends at all wells except for PCE concentrations in MW-261S, VC concentrations in MW-266Mb, and PCE and TCE concentrations in MW-267M, at which increasing trends were determined. An increase in degradation products (i.e., cDCE and VC) over time is indicative of an increase in intrinsic biodegradation processes, which are a significant component of natural attenuation.

SUMMARY

A trend of stable or declining chemical concentrations is apparent for most wells within the Northern Area of the Site. A relatively minor number of locations and chemicals showed increasing trends of CVOC constituents. Two of the increasing trends occurred near the source area for the plume, at MW-261S (cDCE and PCE), and the rest occurred at downgradient wells that are interpreted to be off-centerline of the plume. Wells within or close to the centerline of the plume (MW-265M and MW-268M) show stable or decreasing trends for PCE, TCE, cDCE, and/or VC. Since the plume-centerline wells show stable or declining values, it may generally be interpreted from the available dataset that the plume is attenuating or in steady state.

Attachment A

References and Related Notes

<u>Notes on Statistical Analyses for Data Trends, and Related Notes</u>

Data shows no serial correlation – note that serial correlation may over-predict cases where trends occur, but not otherwise, so not correcting for serial correlation is conservative

Graphical – Box Plots – require replicate samples each round
Papastergiou and Papadopoulou-Mourkidou (2001)

Parametric – Sequential T-Test (see Appendix F of EPA, 1992)
Hess et al (2001):

Parametric – Regression Analysis
Gibbs et al (2002)
Pelayo and Evangelista (2003): Linear regression analysis in time – w **groundwater**

Non-Parametric – Mann-Kendall Test
High power, robust test (Manly and MacKenzie, 2000; Hess et al, 2001)

"With the rule of six consecutive data points described above, the chance of erroneously concluding that a trend exists is only 1 in 360, or about 0.3 percent." (EPA, 1992) "In contrast, a rule based on five consecutive points has a 1 in 60 chance (1.6 percent) of erroneously concluding that there is a trend." (EPA, 1992).
"The [Mann-Kendall] trend analysis requires at least four independent sampling events (Wiedemeier et al., 1999)." (from Lee and Lee, 2003).

Yue and Wang:
Yue et al (2002):
Burn and Hag Elnur:
Zetterqvist (1991):

van Belle & Hughes and χ^2
Dixon and Chiswell (1996):
van Belle and Hughes (1984) took the work of Hirsch et al. (1982) a step further, and presented a method for testing the homogeneity assumptions implicit in the use of intrablock methods (which include the seasonal Kendal tests) and aligned rank methods (Farrell, 1980) for trend testing. They showed how χ^2 statistics could be derived to test for overall trend and for site and seasonal heterogeneity and interaction. They also gave advice on the analysis of nonuniformly-sampled data sets.
Berryman *et al.* (1988) reviewed nonparametric tests for trend, and gave a useful flowchart for the selection of a statistical test for a monotonic trend. Their best choices for use with water quality time series were the Mann-Whitney, Spearmen and Kendall tests. Yu et al. (1993) gave a case study of the performance of four, established, nonparametric methods in detecting trends in water quality data of rivers in Kansas. These were the Mann-Kendall, seasonal Kendall and Sen's t-tests, and Sen's estimator of slope. They found that the tests had similar powers at a 0.05 significance

level for data records of over nine years. They also discussed the use of the van Belle and Hughes' χ^2 test for homogeneity of trends with the above tests, and found heterogeneity in station-wide or basin-wide trends.

Gan(1998)

Mass Flux
e.g., Suarez and Rifai (2002)

References

Burn, Donald H. and Mohamed A. Hag Elnur, "Detection of hydrologic trends and variability," Journal of Hydrology, 255:107-122, 2002.

Darken, P. F., Holtzman, G. I., Smith, E. P. and Carl E. Zipper, "Detecting changes in trends in water quality using modified Kendall's tau," Environmetrics 11:312-323, 1999.

Dixon, William and Barry Chiswell, "Review of aquatic monitoring program design," Water Research 30(9):1935-1948, 1996.

Gan, Thian Yew, "Hydroclimatic trends and possible climatic warming in the Canadian Prairies," Water Resources Research, 34(11):3009-3015, 1998.

Gibbs, James T., Williamson, Travis K., Naber, J. Steven J. and Thomas L. Macchiarella, "Multiple Methods for Determining Stability of Attenuating MTBE Groundwater Plume," *Journal of Environmental Engineering*, Vol. 128, No. 9, pp. 891-901, September 1, 2002.

Hamed, Khaled H. and A. Ramachandra Rao, "A modified Mann-Kendall trend test for autocorrelated data," Journal of Hydrology, 204:182 196, 1998.

Hess, Ann, Iyer, Hari and William Malm, "Linear trend analysis: a comparison of methods," Atmospheric Environment 35:5211–5222, 2001.

Lee, Jin-Yong and Kang-Kun Lee, "Viability of natural attenuation in a petroleum-contaminated shallow sandy aquifer," Environmental Pollution 126:201–212, 2003.

Manly, Bryan F. and Darryl MacKenzie, "A cumulative sum type of method for environmental monitoring," Environmetrics, 11:151-166, 2000.

Mann, Henry B., "Nonparametric tests against trend," Econometrica, 13(3):245-259, 1945.

Papastergiou, Asterios and Euphemia Papadopoulou-Mourkidou, "Occurrence and Spatial and Temporal Distribution of Pesticide Residues in Groundwater of Major Corn-Growing Areas of Greece (1996-1997)," Environ. Sci. Technol., 35(1):63-69, 2001.

Pelayo, Aristeo M., and Fe S. Evangelista, "A statistical F test for the natural attenuation of contaminants in groundwater," Environmental monitoring and assessment, 83:47-70, 2003.

Suarez, Monica P. and Hanadi S. Rifai, "Evaluation of BTEX remediation by natural attenuation at a coastal facility," Ground Water Monitoring and Remediation, 22(1):62–77, 2002.

US EPA, "Methods for Evaluating The Attainment Of Cleanup Standards, Volume 2: Groundwater," Environmental Statistics and Information Division (PM-222), EPA 230-R-92-014, July 1992.

US EPA, "Guidance for Data Quality Assessment: Practical Methods for Data Analysis, EPA QA/G-9 QA00 Update," Office of Environmental Information, EPA/600/R-96/084, July 2000.

Yue, Sheng and Chunyuan Wang, "The Mann-Kendall Test Modified by Effective Sample Size to Detect Trend in Serially Correlated Hydrological Series," Water Resources Management 18:201–218, 2004.

Yue, Sheng, Pilon, Paul and George Cavadias, "Power of the Mann-Kendall and Spearman's rho tests for detection of monotonic trends in hydrological series," Journal of Hydrology, 259:254-271, 2002.

Zetterqvist, Lena, "Statistical estimation and interpretation of trends in water quality time series," Water Resources Research, 27(7):1637-1648, 1991.

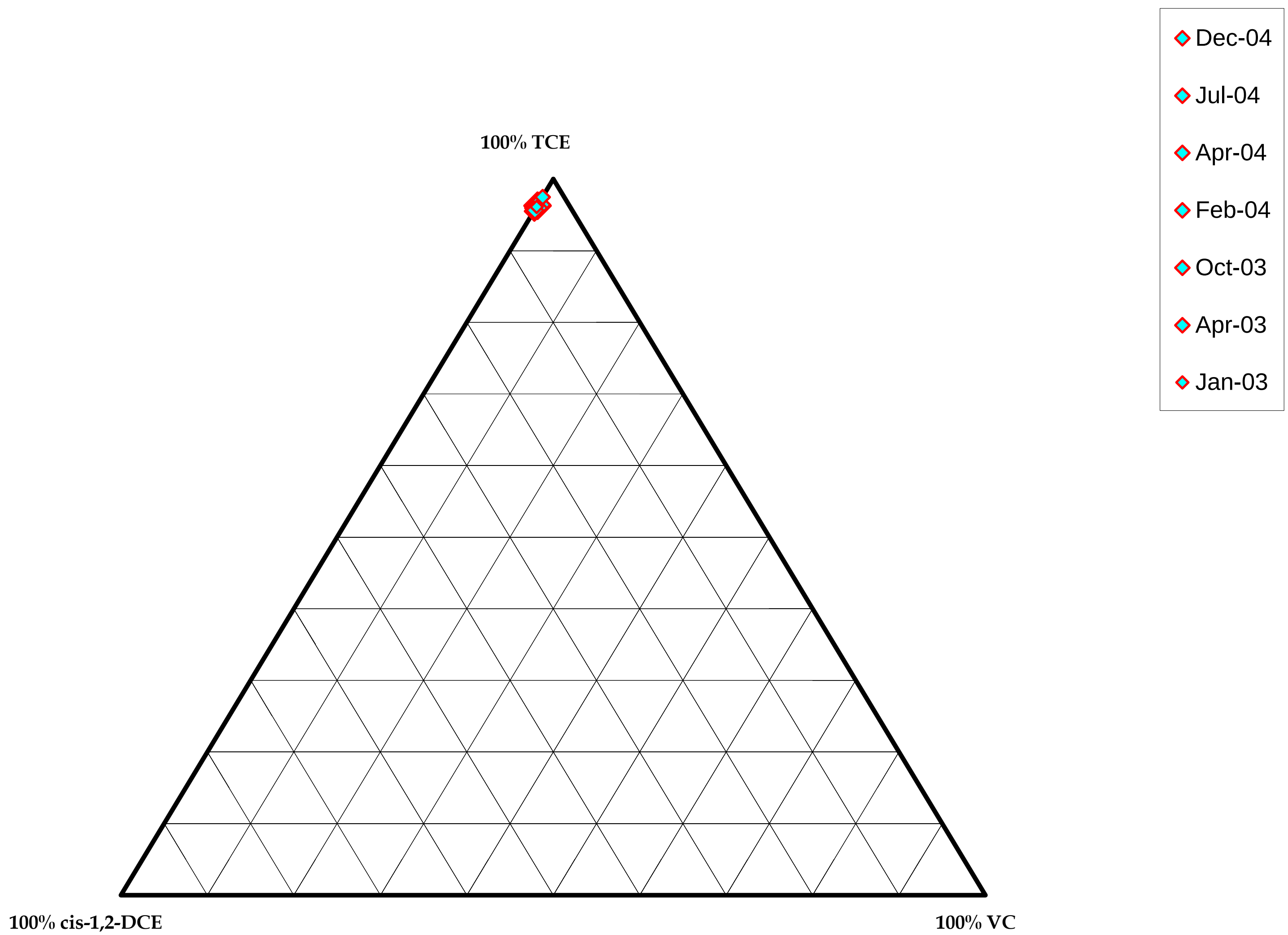
Gauthier, Thomas D., "Detecting trends using Spearman's rank correlation coefficient," Environmental Forensics, 2:359-362, 2001.

MTBE in Groundwater example

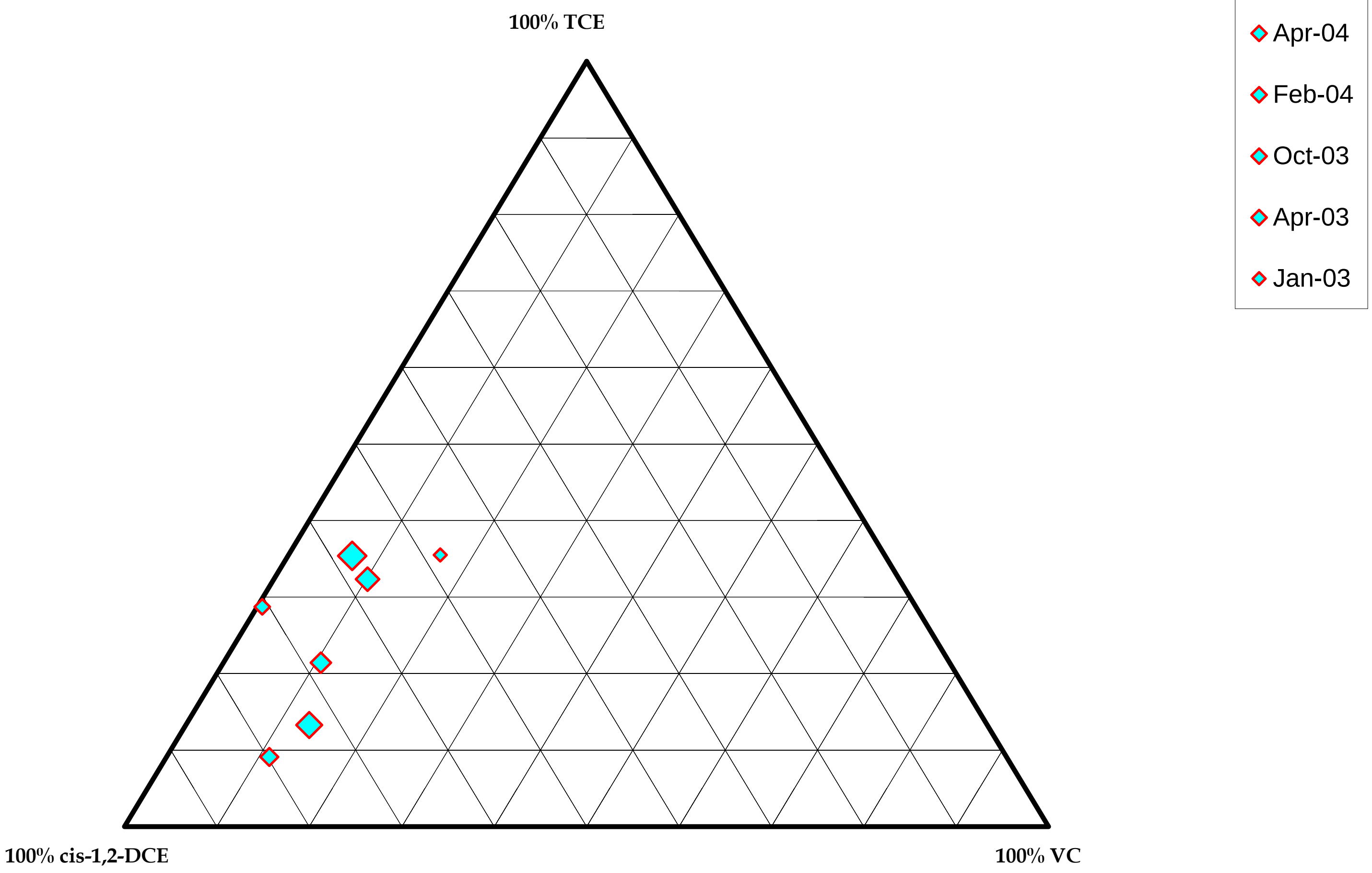
Attachment B

Ternary Diagrams for Hydrochemical Facies Analysis

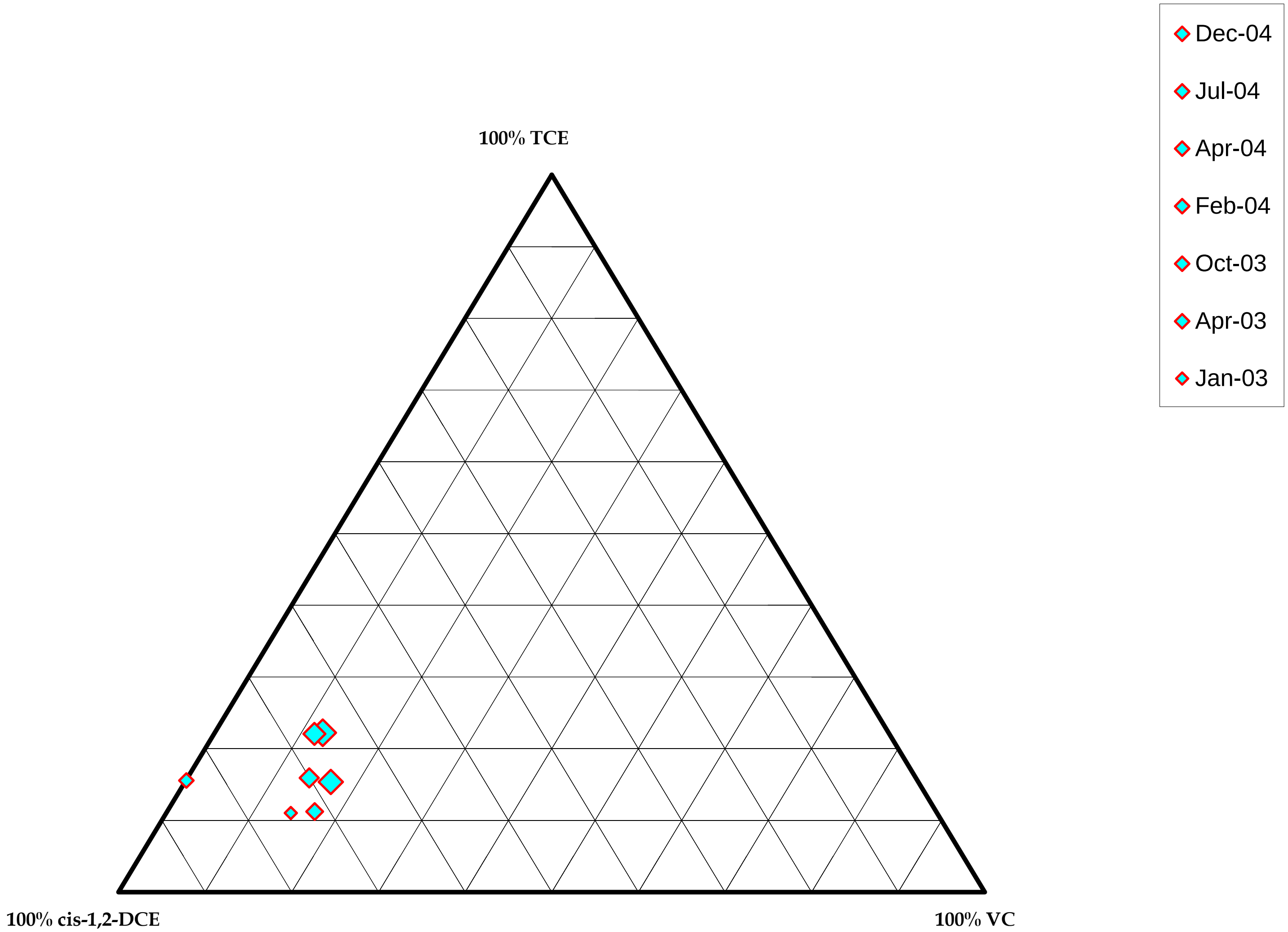
MW-261S TCE-cDCE-VC Time-series



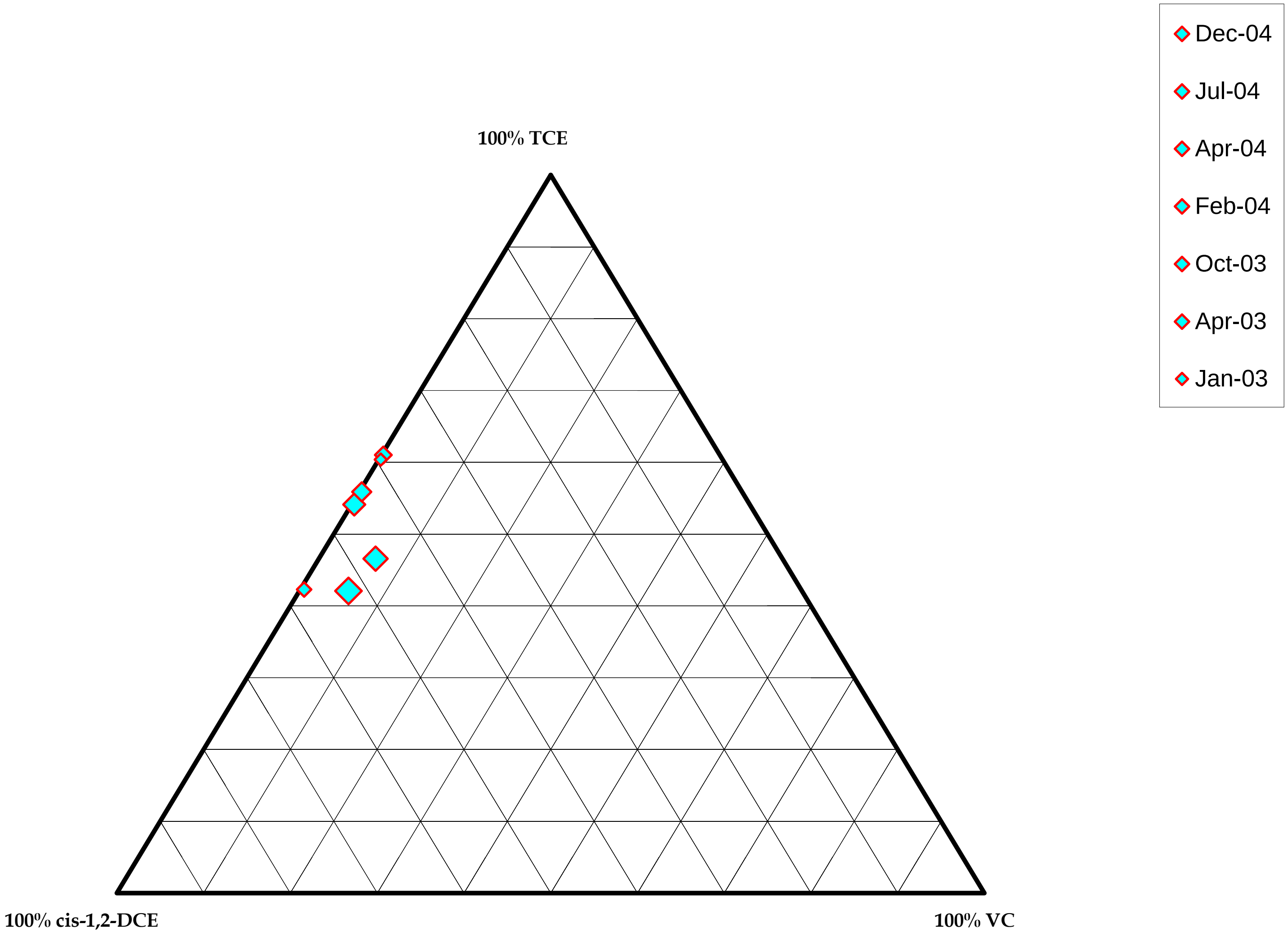
MW-264M TCE-cDCE-VC Time-series



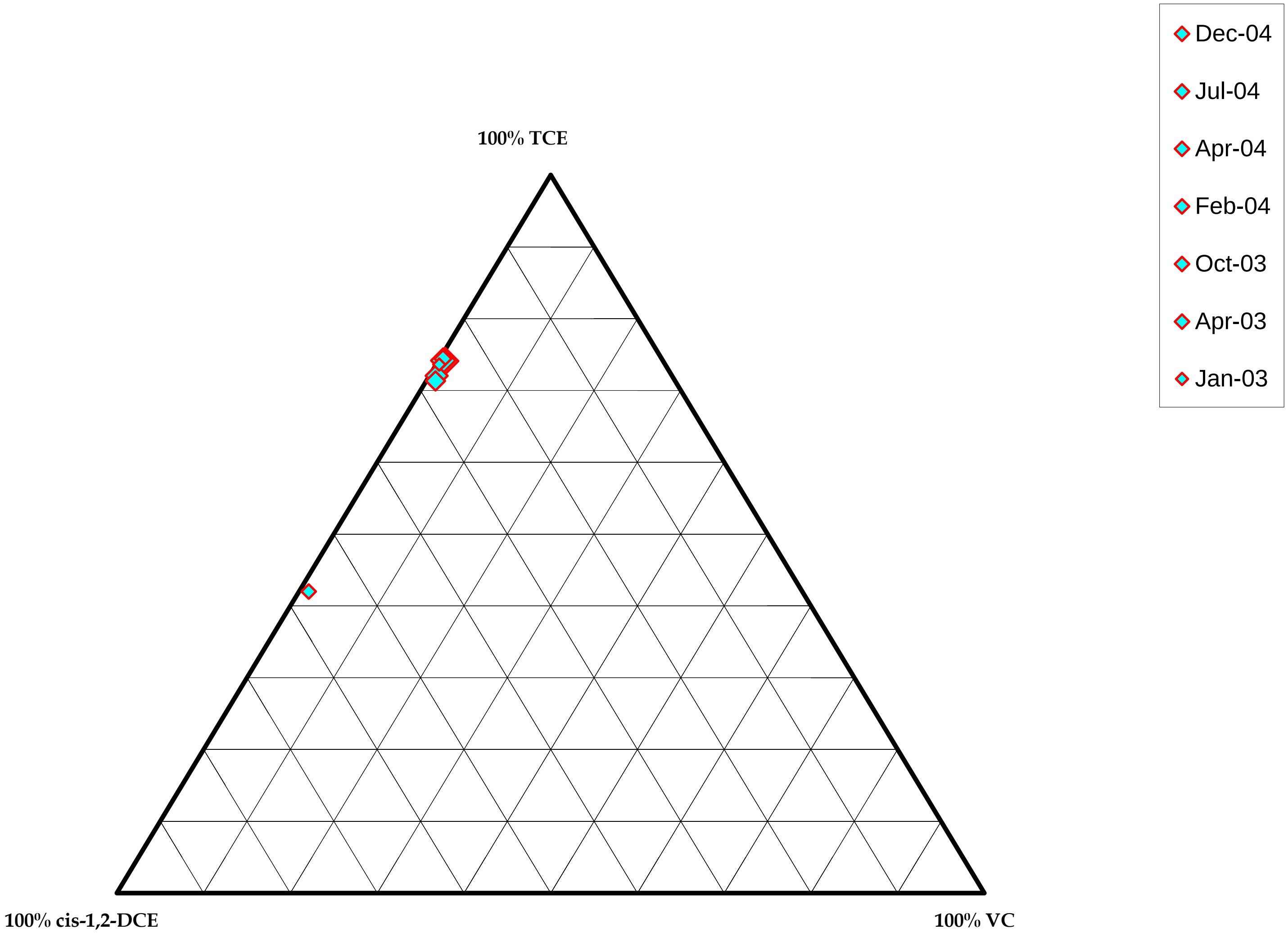
MW-265M TCE-cDCE-VC Time-series

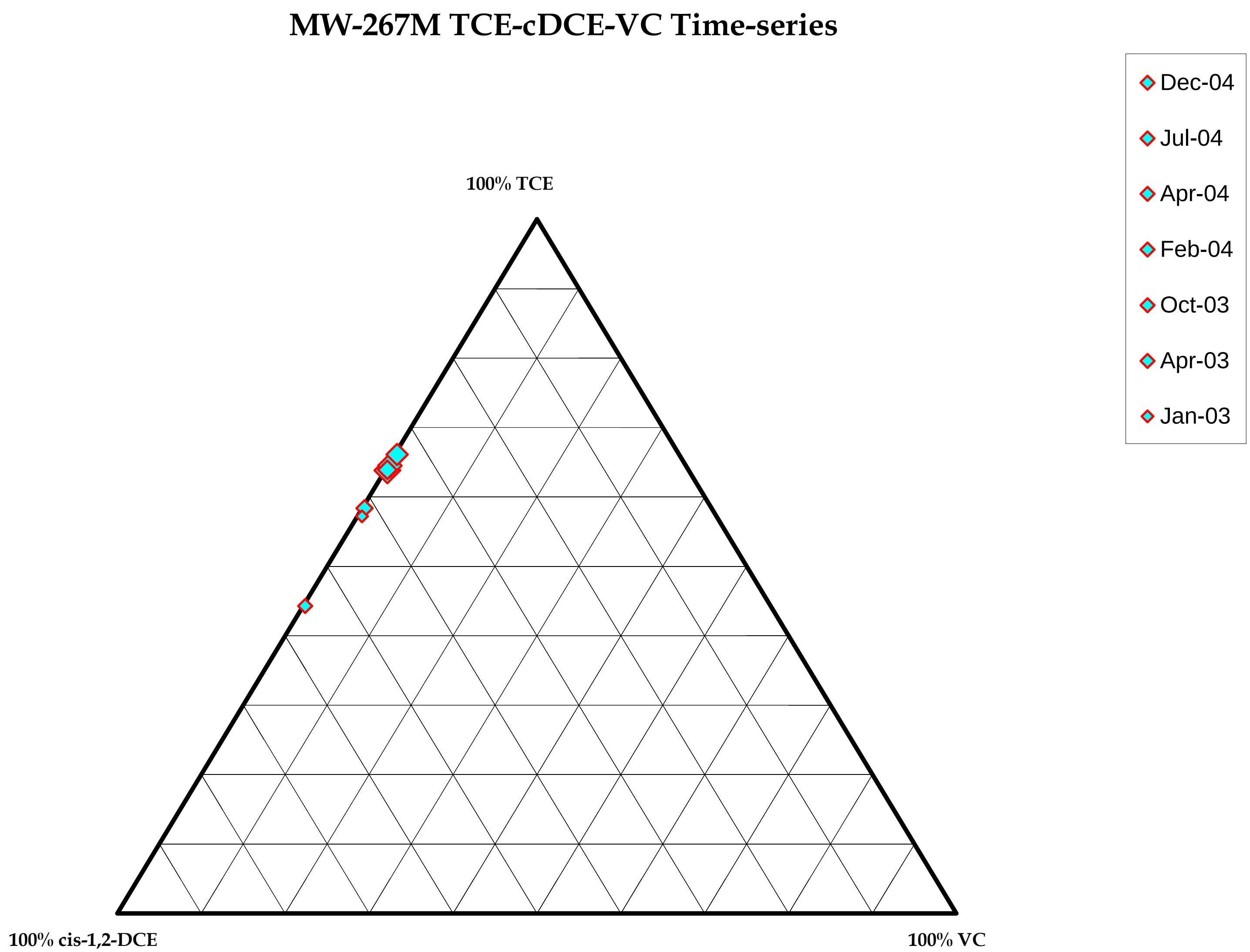


MW-266Mb TCE-cDCE-VC Time-series

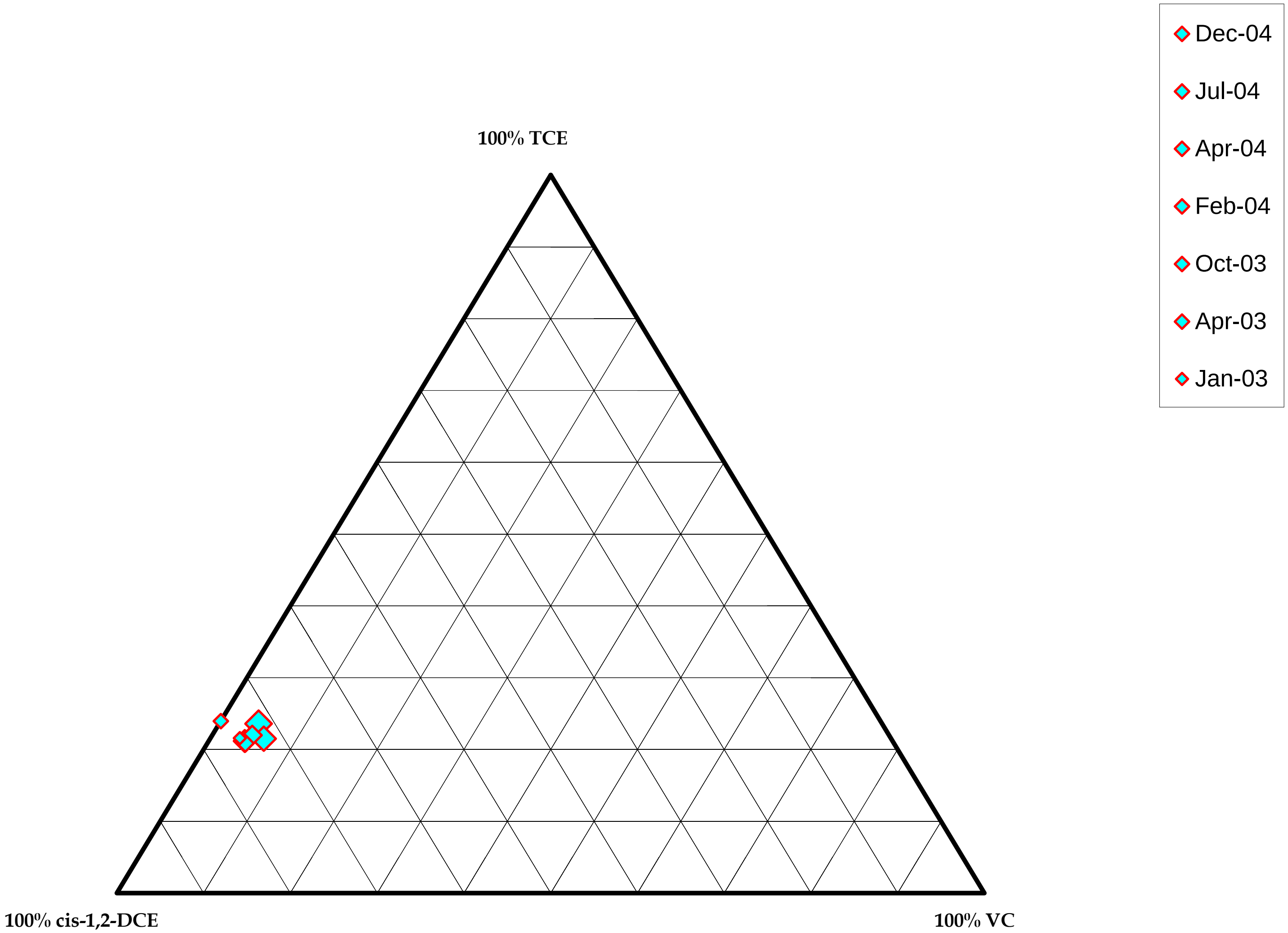


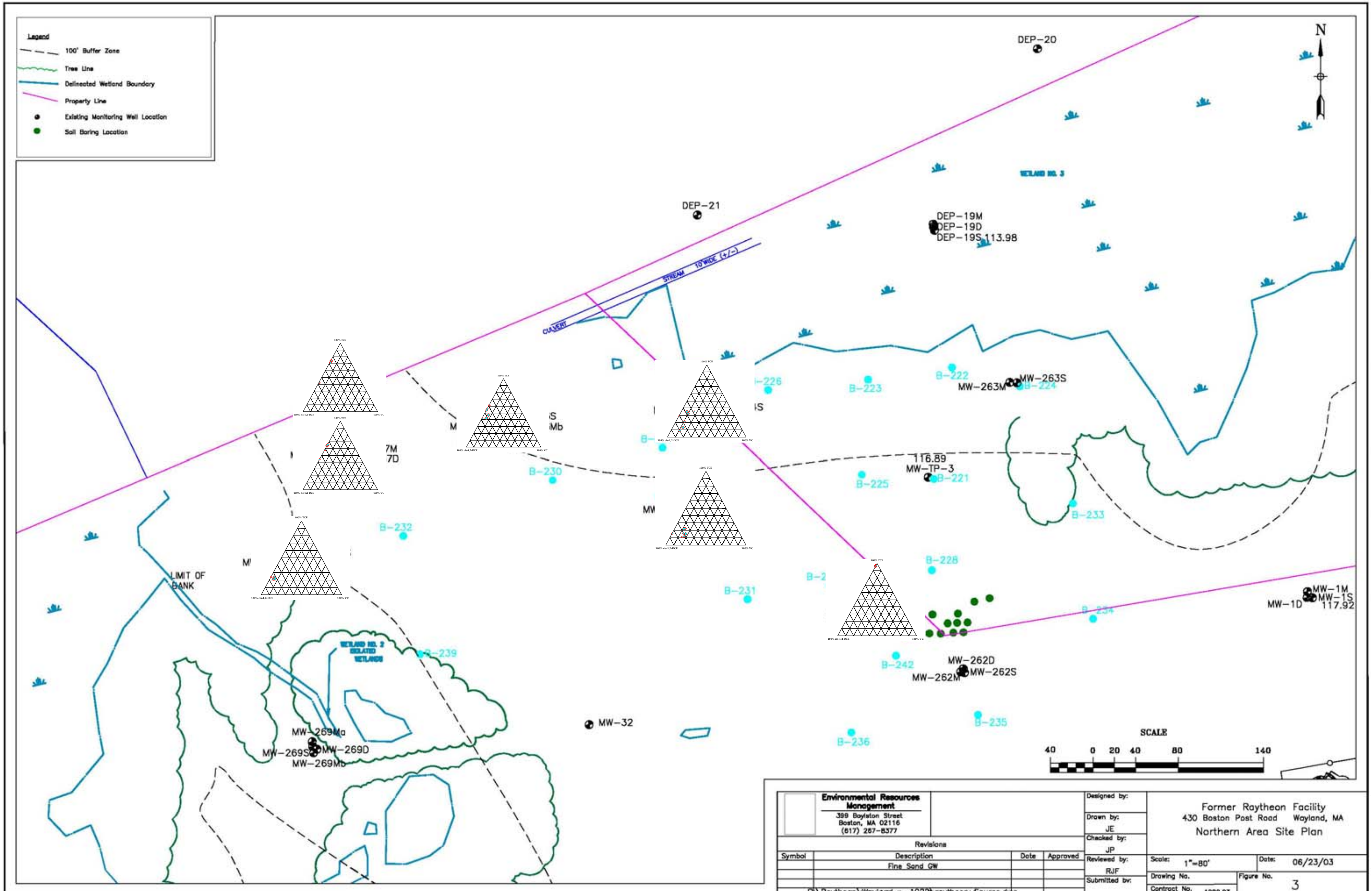
MW-267S TCE-cDCE-VC Time-series




MW-267M TCE-cDCE-VC Time-series
100% TCE
100% cis-1,2-DCE
100% VC
Dec-04
Jul-04
Apr-04
Feb-04
Oct-03
Apr-03
Jan-03

MW-268M TCE-cDCE-VC Time-series





Legend
100' Buffer Zone
Tree Line
Delineated Wetland Boundary
Property Line
Existing Monitoring Well Location
Soil Boring Location
N
DEP-20
WETLAND NO. 3
DEP-21
DEP-19M
DEP-19D
DEP-19S 113.98
STREAM 10'WIDE (+/-)
CULVERT
B-226
B-223
B-222
MW-263S
MW-263M
B-224
B-230
116.89
MW-TP-3
B-221
B-225
B-233
B-232
B-228
B-231
B-234
MW-1M
MW-1S
MW-1D
117.92
LIMIT OF BANK
WETLAND NO. 2 ISOLATED WETLANDS
B-239
B-242
MW-262D
MW-262M
MW-262S
MW-32
B-235
B-236
MW-269Ma
MW-269S
MW-269D
MW-269Mb
SCALE
40 0 20 40 80 140
Environmental Resources Management
399 Boylston Street
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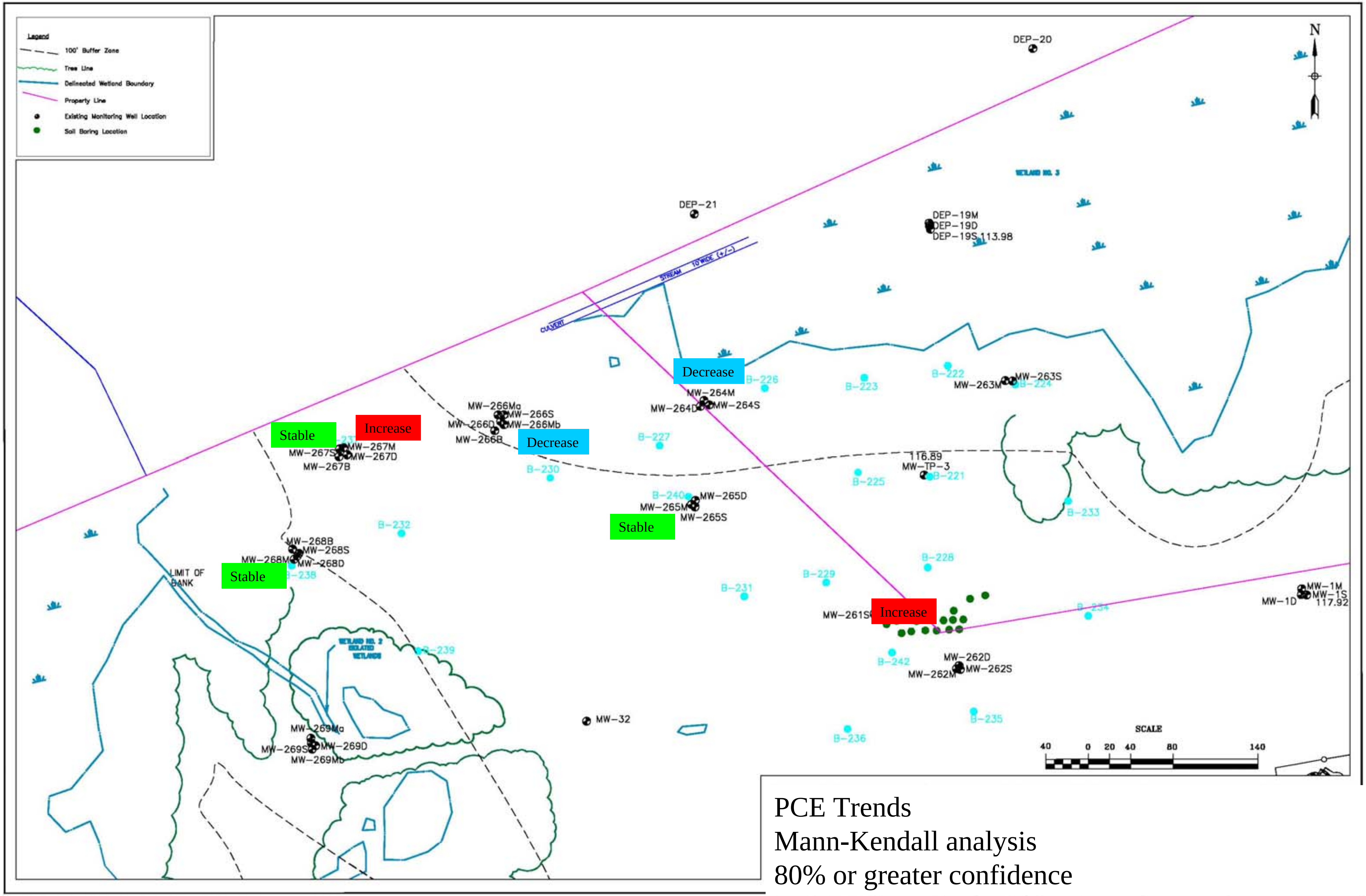
Revisions
Symbol
Description
Date
Approved
Fine Sand GW
Designed by:
Drawn by:
JE
Checked by:
JP
Reviewed by:
RJF
Submitted by:
Former Raytheon Facility
430 Boston Post Road Wayland, MA
Northern Area Site Plan
Scale: 1"=80'
Date: 06/23/03
Drawing No.
Figure No.
3
Contract No. 1922.03

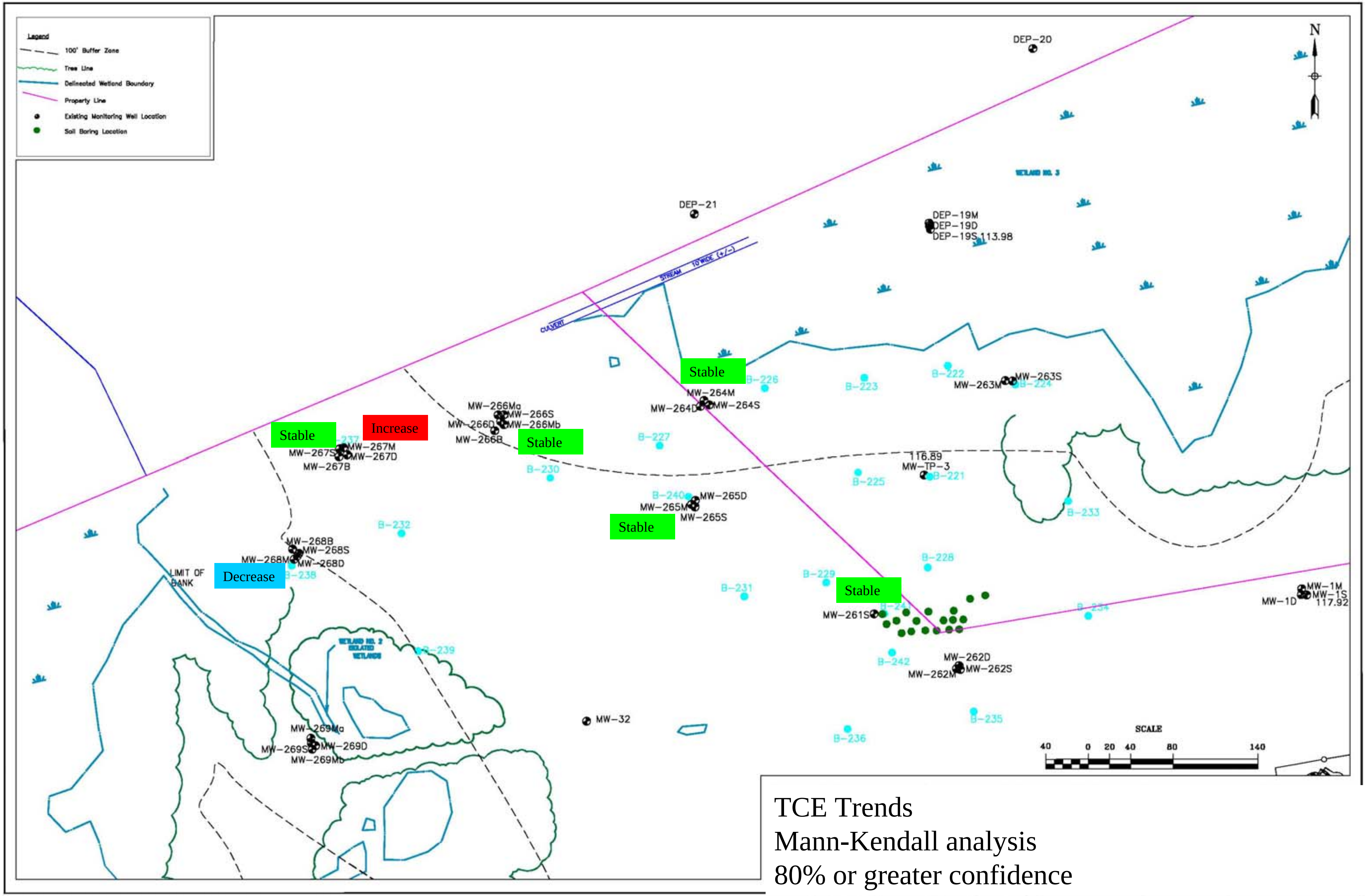
Attachment C

Plan View Results of Individual Mann-Kendall Analyses,

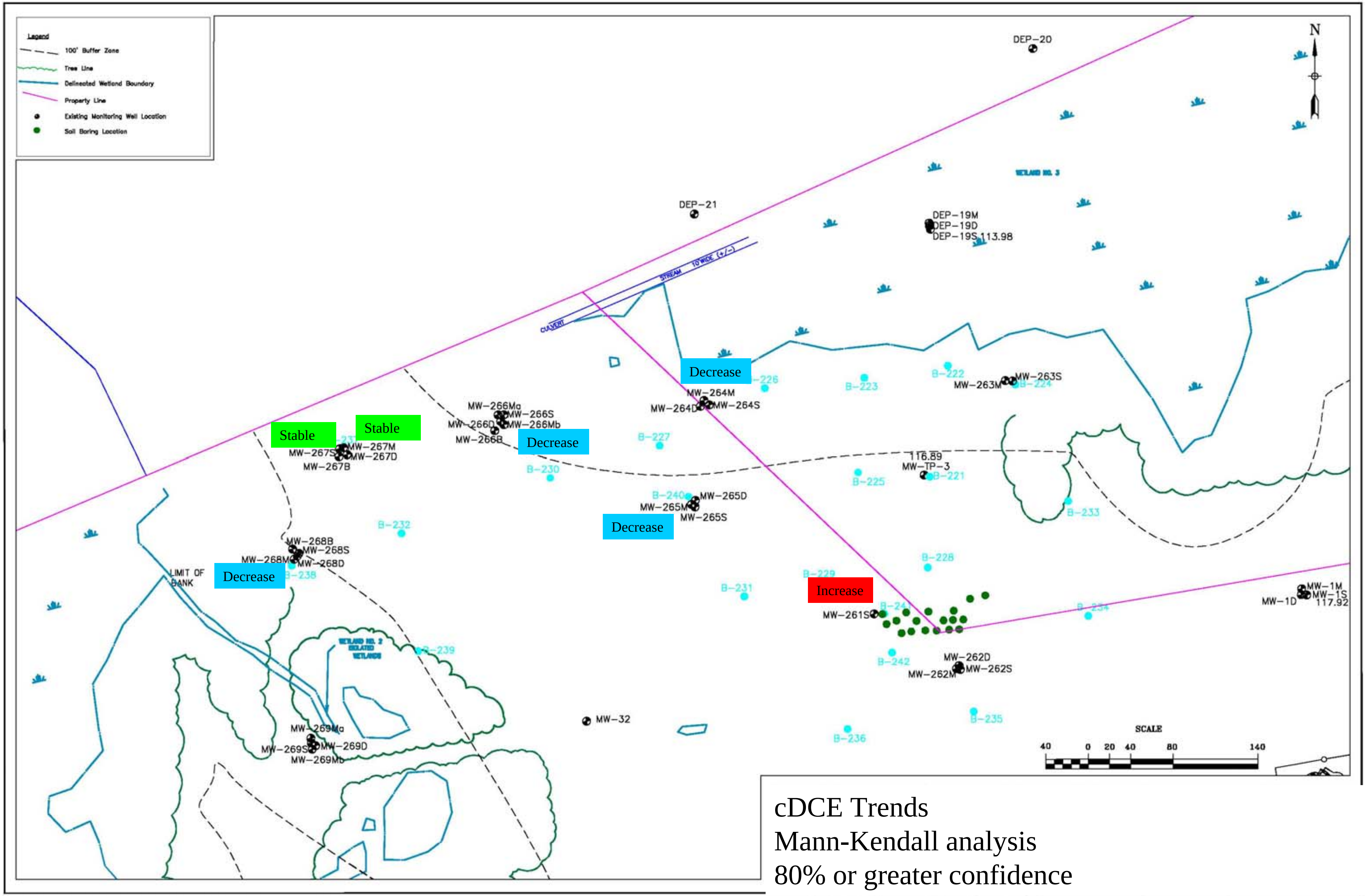
By Constituent, By Well



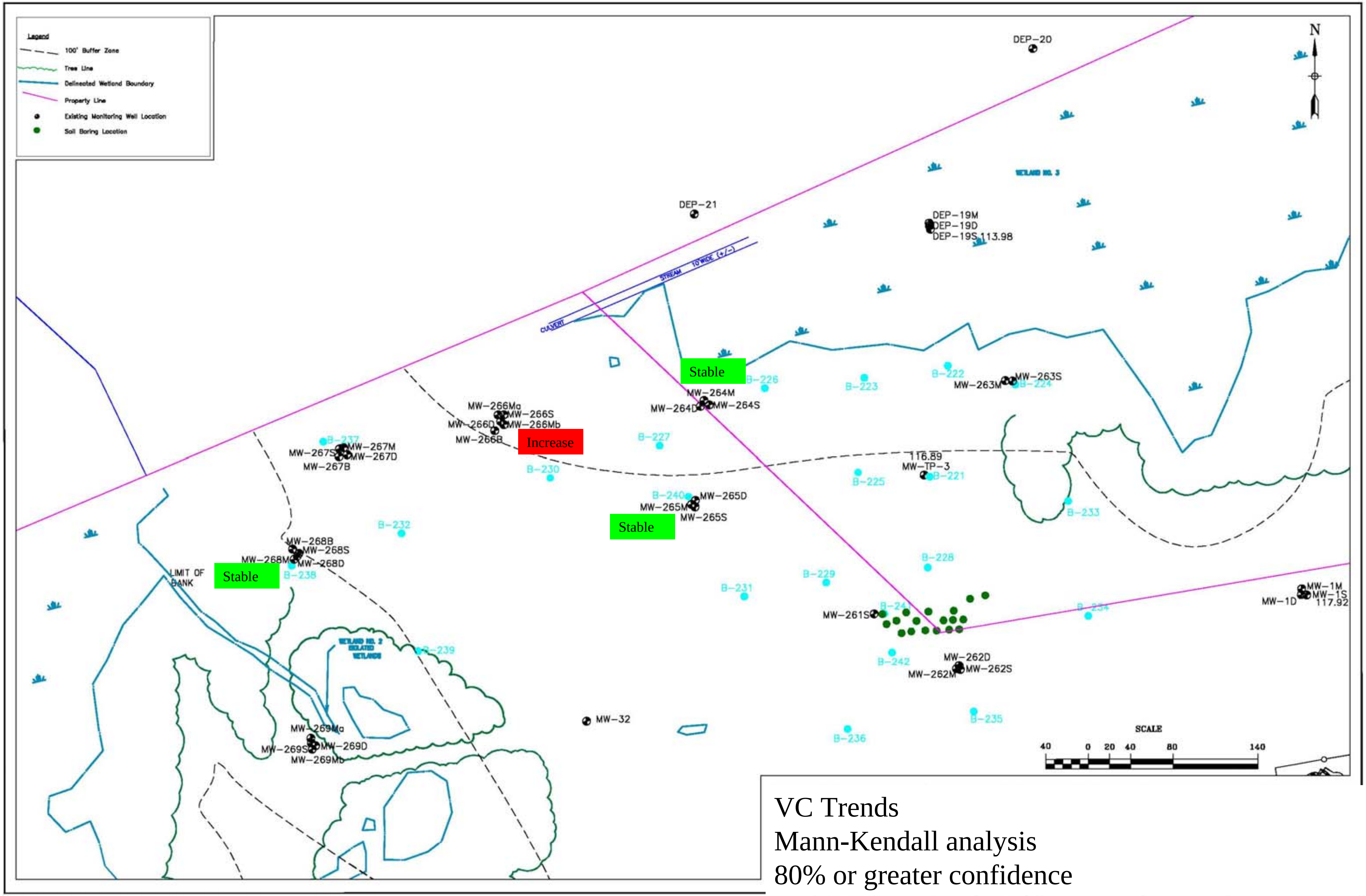
PCE Trends
Mann-Kendall analysis
80% or greater confidence



TCE Trends
Mann-Kendall analysis
80% or greater confidence



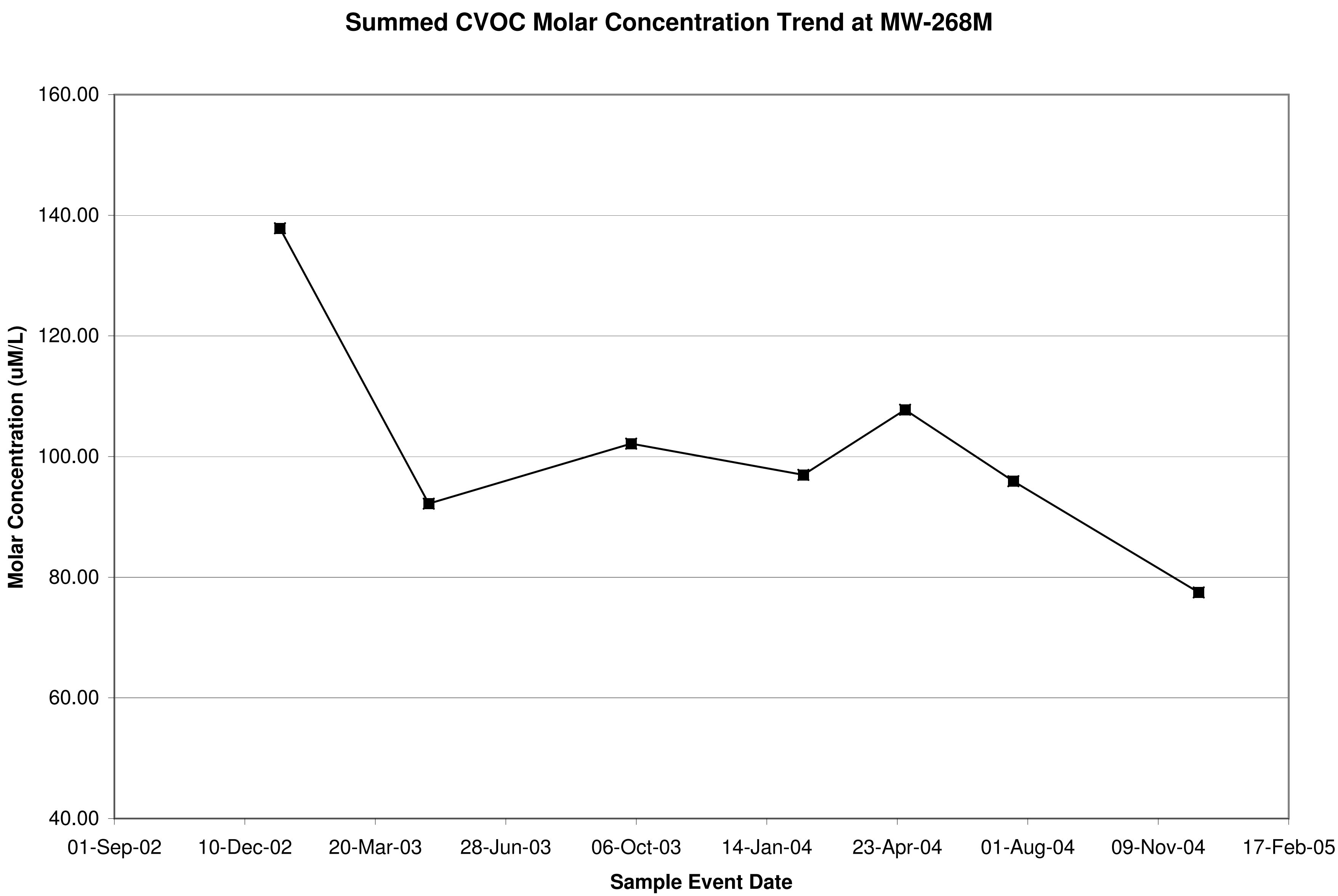
cDCE Trends
Mann-Kendall analysis
80% or greater confidence



VC Trends
Mann-Kendall analysis
80% or greater confidence

Attachment D

MW-268M and Total-Plume Molar Trend Plots and Analyses



Summed CVOC Molar Concentration Trend at MW-268M
160.00
140.00
120.00
100.00
80.00
60.00
40.00
Molar Concentration (uM/L)
01-Sep-02
10-Dec-02
20-Mar-03
28-Jun-03
06-Oct-03
14-Jan-04
23-Apr-04
01-Aug-04
09-Nov-04
17-Feb-05
Sample Event Date

State of Wisconsin
Department of Natural Resources
Remediation and Redevelopment Program

Mann-Kendall Statistical Test
Form 4400-215 (2/2001)

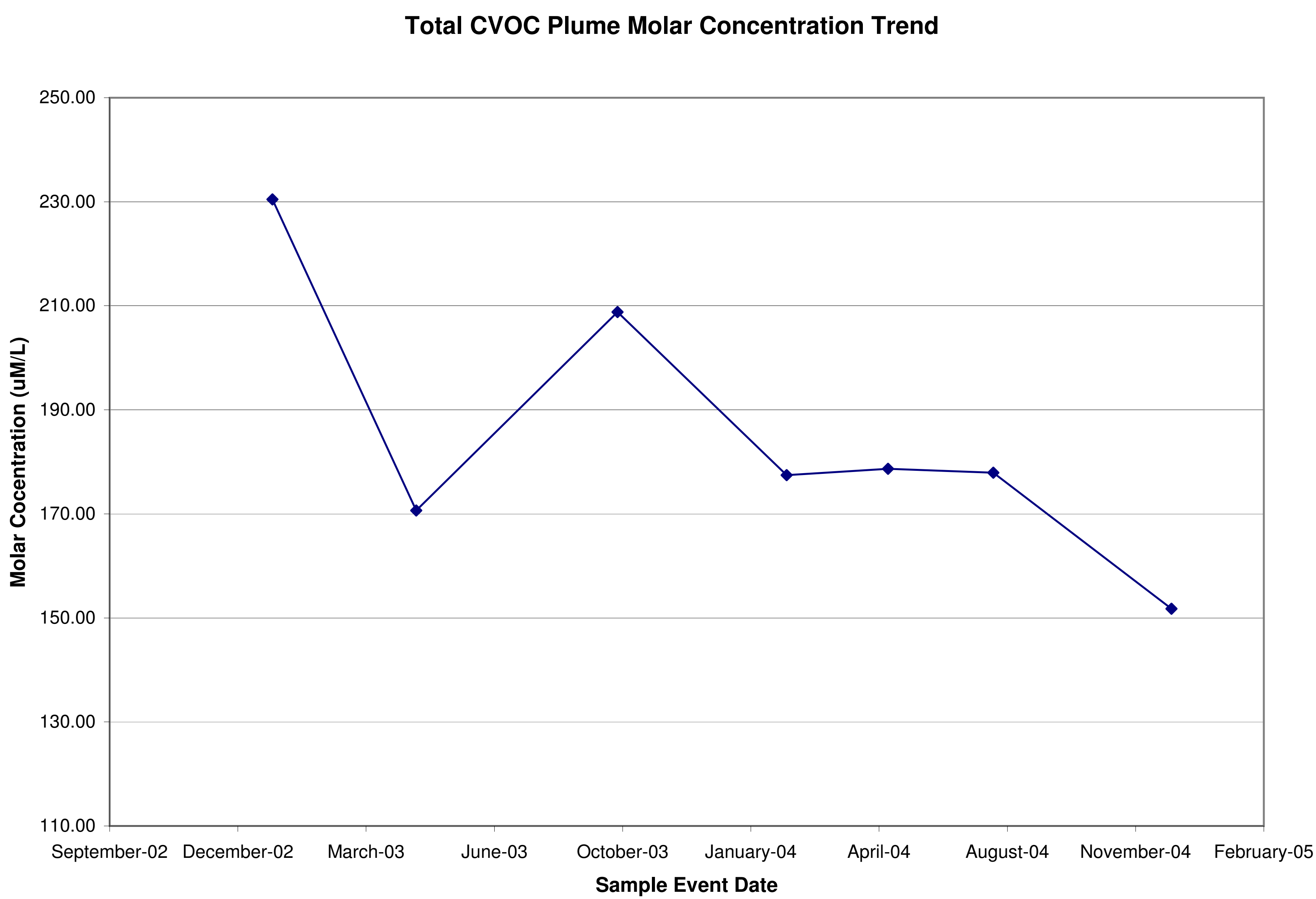
Notice: This form is the DNR supplied spreadsheet referenced in Appendices A of Comm 46 and NR 746, Wis. Adm. Code. It is provided to consultants as an optional tool for groundwater contaminant trend analysis to support site closure requests under s. Comm 46.07, Comm 46.08, NR 746.07, NR 746.08, Wis. Adm. Code. Use this form or a manual method when seeking case closure under those rules. Earlier versions of this form should not be used.

Instructions: Do not change formulas or other information in cells with a blue background, only cells with a yellow background are used for data entry. To use the spreadsheet, provide at least four rounds and not more than ten rounds of data that is not seasonally affected. Use consistent units. The spreadsheet contains several error checks, and a data entry error may cause "DATA ERR" or "DATE ERR" to be displayed. Dates that are not consecutive will show an error message and will not display the test results. The spreadsheet tests the data for both increasing and decreasing trends at both 80 percent and 90 percent confidence levels. If a declining trend is present at 80 percent but not at 90 percent, a site is still eligible for closure under Comm 46 and NR 746 provided that other conditions in those rules are met. If an increasing or decreasing trend is not present, an additional coefficient of variation test is used to test for stability, as proposed by Wiedemeier et al, 1999. For additional information, refer to the Interim Guidance on Natural Attenuation for Petroleum Releases, dated October 1999. Refer to the guidance for recommendations on data entry for non-detect values.

Site Name = Former Raytheon Facility | BRRTS No. = | Well Number = MW-268M

Event Number	Sampling Date (most recent last)	Molar CVOC Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)
1	6-Jan-03	137.86					
2	30-Apr-03	92.22					
3	2-Oct-03	102.12					
4	11-Feb-04	96.97					
5	29-Apr-04	107.77					
6	21-Jul-04	95.93					
7	10-Dec-04	77.49					
8							
9							
10							
	Mann Kendall Statistic (S) =	-9.0	0.0	0.0	0.0	0.0	0.0
	Number of Rounds (n) =	7	0	0	0	0	0
	Average =	101.48	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	Standard Deviation =	18.602	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	Coefficient of Variation(CV)=	0.183	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Error Check, Blank if No Errors Detected			n<4	n<4	n<4	n<4	n<4
Trend ≥ 80% Confidence Level		**DECREASING**	n<4	n<4	n<4	n<4	n<4
Trend ≥ 90% Confidence Level		No Trend	n<4	n<4	n<4	n<4	n<4
Stability Test, If No Trend Exists at 80% Confidence Level		NA	n<4 n<4	n<4 n<4	n<4 n<4	n<4 n<4	n<4 n<4

Data Entry By = JDF | Date = 28-Sep-05 | Checked By =



Total CVOC Plume Molar Concentration Trend
Molar Cocentration (uM/L)
250.00
230.00
210.00
190.00
170.00
150.00
130.00
110.00
September-02
December-02
March-03
June-03
October-03
January-04
April-04
August-04
November-04
February-05
Sample Event Date

State of Wisconsin
Department of Natural Resources
Remediation and Redevelopment Program

Mann-Kendall Statistical Test
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Instructions: Do not change formulas or other information in cells with a blue background, only cells with a yellow background are used for data entry. To use the spreadsheet, provide at least four rounds and not more than ten rounds of data that is not seasonally affected. Use consistent units. The spreadsheet contains several error checks, and a data entry error may cause "DATA ERR" or "DATE ERR" to be displayed. Dates that are not consecutive will show an error message and will not display the test results. The spreadsheet tests the data for both increasing and decreasing trends at both 80 percent and 90 percent confidence levels. If a declining trend is present at 80 percent but not at 90 percent, a site is still eligible for closure under Comm 46 and NR 746 provided that other conditions in those rules are met. If an increasing or decreasing trend is not present, an additional coefficient of variation test is used to test for stability, as proposed by Wiedemeier et al, 1999. For additional information, refer to the Interim Guidance on Natural Attenuation for Petroleum Releases, dated October 1999. Refer to the guidance for recommendations on data entry for non-detect values.

Site Name = Northern Area Plume of Former Raytheon Facility				BRRTS No. =		Well Number =	Molar Sum
	Compound ->	Molar CVOC					
Event Number	Sampling Date (most recent last)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)	Concentration (leave blank if no data)
1	6-Jan-03	230.46					
2	28-Apr-03	170.67					
3	2-Oct-03	208.80					
4	11-Feb-04	177.45					
5	30-Apr-04	178.66					
6	21-Jul-04	177.92					
7	7-Dec-04	151.74					
8							
9							
10							
	Mann Kendall Statistic (S) =	-9.0	0.0	0.0	0.0	0.0	0.0
	Number of Rounds (n) =	7	0	0	0	0	0
	Average =	185.10	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	Standard Deviation =	26.113	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	Coefficient of Variation(CV)=	0.141	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Error Check, Blank if No Errors Detected			n<4	n<4	n<4	n<4	n<4
Trend ≥ 80% Confidence Level		**DECREASING**	n<4	n<4	n<4	n<4	n<4
Trend ≥ 90% Confidence Level		No Trend	n<4	n<4	n<4	n<4	n<4
Stability Test, If No Trend Exists at 80% Confidence Level		NA	n<4 n<4	n<4 n<4	n<4 n<4	n<4 n<4	n<4 n<4
	Data Entry By =	JDF	Date =	28-Sep-05	Checked By =		

Attachment E

Plan View Results of Three Statistical Analyses, by Well

Statistics to 90% Confidence