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# Chapter NR 746

# Nonparametric Statistical Tests for Determining the Effectiveness of Natural Attenuation

Two nonparametric statistical tests are described here: the Mann–Kendall (S) and Mann–Whitney (U) statistical tests. These tests can be used to show whether groundwater contaminant concentrations in a monitoring well are increasing, stable or decreasing. However, neither test is able to determine the rate in which the concentrations are changing over time. The Mann–Kendall Test can be used with a minimum of 4 rounds of sampling results; however, the Mann–Kendall Test is not valid for data that exhibit seasonal behavior. The Mann–Whitney U Test is applicable to data that may or may not exhibit seasonal behavior, but the test requires 8 consecutive rounds of quarterly or semi–annual sampling results. To demonstrate that natural attenuation is effective, the chosen statistical test must show decreasing contaminant concentrations at an appropriate confidence level, given in the test methodologies that follow.

#### Mann-Kendall Test

1. Assemble well data for at least 4 sampling events for each contaminant in the order in which the data was collected. Include all contaminants that have exceeded the ES at one or more monitoring wells. Include data from:

a. One or more contaminated monitoring wells near the downgradient plume margin, which may include piezometers,

b. A monitoring well near the source zone, and

c. At least one monitoring well along a flow line between the source zone well and plume margin well.

2. For purposes of the Mann–Kendall test, all non–detect data values should be assigned a single value that is less than the detection limit, even if the detection limit varies over time.

3. Tests for Seasonality in Data. For seasonally affected data, either remove the seasonality in the data (e.g., by only testing data from the seasons with the highest contaminant concentrations) or use a statistical test that is unaffected by seasonality, such as the Mann–Whitney U Test. To test for data seasonality:

a. Determine if groundwater flow direction changes with season by comparing a water table map from each season that the contaminant concentrations are measured. If the flow direction changes from one sampling period to another and shifts the plume away from the wells being used in the statistical test, then data from those seasons that are shifted away from the centerline monitoring wells can not be used in the Mann–Kendall Test.

b. Determine if groundwater elevation and contaminant concentration change seasonally. Plot contaminant concentration versus groundwater level for each well to be assessed by the Mann–Kendall Test. If groundwater concentrations change as water level changes, then the data is seasonally affected. The seasons with the highest contaminant concentrations should be included in the Mann–Kendall Test.

4. Calculate the Mann–Kendall Statistic (S) using a manual method or a DNR supplied spreadsheet. Assess all contaminants in the plume for the selected wells being assessed with the Mann–Kendall Test. Enter data for each contaminant in the order it was collected.

a. Manual Method to Calculate Mann–Kendall Statistic. Compare data sequentially, comparing sampling event 1 to sampling events 2 through n, then sampling event 2 to sampling events 3 through n, etc. Each row is filled in with a 1, 0 or -1, as follows:

Along row 2, if:

- Concentration of event  $x_i >$  event 1: Enter +1
- Concentration of event  $x_i$  = event 1: Enter 0
- Concentration of event  $x_i < \text{event } 1$ : Enter 1

Where: n = total number of sampling events

 $x_i$  = value of given sample event, with i = 2 to n

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Continue for the remaining rows. Sum each row and enter result at the end of the row. Add the sum of each row down to obtain the Mann–Kendall Statistic (S). See Table A as an example.

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	Sampling Event 1	Sampling Event 2	Sampling Event 3	Sampling Event 4	Sampling Event 5	
Contaminant concentra-						Sum Rows
tion $\rightarrow$	100	50	85	75	50	
Compare to Event 1	$\rightarrow$	-1	-1	-1	-1	- 4
Compare to Event 2		$\rightarrow$	+1	+1	0	+ 2
Compare to Event 3			$\rightarrow$	-1	-1	- 2
Compare to Event 4				$\rightarrow$	-1	- 1
		Mann Kendall Statistic (Total) =			- 5	

Table AMann–Kendall Statistic

b. Manual Mann–Kendall Statistic Look up Table. Table B gives the maximum S statistic ( $S_{max}$ ) to accept a declining trend alternative at an  $\alpha$  level of significance. If the computed S is greater than  $S_{max}$  (or S is a smaller negative number than  $S_{max}$ ), then there is either a no–trend or an increasing trend in the data.

Table B Mann–Kendall Statistic Look Up Table			
N	Range of S	$S_{max}$ $\alpha = 0.2^*$	
4	-6  to  + 6	- 4	
5	-10 to $+10$	- 5	
6	- 15 to + 15	- 6	
7	- 21 to + 21	-7	
8	-28 to $+28$	- 8	
9	- 36 to + 36	-10	
10	– 45 to +45	-11	

\* The probability that the computed Mann–Kendall statistic  $S \le S_{max}$  is at most  $\alpha$ .

5. Test for a declining trend. Evaluate data trends for each contaminant identified in the plume. Evaluate the null hypothesis of no trend against the alternative of a decreasing trend. The null hypothesis can be rejected in favor of a decreasing trend if both of the following conditions are met:

a. S is a large negative number (see Table B for magnitude of S)

b. The probability value, given n (number of data) and the absolute value of S, is LESS than the a priori significance level,  $\alpha$ , of the test. An  $\alpha \leq 0.2$  is acceptable.

6. Test for an increasing trend. An increasing trend alternative (i.e., an advancing plume) is shown if both of the following conditions are met:

a. S is positive.

b.  $S \ge |S_{max}|$  at a given  $\alpha$  level of significance (see Table B). If the computed S is equal to or greater than the absolute value of  $S_{max}$ , then it can be concluded the plume is advancing at an  $\alpha$  level of significance. An  $\alpha \le 0.2$  is acceptable for this test.

7. Test for Plume Stability. If the Mann–Kendall Test indicates no–trend is present, perform the coefficient of variation test. As a non–parametric test, the Mann–Kendall Test does not take into account the magnitude of scatter in the data. A data set with a great deal of scatter may return a Mann–Kendall test indicating there is no trend, when, in fact, no conclusion can be drawn regarding trend because of data variability. In this case, additional data collection may be necessary to determine that the plume is stable, declining or advancing. As a simple test, the coefficient of variation can assess the scatter in the data:

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 $CV = \frac{standard \ deviation}{arithmetic \ mean}$ 

Where: CV = coefficient of variation

CV should be  $\leq 1$  to say that the no-trend hypothesis also indicates a stable plume configuration.

Mann-Whitney U Test. This test is equivalent to the Wilcoxon Rank Sum Test.

1. Assemble well data for the most recent 8 consecutive quarterly or semi–annual sampling events for each contaminant that has exceeded the ES at one or more monitoring wells. Include data from:

a. One or more contaminated monitoring wells near the downgradient plume margin, which may include piezometers,

b. A monitoring well near the source zone, and

c. At least one monitoring well along a flow line between the source zone well and plume margin well.

2. Enter the data into a DNR supplied spreadsheet or manually assemble the data into a table (e.g., Table C) in the order the data was collected. Assign a rank to each sample value, with the smallest value ranked #1 and the largest value ranked #8.

3. For purposes of the Mann–Whitney U test, all non–detect values should be assigned a data value of zero (0).

	Benzene		Rank Sum of
Year/Date	Concentration (ug/l)	Rank	1 <sup>st</sup> Year (Wrs)
1 <sup>st</sup> Year, 1 <sup>st</sup> Quarter	160	8 )	
1 <sup>st</sup> Year, 2 <sup>nd</sup> Quarter 1 <sup>st</sup> Year, 3 <sup>rd</sup> Quarter	130	7	25
	80	4	25
1st Year, 4th Quarter	100	6	
2 <sup>nd</sup> Year, 1 <sup>st</sup> Quarter	89	5	
2 <sup>nd</sup> Year, 2 <sup>nd</sup> Quarter	0	1	
2 <sup>nd</sup> Year, 3 <sup>rd</sup> Quarter	53	3	
2nd Year, 4th Quarter	24	2	
		U = 26	<b>–</b> Wrs = 1

 Table C

 Example Data Set for the Mann–Whitney U Statistical Test

4. Sum the ranks for the data in the 1<sup>st</sup> year. Denote this sum as Wrs (or the Wilcoxon rank sum).

5. Calculate the U Statistic. U = 26 - Wrs

6. Interpreting U Statistic. For 2 groups of 4 samples, at  $U \le 3$ , the probability that year 2 data show a decrease relative to year 1 data is at least 90%, and so  $U \le 3$  will be acceptable to show that contaminant concentration is declining.

7. If there are ties in sample data, calculate an average rank value for the tied data and assign this average rank to the tied sample data. See example in Table D.

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E	Table DExample of Rank Sum Value for Tied Data			
	Benzene	Check for		Rank Sum of
Year/Date	Concentration (ug/ l)	Ties	Rank	1 <sup>st</sup> Year (Wrs)
1 <sup>st</sup> Year, 1 <sup>st</sup> Quarter	300		8	
1 <sup>st</sup> Year, 2 <sup>nd</sup> Quarter	280		7	24.5
1 <sup>st</sup> Year, 3 <sup>rd</sup> Quarter	105		4	> 24.5
1 <sup>st</sup> Year, 4 <sup>th</sup> Quarter	110	*	5.5 J	
2 <sup>nd</sup> Year, 1 <sup>st</sup> Quarter	83		3	
2 <sup>nd</sup> Year, 2 <sup>nd</sup> Quarter	50	$\checkmark$	1.5	
2 <sup>nd</sup> Year, 3 <sup>rd</sup> Quarter	110	*	5.5	
2 <sup>nd</sup> Year, 4 <sup>th</sup> Quarter	50	$\checkmark$	1.5	
			U = 26	-Wrs = 1.5

8. Probability and the U Statistic. Table E shows the  $\alpha$  value and the confidence level for values of U calculated for 2 groups of 4 samples each.

Table EProbability and U Statistic(For 2 Groups of 4 samples each)				
U Statistic	Level of significance $\alpha$	Confidence Level (%)		
0	0.014	98.6		
1	0.029	97.1		
2	0.057	94.3		
3	0.100	90.0		

9. If more than 8 consecutive rounds of data are available, a Mann–Whitney U statistic can be calculated similar to the method presented here. Each set of data to be compared should represent the same span of time (e.g. 1 year) and the same time interval between samples (e.g., quarterly). The test must be conducted at a level of significance ( $\alpha$ ) of  $\leq 0.10$ .

## References:

Conover, W.J., Practical Nonparametric Statistics, 2<sup>nd</sup> Ed., John Wiley & Sons, 1971, pp. 216–223.

Gilbert, R.O., Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, 1987, pp. 204 – 240 and 272.