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REPORT

# Groundwater Contamination Plume Stability

## *Review of Assessment Methods*

Submitted to:

**CSAP Society**

Technical Review Committee

Submitted by:

**WSP Canada Inc.**

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## 1.0 INTRODUCTION

The Society of Contaminated Sites Approved Professionals of British Columbia (CSAP) retained WSP Canada Inc. (WSP) to prepare this review of groundwater contaminant plume stability trend analysis methods. Plume trend analysis can be a component of a screening level risk assessment or a detailed human health and ecological risk assessment in accordance with the framework established by the British Columbia (BC) Contaminated Sites Regulation (BC Reg. 375/96). The framework includes protocols for conducting risk assessment. Protocol 1 for Contaminated Sites on *Detailed Risk Assessment* stipulates a stable or declining plume as a pre-requisite in Section 2.4. Protocol 13 for Contaminated Sites on *Screening Level Risk Assessment* describes plume stability requirements in Section 6. In both cases practitioners must demonstrate that groundwater contaminant plumes are stable or decreasing before proceeding with risk assessment. Plume stability and trend analysis may also be a component of a performance verification plan associated with a Certificate of Compliance. It is also worth noting that plume stability arguments can be used in Protocol 21 for Contaminated Sites on *Water Use Determination*, when evaluating the applicability of aquatic life water use and current drinking water use.

The purpose of this document is to provide practitioners with a summary of various plume stability assessment techniques, considerations for conducting a plume stability assessment and examples of plume stability applications. The intended audience for this document is the CSAP Society and contaminated sites practitioners.

### 1.1 Definition of Plume Stability

The overall purpose of a plume stability assessment is to use quantitative data to understand the behaviour of a groundwater plume with regard to future risks related to groundwater contamination migration. This is accomplished by demonstrating that a groundwater contaminant plume will not expand or migrate such that the conceptual site model is no longer accurate or that unacceptable risks are actually or potentially created.

A simple definition of plume stability is a condition in which a groundwater contaminant plume is not increasing (physical dimension and/or mass) and the plume footprint is not moving in an undesirable direction. For a stable groundwater plume, the rate of contaminant mass into the plume from a source is equal to the rate of contaminant mass lost from the plume. For a plume that is not stable, the rate of contaminant mass into the plume is greater than (increasing plume) or less than (decreasing plume) the rate of contaminant mass lost from the plume.

### 1.2 General Considerations for Plume Stability Assessments

Because the intent of a plume stability assessment is to validate the conceptual site model related to a groundwater contaminant plume, there are several general requirements to consider prior to conducting the assessment.

- A plume stability assessment is intended to be an empirical evaluation of site data and is therefore best performed following the establishment of an adequate groundwater monitoring well network (based on site investigations) and the collection of sufficient and representative data from that network. The location of the wells should include source areas, distal areas (both downgradient and side-gradient) and delineation areas (laterally and vertically). Lack of delineation of a groundwater contaminant plume may, but does not always, present a data gap that limits the ability of the dataset to adequately yield accurate conclusions of plume stability.



- The quantity of data in terms of the number of sampling events and the temporal period covered by sampling should be considered prior to conducting a plume stability assessment and when assessing the strength of plume stability conclusions. In general, monitoring must be conducted enough times over a sufficient period to show a reliably consistent trend in contaminant concentrations. See Section 2.1 for more details.
- Every effort should be made to sample a consistent network of monitoring wells for a plume stability assessment. It is understood that periodically a sample cannot be collected due to various reasons. For whole plume-based stability methods, such as the Ricker Method® plume stability analysis (Ricker 2008), missing events should be assigned numeric values using scientific procedures or professional judgement. See Section 3.3.2 for more details.
- Nearly all datasets used in plume stability assessments include non-detect results. Non-detect results must be assigned numeric values for use in a plume stability assessment. Detection limits higher than delineation standard are referred to as “elevated non-detects”. Elevated non-detects ultimately represent a data gap. Therefore, every effort should be made to coordinate with project laboratories to achieve detection limits that meet the delineation criterion for a particular contaminant. If lower detection limits are not achievable, elevated non-detects must still be assigned numeric values for plume stability assessments. See Section 2.2 for further detail on assigning numeric values for non-detect results.
- If a groundwater contaminant plume is in active remediation, conclusions of plume stability cannot be disassociated from the effects of ongoing remediation. A plume stability assessment during active remediation may be useful to validate the effectiveness of a remediation system. Plume stability assessments that are conducted as part of a closure evaluation (e.g. Certificate of Compliance submission or risk-based performance verification plan) should be based on post-corrective action data so conclusions of plume stability can be attributed to the natural conditions of the site.
- The presence and/or mobility of source areas (e.g., non-aqueous phase liquids, NAPLs) should be considered along with trend conclusions as part of an overall evaluation of plume stability.

### 1.3 General Considerations for Chlorinated Solvents

Chlorinated volatile organic compounds (CVOCs) are commonly observed at many contaminated sites. Moreover, many CVOCs dissolved in groundwater are known to be susceptible to degradative natural attenuation processes (USEPA 2012). When evaluating CVOC plume stability, care should be taken in how the data are evaluated. For example, most CVOC sites are composed of families of compounds where parent compounds degrade into daughter compounds. In these instances, trend analyses on individual contaminants may yield conflicting results. For example, tetrachloroethene (PCE) and trichloroethene (TCE) are known to biodegrade to cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride (VC). It is common at CVOC sites to observe decreasing trends in TCE coupled with increasing trends in daughter compounds cis-1,2-DCE and VC. The practitioner is then left with the challenging task of communicating to stakeholders the presence of increasing trends for some contaminants of concern (COCs) while overall contaminant mass is stable or decreasing.

To alleviate this issue, some practitioners will conduct a trend analysis on the sum of total chloroethenes. Theoretically, the total chloroethenes trend would be decreasing if there was complete mineralization of the parent compound. However, in many cases there is incomplete mineralization, and although the total chloroethenes weight-based concentration may decrease, the molar-based concentration would theoretically remain unchanged.

This is because one molecule of a parent compound degrades to one molecule of a daughter compound that weighs less. For this reason, it is more accurate to assess plume stability for total chloroethenes (or any other family of contaminants) on a molar basis. The following exhibit adapted from Ricker, et al. (2019) is an example showing the importance of using molar-based data when evaluating chlorinated solvent data.

### Exhibit 1.1 Hypothetical example for CVOC data analysis

For this example, imagine there are 30 molecules of PCE that degrade over time to 10 molecules each of TCE, cis-1,2-DCE, and VC. This would be analogous to a PCE molar concentration of 30  $\mu\text{mol/L}$  that degrades to molar concentrations of 10  $\mu\text{mol/L}$  each of TCE, cis-1,2-DCE, and VC. In this example, the sum of the individual contaminant molar concentrations of the initial “total CVOC” and final “total CVOC” concentrations remain unchanged at 30  $\mu\text{mol/L}$ . However, if the molar concentrations are expressed as weight concentrations, the initial “total CVOC” concentration would be 4,975  $\mu\text{g/L}$  and the final total CVOC concentration would be 2,908  $\mu\text{g/L}$ . This phenomenon is illustrated in the following table.

	Molecular Weight g/mol	Initial		Final	
		Molar Concentration $\mu\text{mol/L}$	Weight Concentration $\mu\text{g/L}$	Molar Concentration $\mu\text{mol/L}$	Weight Concentration $\mu\text{g/L}$
PCE	165.83	30	4,975	0	0
TCE	131.4	0	0	10	1,314
DCE	96.95	0	0	10	970
VC	62.498	0	0	10	625
Total CVOCs		30	4,975	30	2,908

The practitioner or other project stakeholders might assume that substantial remedial progress is being made because the “total CVOCs” decreased (ostensibly) by 41%, when in fact on a molar basis the “total CVOCs” is unchanged. Further to the point, consider an example where a second CVOC contaminant source becomes commingled with the original source as illustrated in the following table.

	Molecular Weight g/mol	Initial		Final	
		Molar Concentration $\mu\text{mol/L}$	Weight Concentration $\mu\text{g/L}$	Molar Concentration $\mu\text{mol/L}$	Weight Concentration $\mu\text{g/L}$
PCE	165.83	30	4,975	0	0
TCE	131.4	0	0	15	1,971
DCE	96.95	0	0	15	1,454
VC	62.498	0	0	15	937
Total CVOCs		30	4,975	45	4,363

In this example, there is the same degradation as above; however, a second source is added that results in additional concentrations of 5  $\mu\text{mol/L}$  each of TCE, cis-1,2-DCE, and VC (total 15  $\mu\text{mol/L}$ ). In this case, the initial total CVOC weight concentration would be 4,975  $\mu\text{g/L}$  and the final total CVOC weight concentration would be 4,363  $\mu\text{g/L}$ , even though additional mass was added from the second source. On a weight-concentration basis it appears that attenuation is occurring. However, on a molar concentration basis there is evidence of co-mingled contamination plumes, because the molar concentration increased from 30  $\mu\text{mol/L}$  to 45  $\mu\text{mol/L}$ . This example shows how molarity provides better clarity when assessing CVOC groundwater plumes.

## 2.0 DATA CONSIDERATIONS

### 2.1 General Considerations

Because a plume stability assessment is an empirical evaluation of data, proper scrutiny of data used in any assessment is foundational to achieving results with the most potential to reveal the true nature of plume stability. The quantity of data in terms of the location of sampled wells, the number of sampling events and the temporal period covered by sampling should be considered prior to conducting a plume stability assessment and when assessing the strength of plume stability conclusions.

The design of a monitoring well network and the sampling program are fundamental to providing adequate spatial coverage to support a plume stability assessment. Guidance on groundwater well placement is provided in Technical Guidance 8 on Contaminated Sites Groundwater Investigation and Characterization (ENV 2021). Consistent with this guidance, the locations of wells should include source areas, distal areas (both downgradient and side-gradient) and non-detect areas. Source area wells often exhibit the most change over time and are therefore critical for capturing changes in plume mass over time. A network consisting entirely of perimeter or sentinel wells will most likely not provide sufficient data to assess plume stability. However, source area wells alone are also not adequate. Distal wells are necessary to provide data on the areal footprint of the plume and concentration gradients with respect to distance from the source area. The practitioner must not forget that plumes extend out from the source area not only through advective movement but also dispersion or diffusion. Therefore, hydraulically side-gradient wells are also important. Dispersive spreading and diffusive transport may play a more significant role in plume expansion on sites with low groundwater potentiometric gradients. Non-detect wells also provide important data concerning the ultimate extent of a plume. If a plume is not delineated by non-detect wells, or wells with concentrations below a standard, the potential exists that decreasing trend conclusions may be the result of mass leaving the system (i.e., well network). However, complete delineation is not always required in a particular direction (in the context of plume trend analysis) as long as sufficient data exist to demonstrate consistently decreasing contaminant gradients in that direction, and therefore adding a well to refine the plume extent will likely reveal what is already reasonably assumed through professional judgement.

The number of sampling events and temporal period covered by sampling are also important for yielding strong conclusions from a plume stability assessment. For example, a minimum of four events are required for a Mann-Kendall test. However, a dataset with four quarterly events, covering a one-year period, is likely to reveal less about the true nature of plume stability and possible attenuation rates than a dataset with four annual events. Frequent sampling, such as quarterly, may be appropriate when establishing a baseline understanding of plume stability. Once a baseline understanding is established, a less frequent sampling program, such as annual or biennial, is often appropriate to continue plume stability evaluations. The practitioner must consider the expected rate of attenuation, the sensitivity of receptors, and regulatory requirements when designing a sampling program. Technical Guidance 8 (ENV 2021) recommends a minimum of two years of groundwater monitoring for most contamination plumes.

### 2.2 Special Considerations for Non-detect Data

Nearly all datasets used in a plume stability assessment will include non-detect data. Non-detect results must be assigned numeric values for use in a plume stability assessment. Detection limits higher than the plume delineation standard, are referred to as “elevated non-detects”. Elevated non-detects ultimately represent a data gap. Therefore, every effort should be made to coordinate with project laboratories to achieve detection limits that meet the delineation standard for a particular contaminant. If lower detection limits are not achievable, elevated non-detects must still be assigned numeric values for plume stability assessments.

Treatment of non-detect data is an imperfect science as it is impossible to know the true value for a censored result. Common industry practices for assigning values for non-detect results are to 1) use the full value of the detection limit, 2) use half the value of the detection limit, or 3) use some other value based on professional judgement. Care should be exercised when applying option 1 or 2 as using the full detection limit or a pre-determined fraction of the detection limit may be somewhat arbitrary and could potentially skew results (Gardner 2011). For example, the following is a dataset for benzene in a monitoring well used in a plume stability assessment reviewed by the authors.

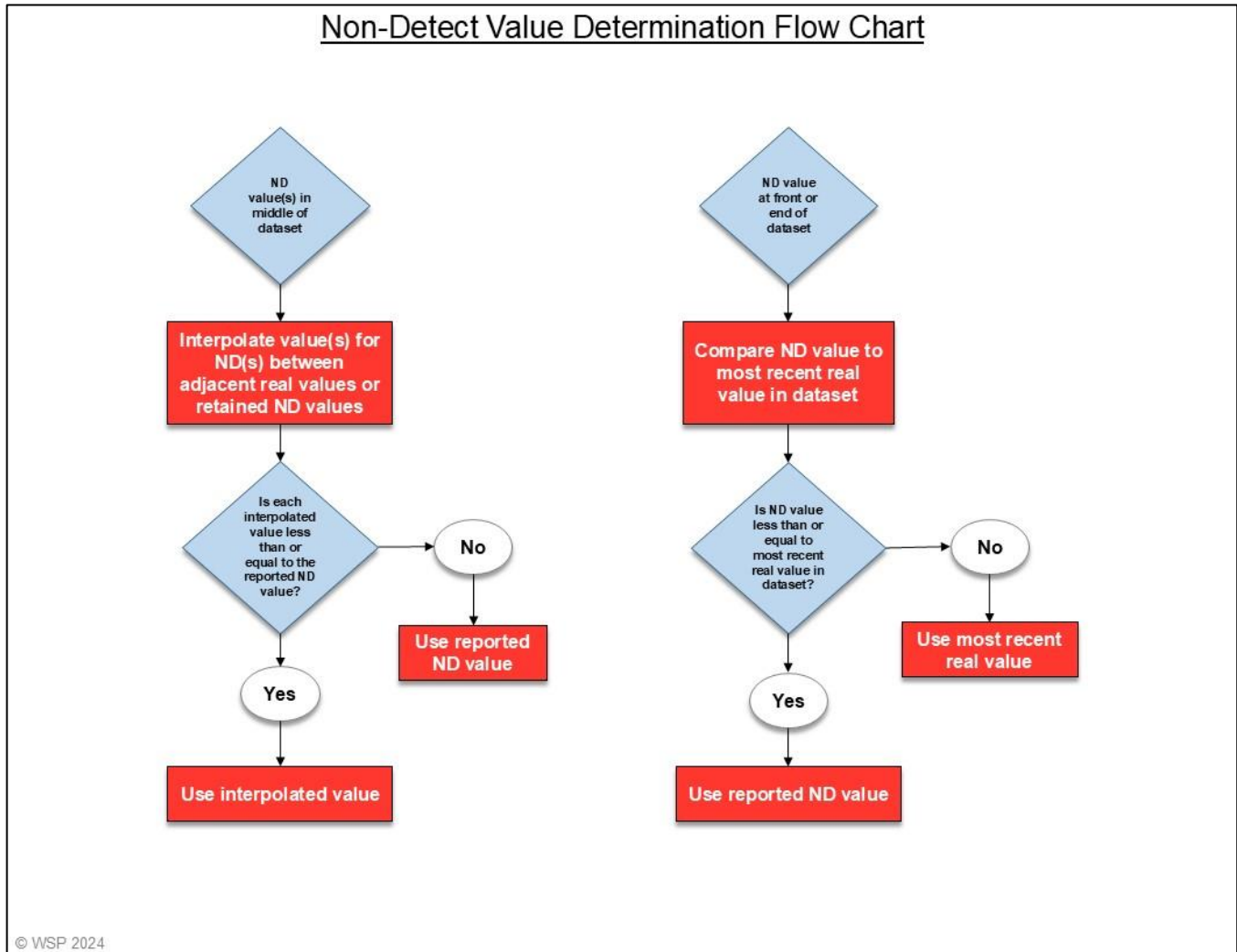
Benzene Results (µg/L)							
May 2017	Aug 2017	Nov 2017	Feb 2018	May 2018	Aug 2018	Feb 2019	May 2019
467	371	425	400	389	543	<1,000	<1,000

As observed above, the last two results are non-detect at elevated reporting limits (required reporting limit was 10 µg/L). If the reporting limits of 1,000 µg/L are used in a statistical trend analysis, the result would be an increasing trend. However, if ½ of the reporting limits are used (i.e., 500 µg/L), then a stable or indeterminate trend would result. Another potential problem that may exist is detection limits over time may skew conclusions if the full value of the detection limit is used.

To aid in value selection when handling non-detects, a logic diagram is included below (Figure 2-1) that outlines a consistent procedure for assigning values. This procedure applies criteria based on other data available in the dataset rather than applying an arbitrary rule. This procedure has been developed based on review of hundreds of plume stability assessments for numerous contaminants. While assigning values for non-detects is an inexact science, the algorithm provides a consistent procedure for handling non-detects. It is reiterated here that because of the nature of elevated non-detects, every effort should be made to achieve required reporting limits when collecting data for plume stability analysis.

Numeric values for non-detect results can be assigned in a consistent manner depending on several factors including the magnitude of the non-detect value relative to surrounding measured values and the position of the non-detect in the dataset. As shown in Figure 2-1, the procedure for assigning non-detect values that occur at the beginning or end of a dataset is different than for values occurring in the middle of a dataset. In all cases, the non-detect values are assigned based on actual measured values from the same dataset.

Figure 2-1: Non-detect Value Determination Flow Chart



As summarized above, if one or more elevated non-detects occur in the middle of a data set (i.e., real measured value on either side of the non-detect[s]), then new values for each non-detect should be calculated using linear interpolation. Each interpolated value is then compared to its respective reported non-detect value. If the interpolated value is less than or equal to the reported value, then the interpolated value should be used in plume stability calculations. If the interpolated value is greater than the reported value, then the reported value should be used in plume stability calculations.

### Interpolation Example

Linear interpolation is the process of estimating unknown values that fall between known values, with each unknown value being calculated using the following formula.

$$y = \frac{y_2 - y_1}{x_2 - x_1} (x - x_1) + y_1$$

Where,

y = interpolated value

y<sub>1</sub> = first known value

y<sub>2</sub> = second known value

x = known date for new interpolated value (as integer)

x<sub>1</sub> = first known respective date (as integer)

x<sub>2</sub> = second known respective date (as integer)

### 3.0 OVERVIEW OF PLUME STABILITY ASSESSMENT METHODS

There are many methods for assessing plume stability. Most methods can be characterized by two main qualities: 1) qualitative versus quantitative and 2) well-by-well or plume-based. Table 3-1 provides a summary of common plume stability assessment methods including descriptions, applicability, limitations and available tools.

**Table 3-1: Plume Stability Assessment Methods Summary**

Method	Description	Applicability	Limitations	Available Tools
<b>Qualitative Methods</b>				
Concentration vs. time plots	A straightforward component of the evaluation of contaminant plume characteristics is the plotting of contaminant concentrations over time at each monitoring location, as well as the graphing of contaminant concentrations versus distance downgradient along the plume flow path over several sampling events.	Typically, can be used as a first step in plume stability analysis. There are minimal data requirements and outputs can be created using industry standard tools. Allows visual identification of trends and patterns that lead to more robust analysis (e.g., statistical trend analysis). These methods are generally applicable to smaller and less complex sites.	Susceptible to arbitrary practitioner choices in scale selection. Noisy datasets may obscure subtle trends. Data interpretation can be difficult with large datasets.	<ul style="list-style-type: none"> <li>Spreadsheet (e.g., Excel)</li> </ul>
Concentration vs. distance plots				

Method	Description	Applicability	Limitations	Available Tools
Concentration isopleth maps	Isopleth maps are prepared by plotting the concentration of the contaminant on a base map prepared using surveyed data. Lines of equal contaminant concentration (isopleths) are then drawn and labeled.	Typically, can be used as a first step in plume stability analysis. Provides spatial representation of contaminant concentrations across a site.	Susceptible to practitioner bias in isopleth interval. This method is not applicable for small or poorly defined well networks.	<ul style="list-style-type: none"> <li>▪ Surfer®</li> <li>▪ RockWorks</li> <li>▪ Leapfrog Works</li> <li>▪ Earth Volumetric Studio (EVS)</li> </ul>
<b>Well-by-Well Methods</b>				
Mann-Kendall	A nonparametric statistical test for monotonic trends, such as concentrations that are either consistently increasing or decreasing over time. The advantages of the test include no assumption of normality or other distribution.	Can be easily used on most sites where temporal data are available.	May not be useful when evaluating cyclical trends (e.g., seasonal variation). Trends can be masked by large concentration changes. Requires at least four sampling events.	<ul style="list-style-type: none"> <li>▪ WSP Mann-Kendall Tool</li> <li>▪ MAROS</li> <li>▪ GSI Mann-Kendall Toolkit</li> <li>▪ Spreadsheet (e.g., Excel)</li> <li>▪ ProUCL</li> </ul>



Method	Description	Applicability	Limitations	Available Tools
Linear regression	A parametric statistical technique used to estimate a trend via a linear relationship between multiple data points (analytical results). A line with a positive slope indicates an increasing trend, whereas a negative slope is indicative of a decreasing trend. Linear regression analysis offers advantages where magnitude is considered, can work with seasonality of data, and is generally easy to compute with readily available tools and software packages.	Can be easily used on most sites where temporal data are available.	Assumes the residuals are independent and normally distributed with a constant variance.	<ul style="list-style-type: none"> <li>▪ Spreadsheet (e.g., Excel)</li> <li>▪ ProUCL</li> </ul>
<b>Plume-Based Methods</b>				
Plume area	Provide a more robust evaluation of plume stability. For example, the trend of total dissolved mass within the extent of the monitoring well network is an unambiguous measure of plume stability.	Typically applied to more complex sites with large datasets but can be used on smaller sites with well-defined well networks.	Can be more expensive and time consuming than simpler well-by-well methods.	<ul style="list-style-type: none"> <li>▪ Ricker Method®</li> <li>▪ MAROS</li> <li>▪ GWSDAT</li> </ul>
Plume mass				
Plume centre of mass				
Plume spread of mass				

Method	Description	Applicability	Limitations	Available Tools
Mass flux	Mass flux combines contaminant concentration and groundwater flow rate to calculate the contaminant mass moving across a unit area of the aquifer. The unit plane is defined by a transect, such as the downgradient edge of the source zone, property boundary, or surface water body.	Typically used for complex sites with boundary monitoring constraints.	Requires clustered sampling points, placed perpendicular to the longitudinal axis of the plume.	<ul style="list-style-type: none"><li>▪ Mass Flux Toolkit (Farhat et al. 2006)</li><li>▪ ITRC (2010)</li></ul>

The dataset provided in Table 3-2 will be used to provide examples of various types of plume stability assessments including qualitative, well-by-well, and plume-based methods in Sections 3.1 to 3.3.

**Table 3-2: Example Dataset**

Well	Coordinates		Benzene Monitoring Data ( $\mu\text{g/L}$ )							
	X	Y	Feb-20	Aug-20	Feb-21	Aug-21	Feb-22	Aug-22	Feb-23	Aug-23
MW-1	2382	2647	1,723	1,372	801	1,042	895	661	538	533
MW-2	2326	2983	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-3	2120	2984	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-4	2026	2716	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-5	2035	2493	35	204	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-6	2215	2370	12,854	14,143	11,786	11,845	--	11,895	13,222	11,400
MW-7	2194	2713	1,643	1,757	624	643	592	758	697	676
MW-8	2492	2787	1,568	1,139	681	927	770	595	484	460
MW-9	2563	2513	563	612	2,020	2,414	803	1,511	1,417	1,387
MW-10	2255	2490	7,541	8,370	5,891	5,838	--	3,749	6,708	6,373
MW-11	2459	2371	10,551	11,680	11,345	7,247	9,650	15,529	11,755	10,932
MW-12	2746	2370	381	635	688	395	423	751	13	12
MW-13	2934	2586	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-14	2711	2851	1,145	1,014	477	807	585	387	266	269
MW-15	1733	2253	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-16	2280	2031	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-17	2602	2008	<1.0	<1.0	<1.0	<1.0	--	<1.0	<1.0	<1.0
MW-18	2732	3013	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
MW-19	2941	2844	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

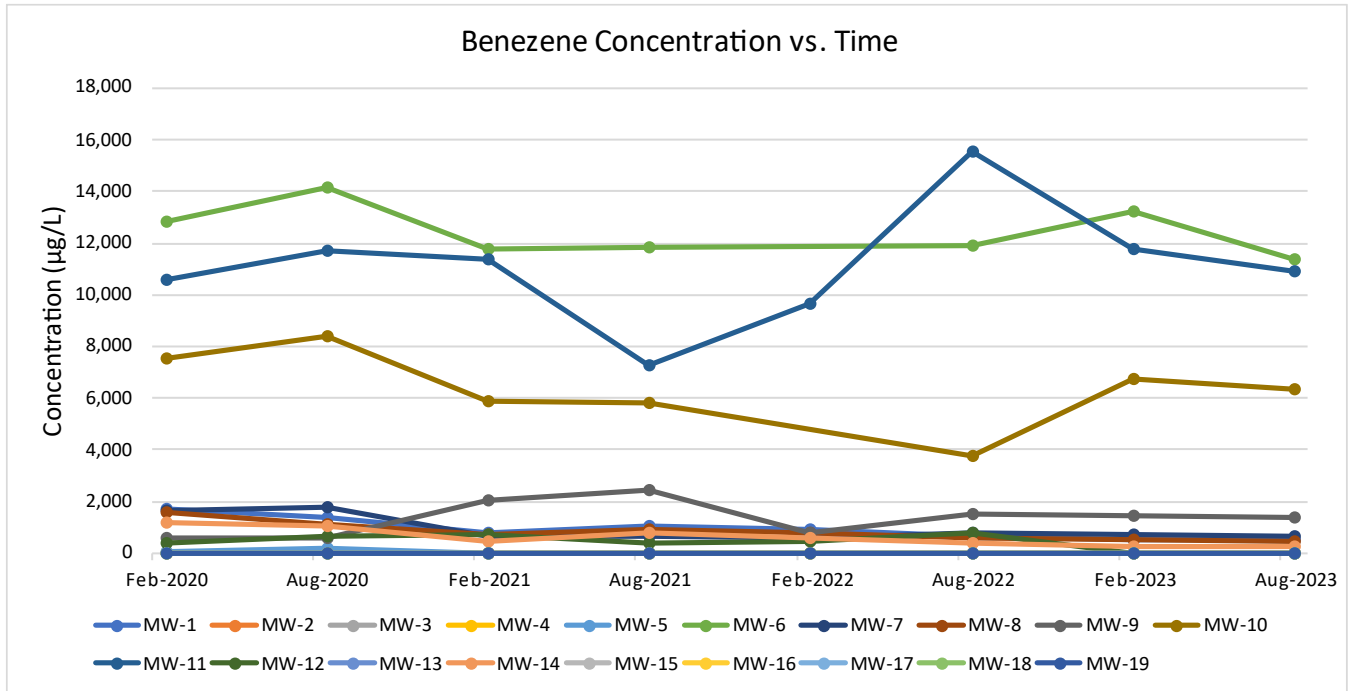
## 3.1 Qualitative Methods

### 3.1.1 Concentration vs. Time and Concentration vs. Distance Plots

A straightforward component of the evaluation of contaminant plume characteristics is the plotting of contaminant concentrations over time at each monitoring location, as well as the graphing of contaminant concentrations versus distance downgradient along the plume flow path over several sampling events. Assessments of plume stability can be made if concentrations in each of the wells are generally decreasing over time and with distance. Examples of both techniques are provided below using the example dataset provided in Table 3-2 accomplished using Microsoft Excel.

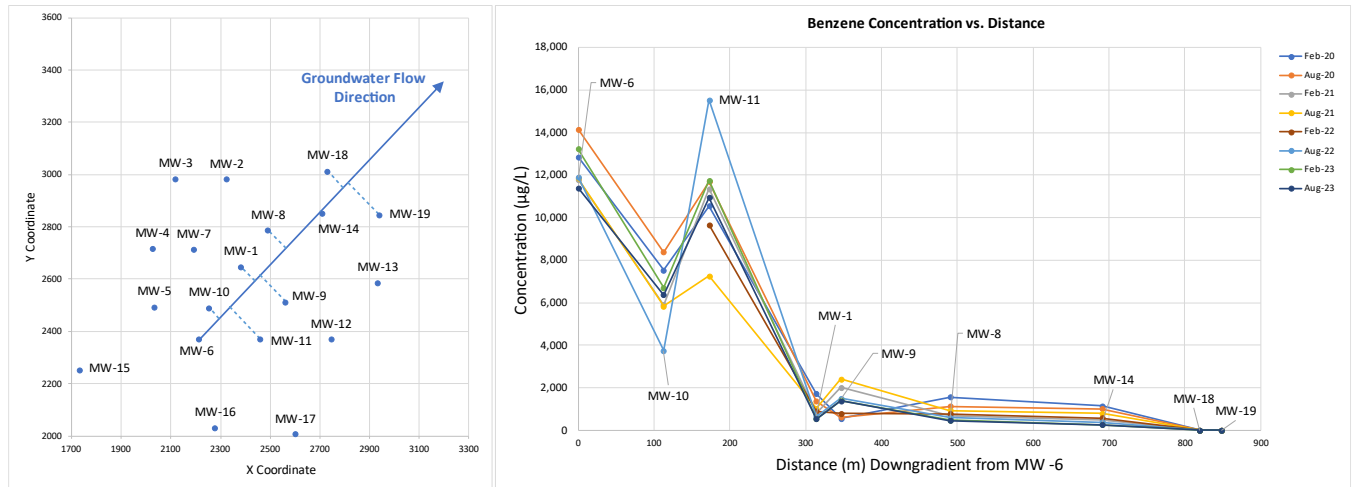
As shown in Figure 3-1, benzene concentrations for each well are plotted for each of the eight sampling events. The well with highest concentration (MW-6) appears to be stable and has a lower concentration at the end of the dataset compared to the start. However, MW-11, the well with the second highest concentrations, appears to be increasing as the average of the last three sampling events (12,739  $\mu\text{g/L}$ ) is greater than the average of the first three sampling events (11,192  $\mu\text{g/L}$ ). Further, in MW-9, there was an early increase in concentrations in February and August 2021 followed by an apparent stable trend. The remaining wells have lower concentrations and apparent stable or decreasing trends over time. It is difficult to draw conclusions on overall plume stability because the graphical evaluation does not show all wells stable or decreasing over time.

**Figure 3-1: Benzene Concentration vs. Time**



As shown in Figure 3-2, the same dataset is plotted as concentration versus distance downgradient. MW-6 is identified as the “source area” well as it generally has the highest benzene concentrations. The concentrations at each well are then plotted in the order of their downgradient distance from the source area well. Multiple events can be added as additional series on the plot. In this plot, concentrations can be seen to be generally decreasing with distance from MW-6. Although farther in the downgradient direction than MW-10, MW-11 is shown to consistently have higher benzene concentrations than MW-10. Review of the locations plot on the left shows MW-11 farther side-gradient than MW-10, suggesting that the source area may be between MW-6 and MW-11. However, a qualitative review of concentrations in the downgradient flow direction from MW-11 can also be accomplished using the same distance plot by assessing the concentration line from MW-11 to MW-9 to MW-19. This second assessment also reveals decreasing concentrations with distance downgradient.

**Figure 3-2: Benzene Concentration vs. Distance**

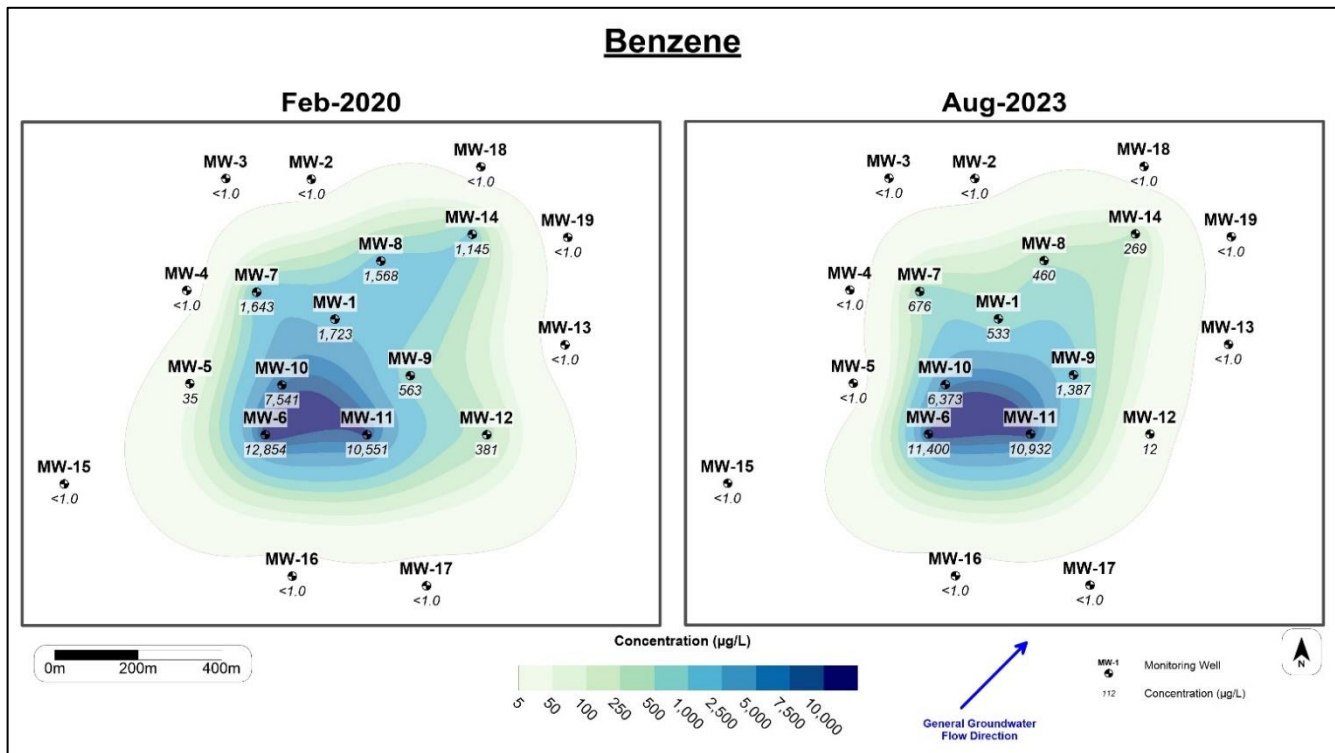


### 3.1.2 Concentration Isopleth Maps

Concentration isopleth maps can be a useful tool for qualitatively assessing plume stability as they depict concentrations with respect to their spatial relationship to each other. An example is provided in Figure 3-3, using the first and last events from the example dataset. Several qualitative statements can be made from this comparison.

- The plume does not appear to be migrating in the downgradient groundwater flow direction because downgradient wells MW-2, MW-13, MW-18, and MW-19 have remained non-detect.
- The plume appears to be decreasing in size because MW-5 has decreased from 35 to <1.0 µg/L.
- However, the “source area,” proximal to wells MW-6, MW-10 and MW-11, appears to be increasing as the amount of darkest blue shading has increased in this area. Although the difference in the amount of darkest blue shading between the two maps is minimal, it does add some uncertainty in the determination of an overall conclusion of stability.

**Figure 3-3: Benzene Concentration Isopleth Map Comparison**



There are several important factors to consider when making qualitative comparisons of concentration isopleth maps. Maintaining a consistent isopleth gradient between maps is important so assessments made on overall shape and magnitude of isopleths are not a result of changes in the concentration gradient intervals depicted. Furthermore, maintaining a consistent network of wells between comparison maps is important so changes in the contours, and subsequent assessments made about their shape, are not the result of difference in the amount of data used to develop the isopleth.

### 3.2 Well-by-Well Analysis Methods

Well-by-well assessment methods are quantitative techniques for assessing plume stability by evaluating trends in data from wells independently from each other. An overall assessment of plume stability may be made provided the conclusions from individual wells agree with each other. Contradictory or inclusive results may make interpretation of plume stability difficult. Two common trend tests used for a well-by-well plume stability assessments are the Mann-Kendall trend test (Gilbert 1987; US EPA 2006;) and linear regression (US EPA 2006). Sections 3.2.1 and 3.2.2 present descriptions and examples of each.

#### 3.2.1 Mann-Kendall Trend Analysis

The Mann-Kendall test is a statistical test that is widely accepted and used in environmental science for evaluating monotonic trends in datasets such as concentrations that are either consistently increasing or decreasing over time (ITRC, 2013). The test is relatively simple, it can be used on small datasets (a minimum of four rounds of sampling data), and the data do not have to be normally distributed. The test can also accommodate datasets with missing values and values below method detection limits (Gilbert, 1987).

One disadvantage of this test is that it is not appropriate for datasets that are cyclic or exhibit seasonal trends (ITRC, 2013). If the dataset has a seasonal trend and is large enough, the data can be divided by season and separate tests can be performed for each season. Otherwise, an alternative test, such as the Mann-Whitney test, would be more appropriate.

The result of a Mann-Kendall test is the calculation of an “S” statistic. The S statistic is the sum of differences between sequential sampling events and provides an indication of whether a trend exists and whether the trend is positive or negative. A positive S value implies that COC concentrations later in time tend to be larger and is therefore indicative of an increasing concentration trend. Conversely, a negative S value indicates that COC concentrations are decreasing over time. An S value of zero or suggests that there is no significant upward or downward trend. The strength of an increasing or decreasing trend increases as the absolute value S increases. If the S statistic does not indicate a statistically significant downward trend, the coefficient of variation (COV) and the sign of the S statistic is used to aid in determining whether the plume may be considered stable. The COV is equal to the standard deviation divided by the mean. The following is a decision matrix that is used in interpreting Mann-Kendall test results where 90% confidence is set as the threshold for a significant trend.

**Table 3-3: Mann-Kendall Interpretation**

<b>Mann-Kendall Interpretation</b>		
<b>Mann-Kendall Statistic</b>	<b>Statistical Confidence</b>	<b>Trend Conclusion</b>
$S > 0$	$\geq 90\%$	Increasing
$S > 0$	$< 90\%$	No Trend
$S \leq 0$	$< 90\%$ and $COV \geq 1$	No Trend
$S \leq 0$	$< 90\%$ $COV < 1$	Stable
$S < 0$	$\geq 90\%$	Decreasing

The Mann-Kendall test can be easily conducted using standard analysis features of Microsoft Excel® or other statistics software packages such as ProUCL software developed by the US EPA or the GSI Mann Kendall Toolkit developed by GSI Environmental Inc. (GSI). For detailed instructions and example calculations on conducting the Mann-Kendall test, the reader is referred to the references above or the user manual supplied with the above-referenced software packages.

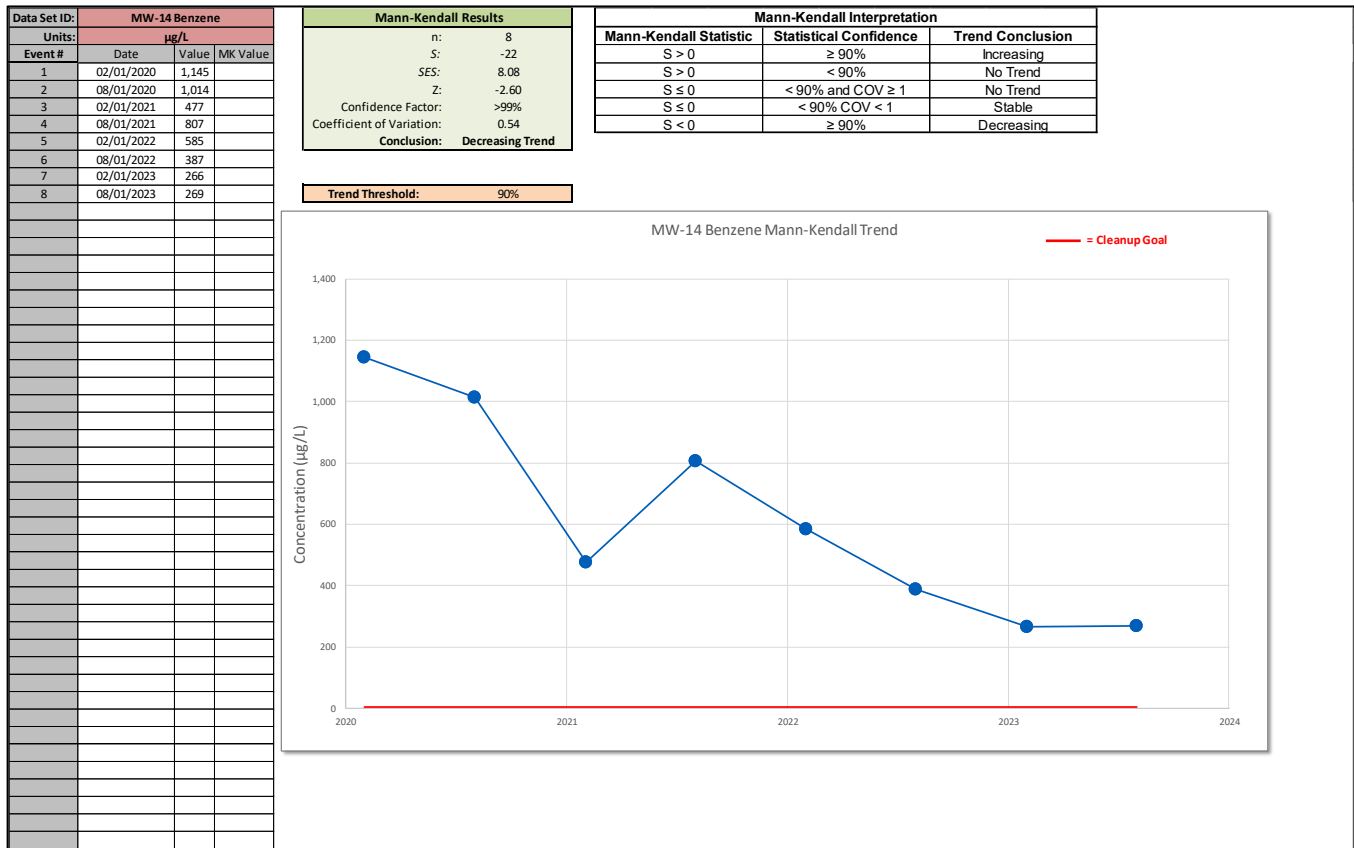
An Excel tool for conducting a Mann-Kendall trend test, developed by WSP, is provided as an attachment to this document and is available for download on the CSAP Society website (<https://csapsociety.bc.ca/for-members/resources/research-technical-studies/groundwater-plume-stability-assessment-methods/>).

Numeric values assigned for non-detects may impact trend conclusions as discussed in Section 2.2. Therefore, the practitioner must exercise careful consideration when assigning these values. The WSP Mann-Kendall tool helps overcome some of the limitations imposed by non-detect data in a Mann-Kendall test by 1) providing visibility of the values assigned for non-detect results in the “MK Value” column and 2) providing options for quickly testing various methods for assigning non-detect values.

Figure 3-4 is an example of the WSP Mann-Kendall tool using MW-14 benzene data from the example dataset. Following completion of a Mann-Kendall trend test for each well, a summary of the conclusions can be developed to aid in assessing overall plume stability. Table 3-4, an example summary table produced by the WSP Mann-Kendall tool, summarizes the calculated Mann-Kendall variables, trend determinations and confidence factor. It

also provides columns to aid in interpretation of the Mann-Kendall results with respect to screening values or site objectives. For example, a stable trend below a cleanup value has a different context in terms of remediation progress than a stable trend above a cleanup value. In the summary table, only wells with detected results were included for a Mann-Kendall trend test. The varying results make an overall assessment of plume stability difficult to determine, which is the main limitation of a well-by-well plume stability assessment approach.

**Figure 3-4: WSP Mann-Kendall Tool Example - MW-14 Benzene**





**Table 3-4: WSP Mann-Kendall Tool Example Summary Table**

Data Set ID	n	S	SES	Z	Confidence Factor	Coefficient of Variation	Conclusion	Most Recent Value	Units	All Values Below Screening Level	Most Recent Value Below Screening Level
MW-6 Benzene	7	-5	6.66	-0.6	72%	0.08	Stable	11,400	µg/L	N	N
MW-7 Benzene	8	-6	8.08	-0.62	73%	0.52	Stable	676	µg/L	N	N
MW-8 Benzene	8	-24	8.08	-2.85	>99%	0.45	Decreasing Trend	460	µg/L	N	N
MW-9 Benzene	8	6	8.08	0.62	73%	0.49	No Trend	1,387	µg/L	N	N
MW-10 Benzene	7	-7	6.66	-0.9	81%	0.23	Stable	6,373	µg/L	N	N
MW-11 Benzene	8	4	8.08	0.37	64%	0.21	No Trend	10,932	µg/L	N	N
MW-12 Benzene	8	-6	8.08	-0.62	73%	0.69	Stable	11.76	µg/L	N	N
MW-14 Benzene	8	-22	8.08	-2.6	>99%	0.54	Decreasing Trend	269	µg/L	N	N

n - number of data points

S - sum of comparisons

SES - square root of variance

Z - Mann-Kendall Statistic

### 3.2.2 Linear Regression Trend Analysis

Linear regression is a parametric statistical test used to evaluate trends in COC concentrations over time (US EPA 2009; ITRC 2013). The test is used to determine if the slope of the trend line is statistically different from zero (USGS 2002; ITRC 2013) using a calculated probability value ( $p$ -value). If the slope of the trend line is significantly different than zero, a trend line with a positive slope indicates that COC concentrations are increasing and a trend line with a negative slope indicates that COC concentrations are decreasing (ITRC 2013). Linear regression assumes that the regression residuals (the difference between the measured concentrations and predicted concentrations from the regression equation) have a constant variance, are normally distributed and are independent of sample date and concentration (USGS 2002; US EPA 2009; ITRC 2013). In some cases, it may be necessary to demonstrate that the data being analyzed do not violate these assumptions (USGS 2002; US EPA 2009; ITRC 2013).

When evaluating trends using linear regression, trends may be obscured by scatter in the data. This condition is typically indicated by a low coefficient of determination ( $R^2$ ) value. As described in the Monitoring and Remediation Optimization System (MAROS) software user's guide (AFCEE 2006), even with low  $R^2$  values (i.e., high degree of scatter), assuming the sign (i.e., positive or negative) of the estimated log-slope is correct, a level of confidence that the slope is not zero can be easily determined.

For the plume trend analysis, significant trends (plume slope is not zero) are concluded when the calculated confidence factor is greater than a predetermined level of significance. If the confidence factor is less than or equal to the predetermined level of significance, the conclusion is that the trend is indeterminate or there is no trend.

Linear regression analysis can easily be conducted using standard analysis features of Excel or other statistics software packages. For detailed instructions and example calculations on conducting linear regression analysis, the reader is referred to the sources above.

### 3.3 Plume-Based Methods

In the assessment of groundwater contamination plumes, a mix of trend conclusions among individual monitoring wells is common. As a result, when data from the individual wells are viewed together, understanding overall plume behaviour can be elusive. An alternative to the well-by-well approach to assessing plume stability is a quantitative plume-based method. The calculation of plume-wide estimates of total dissolved-phase plume mass, plume area, average concentration and centre of mass (COM) have been presented in the literature as powerful tools for determining plume stability (Gibbs et al. 2002; Ricker, 2008; Vanderford, 2010). These methods generally provide a more robust understanding of overall plume behaviour than well-by-well methods. This section focuses on the plume stability evaluation method described by Ricker (2008).

The Ricker Method® (Ricker, 2008) is based on the use of grid files generated from commonly used contouring (Surfer by Golden Software) and spreadsheet computer software (Excel). The overall plume area, average concentration, mass, and COM are calculated for each sampling event. Afterward, an appropriate statistical trend test (e.g., linear regression or Mann-Kendall) is used to assess the trends in the plume metrics of area, average concentration, and mass.

For Ricker Method plume stability analyses, care should be taken when interpreting trends in the plume metrics of area, average concentration, and mass. Each metric describes an aspect of plume behaviour. Therefore, overall plume stability cannot be described by a single metric. Accordingly, an increasing trend in any single plume metric does not necessarily indicate that the plume is not stable or that the plume is expanding. For example, a common phenomenon that has been observed is a condition where the plume area is decreasing, but the plume average concentration is increasing (and plume mass is stable or decreasing). This would be the expected pattern for a groundwater plume undergoing natural attenuation where the fringes of the plume are attenuating at a greater rate than the core of the plume. In this condition, the COCs are becoming more concentrated as the plume footprint gets smaller.

Another example when a single metric does not describe overall plume stability is often observed with the plume COM metric. An increasing trend (i.e., downgradient migration) in COM movement does not necessarily indicate that the plume is increasing or migrating. For example, an upgradient portion of a groundwater plume may undergo rapid attenuation through engineered remediation or natural attenuation, but the downgradient portions of the plume may remain relatively unchanged. In this scenario the COM will migrate in a downgradient direction (i.e., increasing trend in distance from the source) although the plume has undergone a significant reduction in mass and possibly in area and average concentration.

Therefore, the primary plume metric for Ricker Method plume stability demonstrations should be plume mass. Increasing trends in plume metrics area, average concentration, or COM should include discussion of possible causes in the plume stability assessment. However, for plume stability demonstrations, decreasing or stable trends in plume mass should be the primary decision criterion. For detailed instructions on conducting a Ricker Method analysis, the reader is referred to (Ricker 2008) or the example on the Golden Software (2024) website here: [Ricker Method for Plume Stability Analysis](#).

### 3.3.1 Mass Discharge and Mass Flux

Mass discharge and mass flux can aid in assessing plume stability by quantifying plume strength through a transect. Following is definition of mass flux from ITRC (2010).

*Mass flux is a rate measurement specific to a defined area, which is usually a subset of a plume cross section. Mass flux is thus expressed as mass/time/area (e.g., g/d/m<sup>2</sup>). Mass discharge is an integrated mass flux estimate (i.e., the sum of all mass flux measures across an entire plume) and thus represents the total mass of any solute conveyed by groundwater through a defined plane. Mass discharge is therefore expressed as mass/time (e.g., g/d).*

This document focuses on mass discharge as a tool for plume stability assessments. Plume mass discharge is an estimate of the mass of a contaminant that passes through a defined cross-sectional area of the plume over time by combining plume concentrations with the Darcy groundwater velocity (hydraulic conductivity multiplied by the hydraulic gradient). The reader is referred to ITRC (2010) for greater detail on calculation of mass discharge.

Mass discharge can be performed as a supplement to a plume-based stability assessment by defining a transect through the already developed concentration grid files. It can also be performed as a stand-alone analysis if the site well network is not sufficient for gridding, such as a linear network of wells that does not delineate a plume. Mass discharge is useful as an assessment of plume stability by comparing changes in the calculated average transect concentration and discharge rate over multiple sampling events.

The following is an example mass discharge analysis for plume stability assessment using the example dataset provided in Section 3.0. As shown in Figure 3-5, a transect line is defined near a relatively linear network of wells hydraulically downgradient from the source area. Mass discharge for each sampling event was calculated by discretizing the transect line into segments and calculating discrete mass flux values for each segment. The discrete mass flux values are then summed to calculate a mass discharge for each sampling event. Discrete mass flux values are calculated by multiplying a concentration by a groundwater velocity, the plume thickness, and plume segment width at each discrete location along the transect. The width used for each discrete mass flux estimate is the distance between concentration nodes in the contaminant concentration contour. The sum of the segment widths represents the width of the plume at the transect line. Groundwater velocity, or Darcy velocity, is determined by multiplying hydraulic conductivity by the hydraulic gradient. A site-wide average hydraulic conductivity of 30.2 m/d was used for the mass discharge estimates. The hydraulic gradient was calculated for each sampling event using the difference in potentiometric surface elevations between MW-6 and MW-14 and the distance between these wells. Thus, the hydraulic gradient varied between events, averaging 0.0052 m/m over the eight events.

Figure 3-6 depicts the average concentration and mass discharge through the transect over time. The change in these values over time represents the trend in benzene mass discharge from the source of this plume. The trend can be evaluated qualitatively or statistically using Mann-Kendall or linear regression as described in Section 3.2. As shown in Figure 3-6, average concentration and mass discharge are both observed to be decreasing over time.

Figure 3-5: Example Mass Discharge Transect

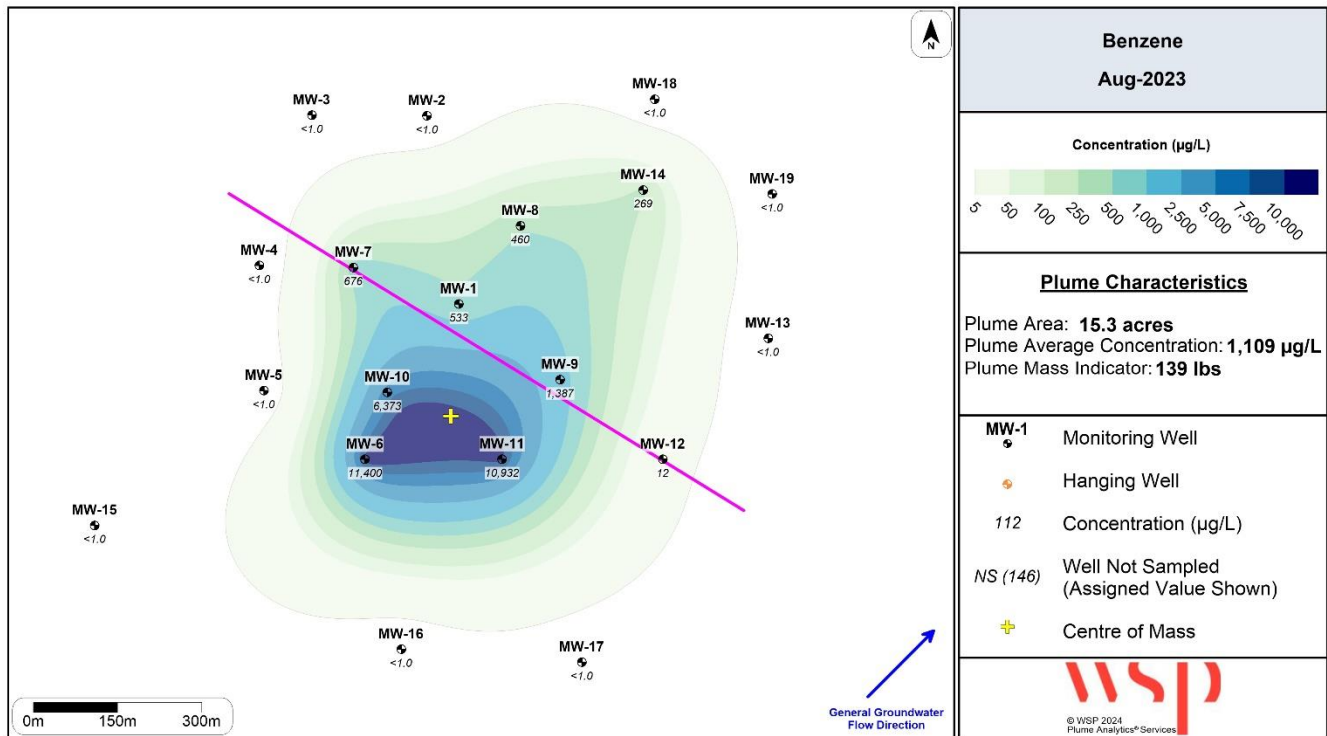
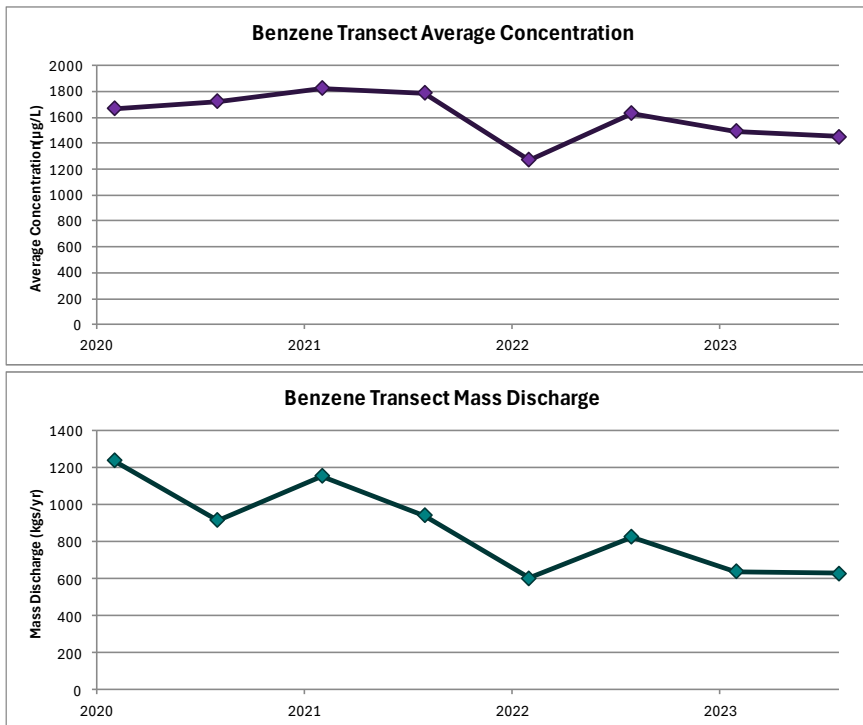


Figure 3-6: Benzene Transect Average Concentration and Mass Discharge



### 3.3.2 Special Considerations for Missing Data in Plume-Based Assessments

For plume-based stability methods, such as the Ricker Method for plume stability analysis, missing events should be assigned numeric values using scientific procedures or professional judgement. Because the intent of a plume-based stability assessment is to evaluate changes in a plume over time, failure to fill missing events may skew results if missing data cause significant change in plume contours.

The example shown in Table 3-5 illustrates the effect of missing data. The example dataset includes eight events. However, three wells (MW-6, MW-10, and MW-17) were not sampled during the February 2022 sampling event (missing values highlighted in yellow below), so the dataset is only complete for seven events. In Table 3-6, the missing values have been assigned numbers using interpolation.

**Table 3-5: Example Dataset with Missing Data**

Well	Coordinates		Benzene Monitoring Data ( $\mu\text{g/L}$ )							
	X	Y	Feb-2020	Aug-2020	Feb-2021	Aug-2021	Feb-2022	Aug-2022	Feb-2023	Aug-2023
MW-1	2382	2647	1,723	1,372	801	1,042	895	661	538	533
MW-2	2326	2983	<1	<1	<1	<1	<1	<1	<1	<1
MW-3	2120	2984	<1	<1	<1	<1	<1	<1	<1	<1
MW-4	2026	2716	<1	<1	<1	<1	<1	<1	<1	<1
MW-5	2035	2493	35	204	<1	<1	<1	<1	<1	<1
MW-6	2215	2370	12,854	14,143	11,786	11,845		11,895	13,222	11,400
MW-7	2194	2713	1,643	1,757	624	643	592	758	697	676
MW-8	2492	2787	1,568	1,139	681	927	770	595	484	460
MW-9	2563	2513	563	612	2,020	2,414	803	1,511	1,417	1,387
MW-10	2255	2490	7,541	8,370	5,891	5,838		3,749	6,708	6,373
MW-11	2459	2371	10,551	11,680	11,345	7,247	9,650	15,529	11,755	10,932
MW-12	2746	2370	381	635	688	395	423	751	13	12
MW-13	2934	2586	<1	<1	<1	<1	<1	<1	<1	<1
MW-14	2711	2851	1,145	1,014	477	807	585	387	266	269
MW-15	1733	2253	<1	<1	<1	<1	<1	<1	<1	<1
MW-16	2280	2031	<1	<1	<1	<1	<1	<1	<1	<1
MW-17	2602	2008	<1	<1	<1	<1		<1	<1	<1
MW-18	2732	3013	<1	<1	<1	<1	<1	<1	<1	<1
MW-19	2941	2844	<1	<1	<1	<1	<1	<1	<1	<1

**Table 3-6: Example Dataset with Interpolated Values**

Well	Coordinates		Benzene Monitoring Data ( $\mu\text{g/L}$ )							
	X	Y	Feb-2020	Aug-2020	Feb-2021	Aug-2021	Feb-2022	Aug-2022	Feb-2023	Aug-2023
MW-1	2382	2647	1,723	1,372	801	1,042	895	661	538	533
MW-2	2326	2983	<1	<1	<1	<1	<1	<1	<1	<1
MW-3	2120	2984	<1	<1	<1	<1	<1	<1	<1	<1
MW-4	2026	2716	<1	<1	<1	<1	<1	<1	<1	<1
MW-5	2035	2493	35	204	<1	<1	<1	<1	<1	<1
MW-6	2215	2370	12,854	14,143	11,786	11,845	11,870	11,895	13,222	11,400
MW-7	2194	2713	1,643	1,757	624	643	592	758	697	676
MW-8	2492	2787	1,568	1,139	681	927	770	595	484	460
MW-9	2563	2513	563	612	2,020	2,414	803	1,511	1,417	1,387
MW-10	2255	2490	7,541	8,370	5,891	5,838	4,785	3,749	6,708	6,373
MW-11	2459	2371	10,551	11,680	11,345	7,247	9,650	15,529	11,755	10,932
MW-12	2746	2370	381	635	688	395	423	751	13	12
MW-13	2934	2586	<1	<1	<1	<1	<1	<1	<1	<1
MW-14	2711	2851	1,145	1,014	477	807	585	387	266	269
MW-15	1733	2253	<1	<1	<1	<1	<1	<1	<1	<1
MW-16	2280	2031	<1	<1	<1	<1	<1	<1	<1	<1
MW-17	2602	2008	<1	<1	<1	<1	<1	<1	<1	<1
MW-18	2732	3013	<1	<1	<1	<1	<1	<1	<1	<1
MW-19	2941	2844	<1	<1	<1	<1	<1	<1	<1	<1

Figure 3-7 depicts the plume in February 2022 if wells MW-6, MW-10, and MW-17 were not assigned values, whereas Figure 3-8 depicts the plume if the missing values were filled using interpolation. As seen by comparing the figures, there is a significant difference in plume concentrations around wells MW-6 and MW-10. Furthermore, the area of the plume expands to the south when MW-17 is not assigned a value. Figure 3-7, Figure 3-8, and Figure 3-9 show a comparison of results from a Ricker Method plume stability analysis between the “missing data” set and the “filled data” set, for all eight events. The difference caused by missing data is evident when comparing the average concentration and mass indicator values for February 2022 between the two sets of charts. The missing data yielded the lowest values for these two metrics throughout the entire eight-event dataset causing a significant change in the linear regression confidence factors and affecting the overall trend conclusions between the two datasets.

Figure 3-7: February 2022 Benzene Plume with Missing Data

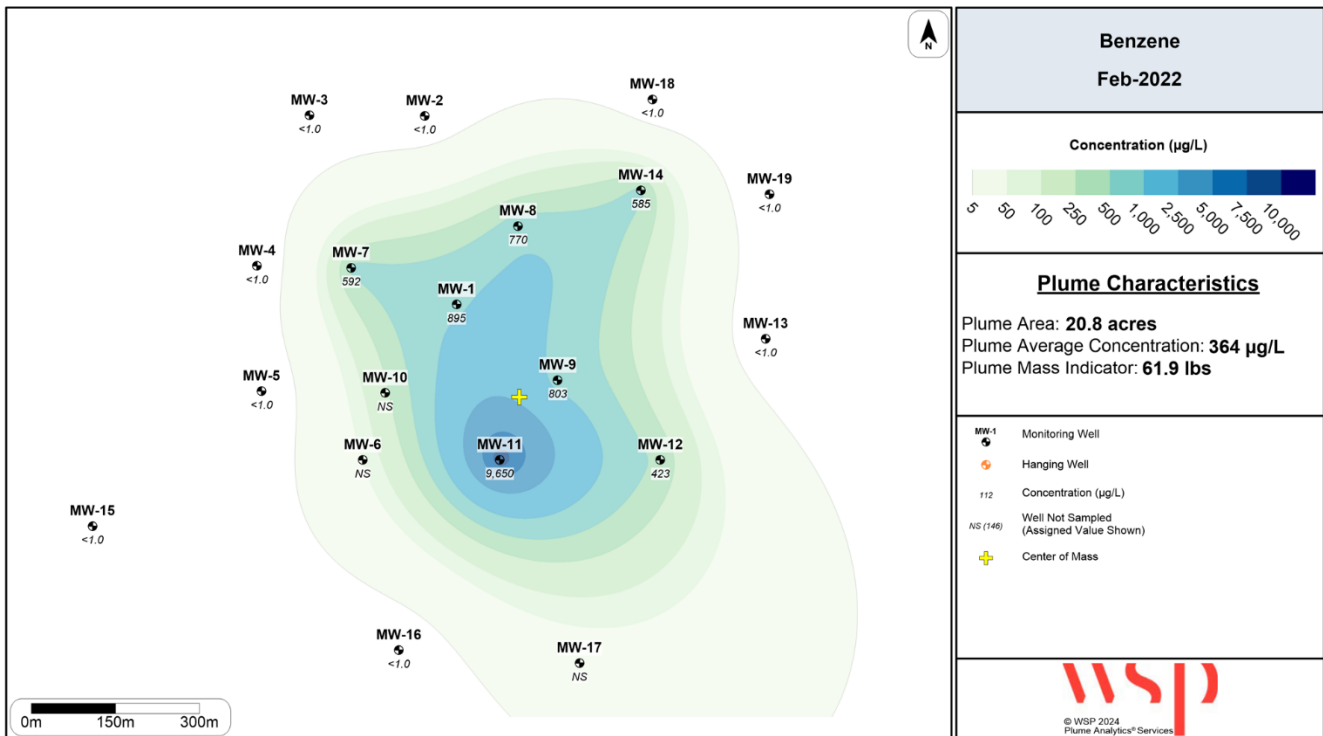
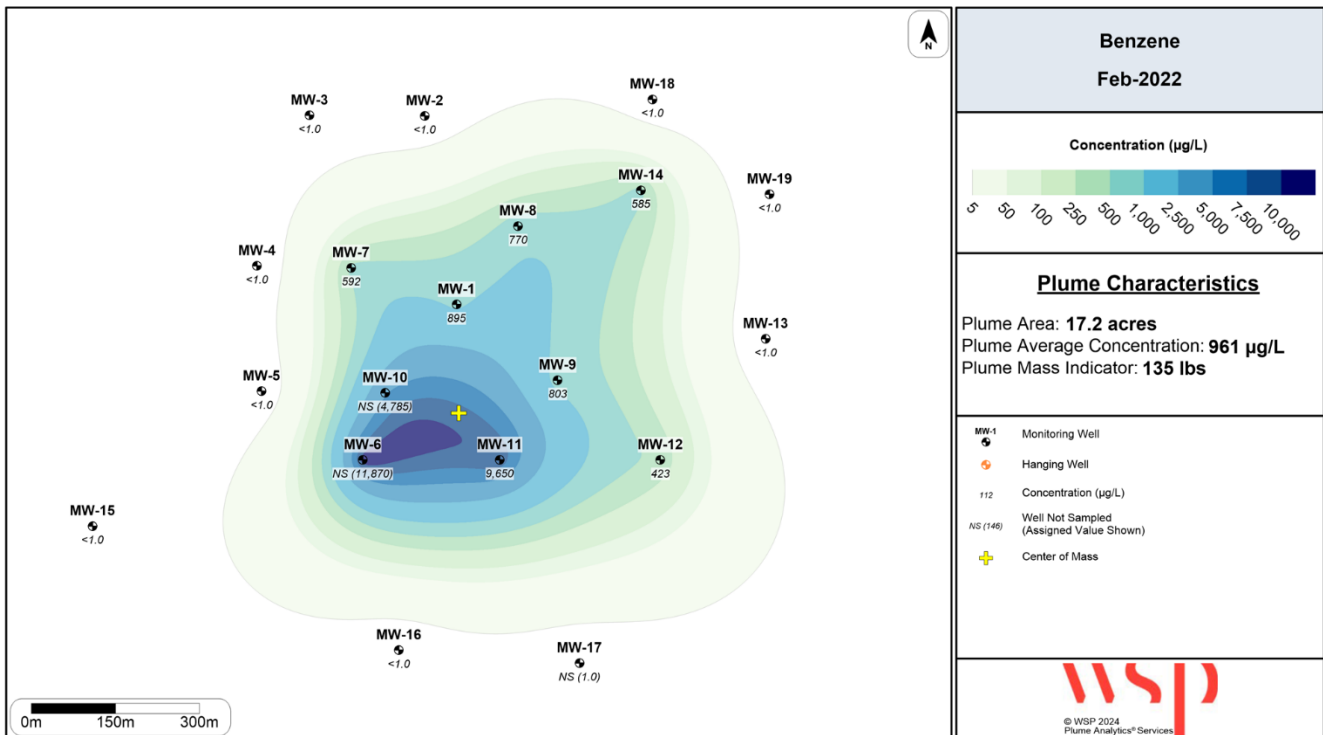
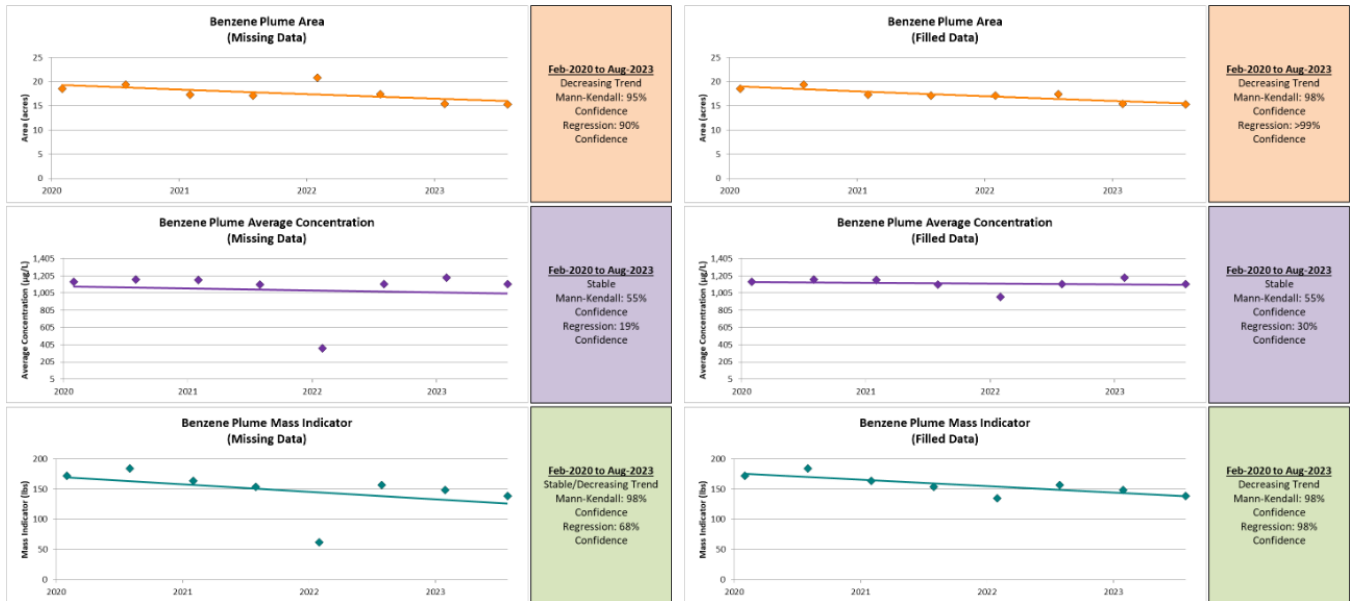


Figure 3-8: February 2022 Benzene Plume with Interpolated Data



**Figure 3-9: Ricker Method® Results Comparison between Missing and Filled Data**





## 4.0 EXAMPLE CONCEPTUAL SITE MODELS

This section presents two example conceptual site models and provides examples of plume stability assessments performed for each site.

### 4.1 Petroleum Hydrocarbon Site

#### 4.1.1 Background

The conceptual site model for a petroleum hydrocarbon site is an active bulk fuel terminal located in northern California. There are two water-bearing zones beneath the site: the shallow A-Zone and deeper B-Zone. Subsurface lithology beneath the site within the A-Zone is characterized by approximately 4.5 to 6.0 m of sandy fill material overlying approximately 3.0 m of interbedded silt and silty sand with clay lenses. Approximately 1.5 to 4.5 m of clay underlies the A-Zone, forming a barrier between the A- and B-Zones, although petroleum hydrocarbon impacts in the B-Zone indicate that this clay layer is not a complete barrier to groundwater or contaminant transport from hydrocarbon impacts in the A-Zone. The B-Zone consists of interbedded sand and silt from approximately 12 to 21 m below ground surface (mbgs).

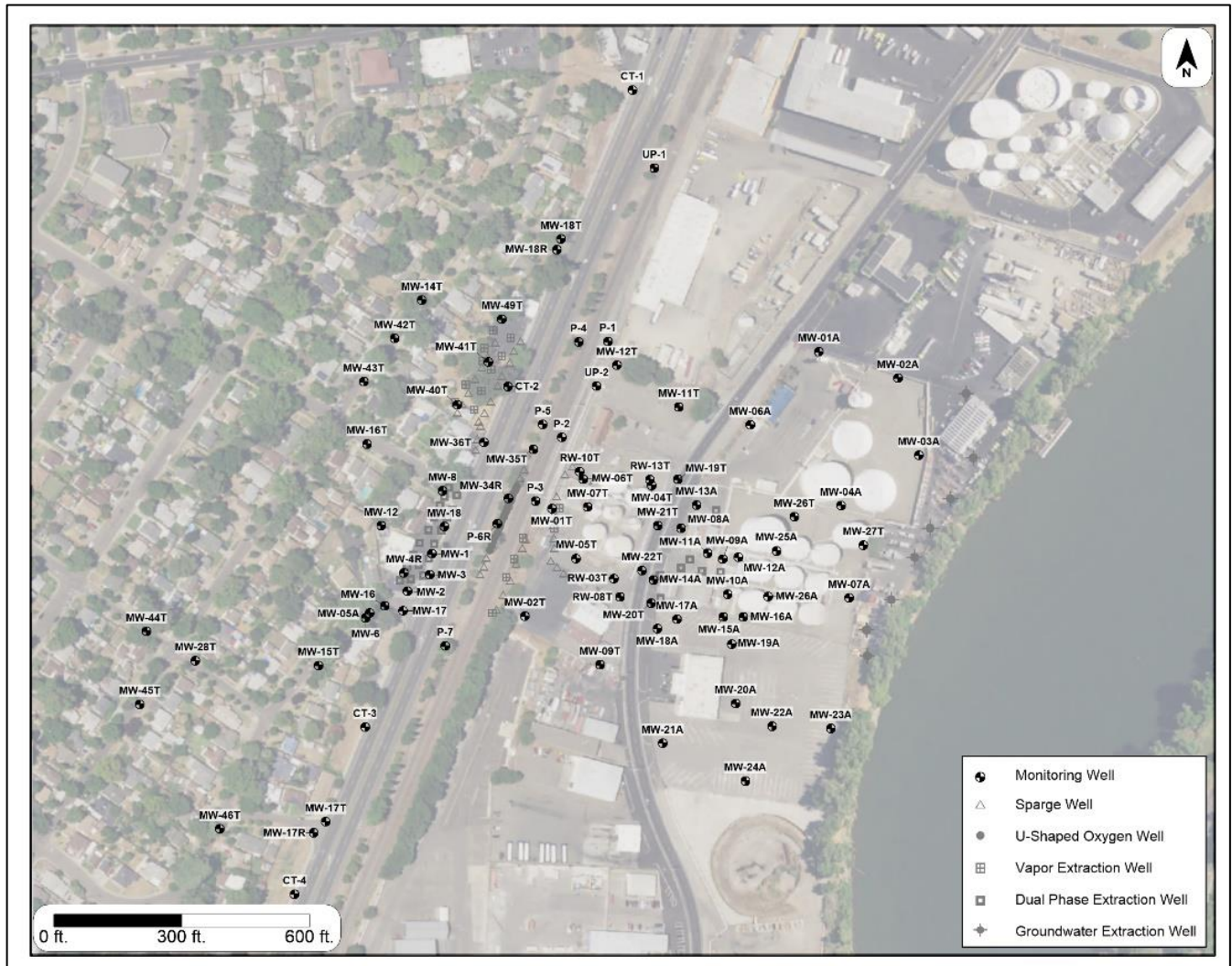
Based on historical groundwater elevation data collected since 1990, groundwater elevations in the vicinity of the site have ranged from approximately 0 to 6 m above mean sea level (approximately 4 to 9.5 mbgs). Groundwater elevations fluctuate seasonally. Historical groundwater flow direction has been variable, but is generally toward the west, away from the river that defines the eastern boundary of the site.

The site contains 20 above-ground storage tanks, above- and below-ground piping, loading racks, and buildings. Numerous remedial technologies have been applied at the site since 1990 that have resulted in significant mass removal. Remediation technologies have been employed at the site from the mid-1990s to 2019 and have included the following systems:

- onsite light non-aqueous phase liquid (LNAPL) recovery system
- multiple soil vapour extraction/air sparge systems
- multiple oxygen injection systems
- off-site dual phase extraction system

Figure 4-1 shows the site and monitoring well network in 2019 prior to optimization.

**Figure 4-1: Monitoring Well Network 2019**



### 4.1.2 Fate and Transport

COCs for the site consist of petroleum hydrocarbons including total petroleum hydrocarbons as gasoline (TPHg); total petroleum hydrocarbons as diesel (TPHd); benzene, toluene, ethylbenzene, xylenes (BTEX); methyl tert-butyl ether (MTBE); and tert-butyl alcohol (TBA). Benzene is the primary COC at the site, as it is the main driver for assessing magnitude of impacts and progress toward cleanup objectives.

The highest soil impacts were primarily encountered within the interbedded silt and sand of the deeper portion of the A-Zone. COC concentrations in soil were relatively low in the overlying sandy fill of the shallower portion of the A-Zone. Lower soil concentrations in the shallower coarse-grained lithology are likely a result of natural attenuation of petroleum hydrocarbons enhanced by soil characteristics and fluctuations in groundwater levels.

Relatively low impacts to shallow soil and strong biodegradation potential of petroleum hydrocarbons are consistent with results of soil vapour surveys conducted on and off site. Soil vapour analytical results indicated that petroleum hydrocarbons attenuated above the groundwater table and were below human health screening levels within 1.5 m of the surface.

Historically, LNAPL has been observed in onsite monitoring wells. LNAPL removal efforts have resulted in only sporadic detections of LNAPL in one monitoring well.

The highest dissolved-phase petroleum hydrocarbon impacts are detected at A-Zone monitoring wells located in the vicinity of the above-ground storage tanks on site. Extensive remediation has been conducted in the western portion of the site and dissolved-phase COC concentrations are relatively low, with stable to decreasing trends. In downgradient offsite areas the plume is more expansive laterally relative to onsite areas. Downgradient monitoring wells, including MW-14T, MW-15T, MW-16T, MW-17R, MW-40T, and MW-49T, provide downgradient delineation of dissolved-phase impacts. The extent of the A-Zone benzene plume, exceeding the California maximum contaminant level of 1 µg/L, is approximately 366 m (1,200 ft) at its greatest length laterally.

### **4.1.3 Plume Stability Analysis**

An initial plume stability analysis was conducted in 2019 as part of an effort to evaluate effectiveness of remediation systems and to optimize the long-term monitoring program. The plume stability analysis was subsequently updated in 2023 to evaluate ongoing natural attenuation after cessation of remediation systems in 2019. TPHg, TPHd, and BTEX were included in the initial analysis based on knowledge of land use and historical releases at the site, which indicated that these compounds presented the most significant risk to nearby potential receptors. The maximum concentrations of MTBE and TBA were relatively low and thus were not included in the plume stability analysis.

The plume stability analysis included a whole plume-based analysis using the Ricker Method as well as a mass flux evaluation. Although not conducted in 2019, a limited well-by-well trend analysis was conducted in 2023 as part of annual reporting for the site. Further details of the plume stability analyses are discussed below. Because the site is in California, imperial units are used in the following discussion.

#### **4.1.3.1 Ricker Method Analysis**

The Ricker Method plume stability analysis compares relative changes in contaminant plume characteristics over time, including area, average concentration, mass, and COM (Ricker, 2008). For this analysis, the term “mass indicator” is used to differentiate between what is represented in the analysis (i.e., dissolved mass estimate) and the total mass in the subsurface. To demonstrate that a plume is stable or decreasing, temporal changes in the calculated values of area, average concentration, and mass indicator should result in an overall stable or decreasing trend. An increasing trend in any of these values may indicate that the plume is not stable and/or is possibly expanding.

The Ricker Method analysis was conducted for both water-bearing zones (A- and B-Zones) at the site. As part of the plume stability analysis, contaminant concentration isopleth maps, or plume maps, were developed using input data from the procedures described in Ricker (2008).

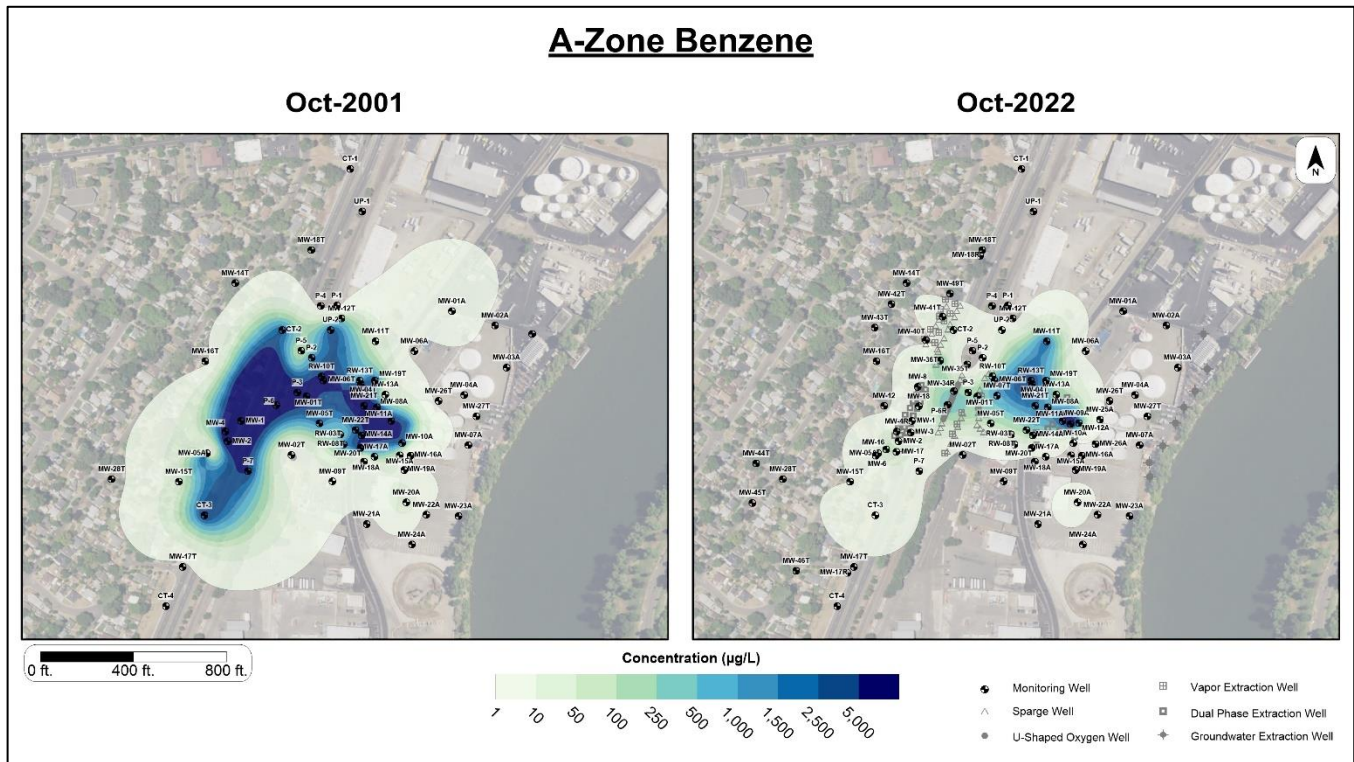
To evaluate the stability of each contaminant plume, the area, average concentration, and mass indicator for each event were plotted to observe changes in each parameter from event to event. Temporal trends of the characteristics for each plume were also evaluated statistically using both linear regression techniques and the Mann-Kendall test. Linear regression analyses were conducted using the regression analysis utility in Excel and the Mann-Kendall tests were conducted using procedures described in Gilbert (1987). The location of the COM was also calculated for each contaminant.

The following is a summary of the plume stability analysis results for benzene.

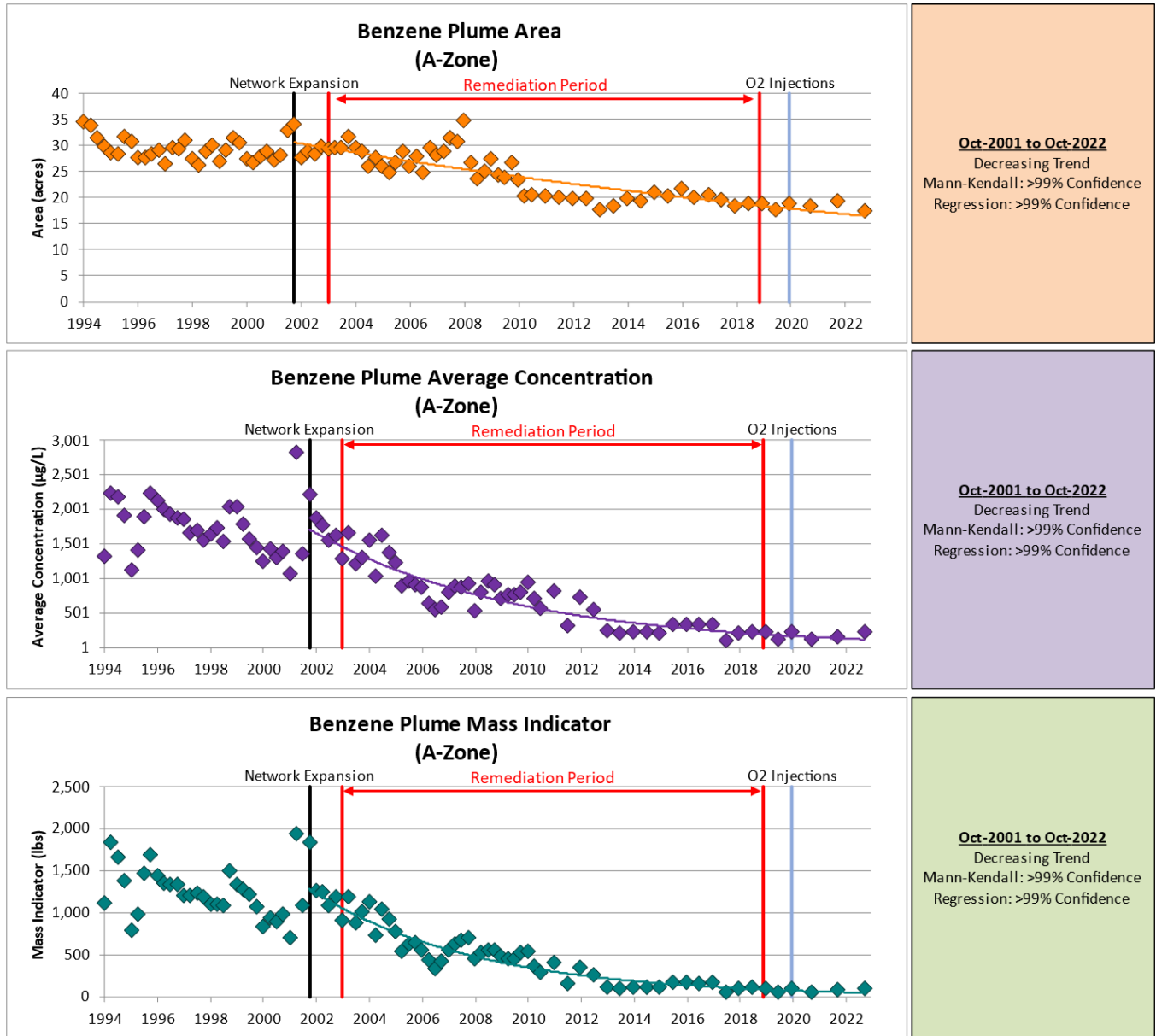
**A-Zone Results**

The benzene plume area, average concentration, and mass in the A-Zone all exhibited decreasing trends over the evaluation period of 2001 to 2022. An illustration of the A-Zone benzene plume extent in 2001 compared to 2022 is shown in Figure 4-2. Temporal trends in plume area, average concentration, and mass indicator during the same period are shown in Figure 4-3.

**Figure 4-2: Benzene A-Zone 2001 vs. 2022**



**Figure 4-3: Benzene A-Zone Ricker Method Plume Stability Trends**



As shown in Figure 4-3, temporal trends in the plume stability metrics were evaluated using both linear regression and the Mann-Kendall test, with each method exhibiting decreasing trends with >99% confidence. Although the benzene plume area decreased from 34.1 acres in 2001 to 17.5 acres in 2022 (49% reduction), the benzene plume mass reduced from 1,839 to 94.5 pounds (95% reduction) during the same period. This is a common phenomenon observed at many sites, whereby the observed reductions in plume average concentration and mass are typically higher than observed reductions in plume area. This highlights the importance of not relying solely on changes in plume footprint (areal extent) when evaluating plume stability.

### B-Zone Results

The benzene plume area, average concentration, and mass in the B-Zone likewise all exhibited decreasing trends over the evaluation period of 2001 to 2022. An illustration of the B-Zone benzene plume extent in 2001 compared to 2022 is shown in Figure 4-4. Temporal trends in plume area, average concentration, and mass indicator during the same period are shown in Figure 4-5.

**Figure 4-4: Benzene B-Zone 2001 vs. 2022**

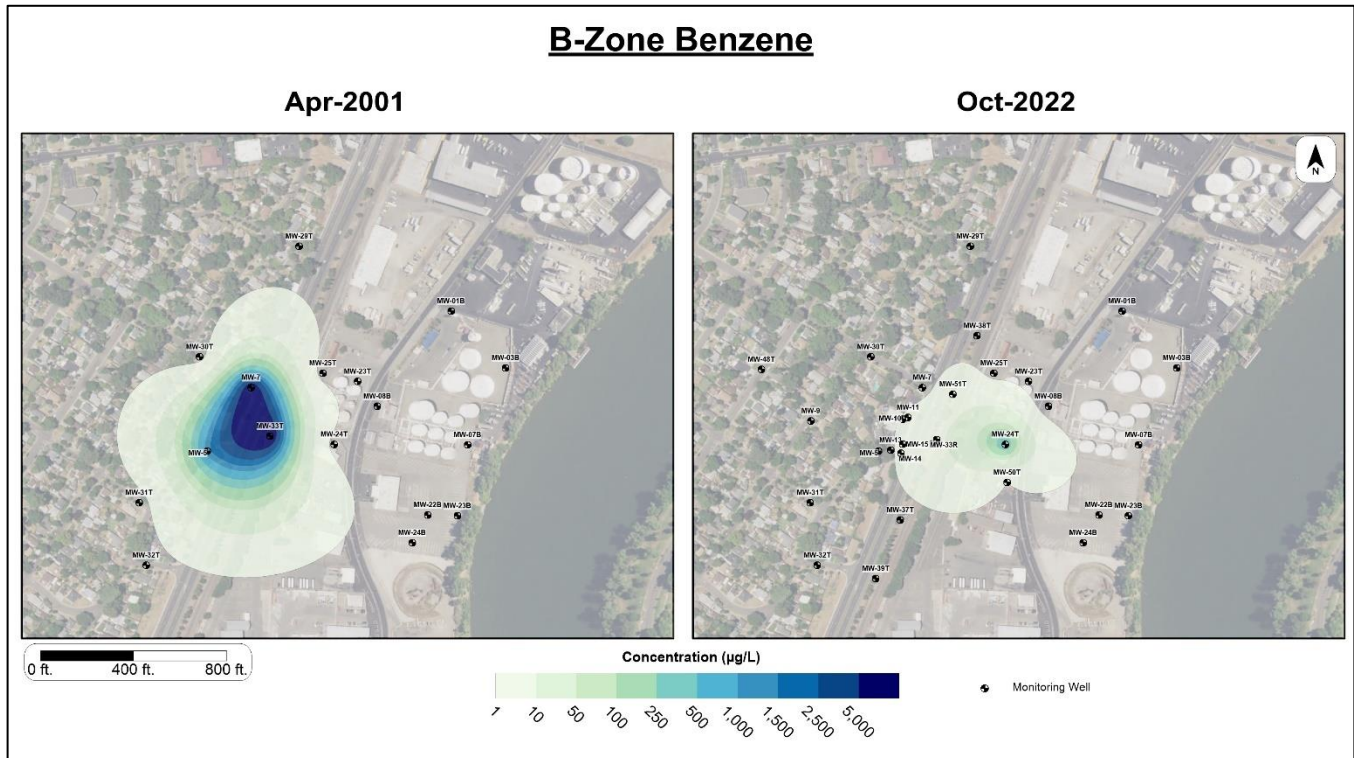
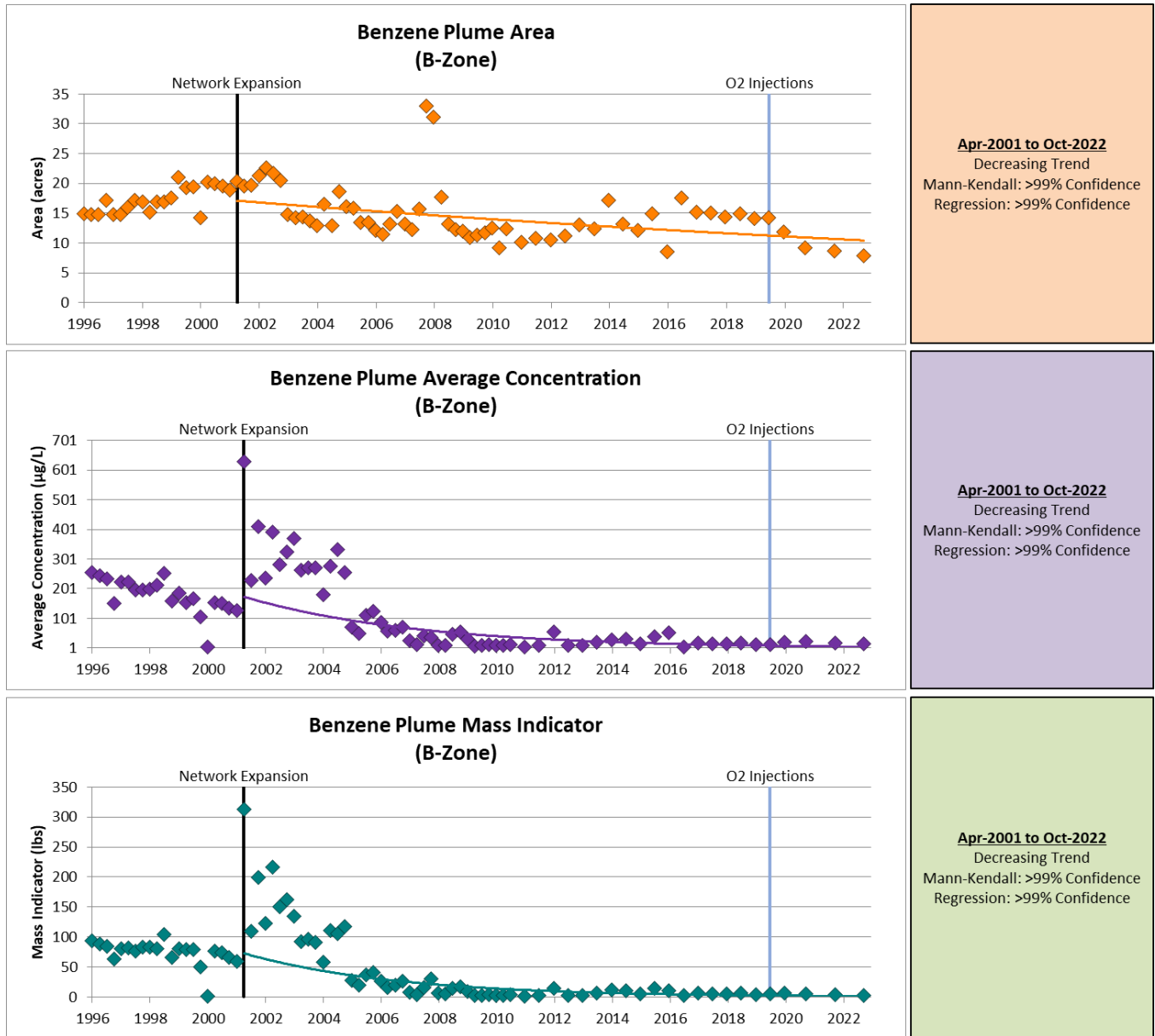


Figure 4-5: Benzene B-Zone Ricker Method Plume Stability Trends



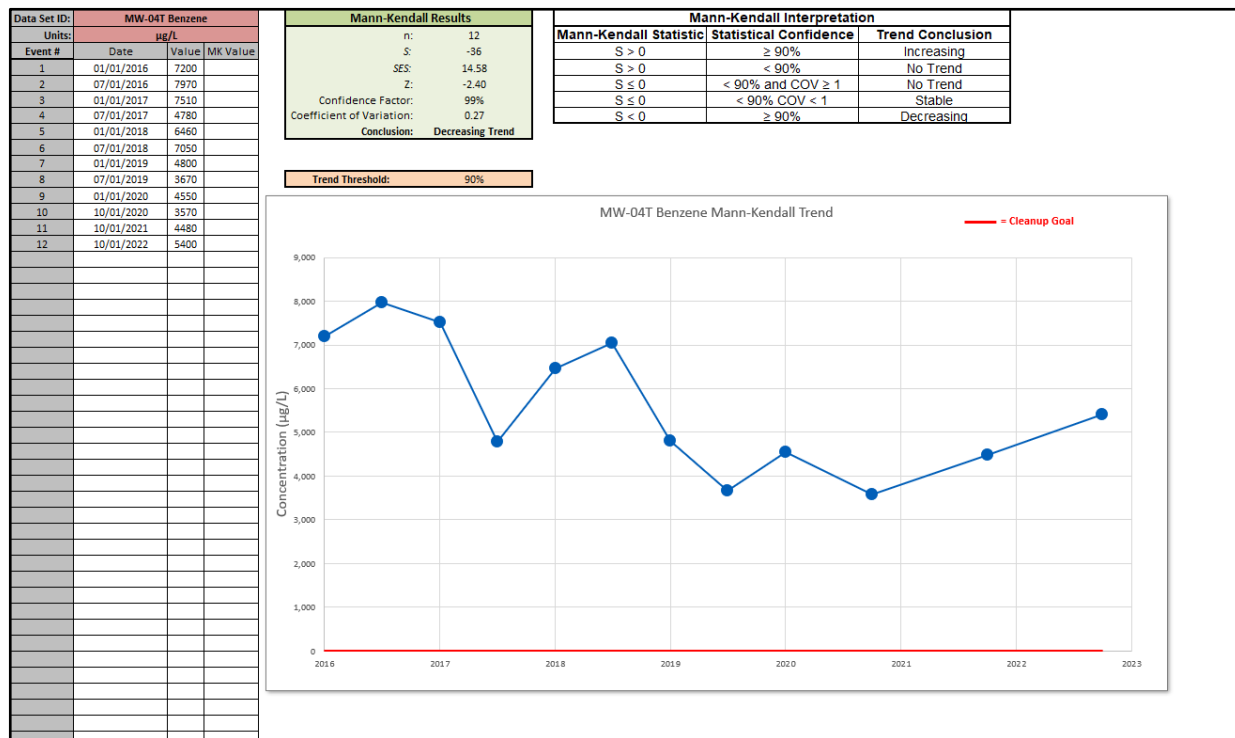
As shown in Figure 4-5, the benzene plume in the B-Zone exhibits strong decreasing trends in all three plume stability metrics. Further, the benzene plume area in the B-Zone decreased from 20.3 acres in 2001 to 8.0 acres in 2022 (61% reduction), the benzene plume mass reduced from 313 to 3.0 pounds (99% reduction) during the same period.

### 4.1.3.2 Temporal Trends in Individual Wells

As noted above, well by well trend analyses were not included in the initial plume stability assessment. However, as part of routine reporting for the site, temporal trends are assessed annually in selected monitoring wells located near source areas and throughout the plume.

The temporal trends were assessed using the WSP Mann-Kendall tool in Excel. Figure 4-6 shows the Mann-Kendall test output for MW-04T for the period of 2016 to 2022. Table 4-1 is a summary of the trend analysis results for each of the wells included in the assessment.

**Figure 4-6: Temporal Trend Assessment Using WSP Mann-Kendall Tool**



**Table 4-1: Summary of Mann-Kendall Trend Analysis Results**

Data Set ID	n	S	SES	Z	Confidence Factor	Coefficient of Variation	Conclusion	Most Recent Value	Units	All Values Below Screening Level	Most Recent Value Below Screening Level
MW-04T Benzene	12	-36	14.58	-2.4	99%	0.27	Decreasing Trend	5400	µg/L	N	N
MW-05T Benzene	10	-5	11.18	-0.36	64%	1.84	No Trend	193	µg/L	N	N
MW-07T Benzene	8	-18	8.08	-2.1	98%	0.47	Decreasing Trend	790	µg/L	N	N
UP-2 Benzene	11	-27	12.85	-2.02	98%	0.88	Decreasing Trend	15.8	µg/L	N	N
CT-2 Benzene	10	-43	11.18	-3.76	>99%	0.74	Decreasing Trend	259	µg/L	N	N
MW-36T Benzene	11	-35	12.85	-2.65	>99%	0.8	Decreasing Trend	4750	µg/L	N	N
MW-8 Benzene	12	14	14.58	0.89	81%	1.84	No Trend	7.6	µg/L	N	N
MW-16 Benzene	11	-49	12.85	-3.74	>99%	0.61	Decreasing Trend	923	µg/L	N	N
MW-01T Benzene	12	5	14.46	0.28	61%	2.4	No Trend	280	µg/L	N	N
MW-06T Benzene	12	-10	14.58	-0.62	73%	1.28	No Trend	1000	µg/L	N	N
P-6R Benzene	12	6	14.58	0.34	63%	0.9	No Trend	670	µg/L	N	N
MW-34R Benzene	11	-11	12.85	-0.78	78%	1.01	No Trend	279	µg/L	N	N

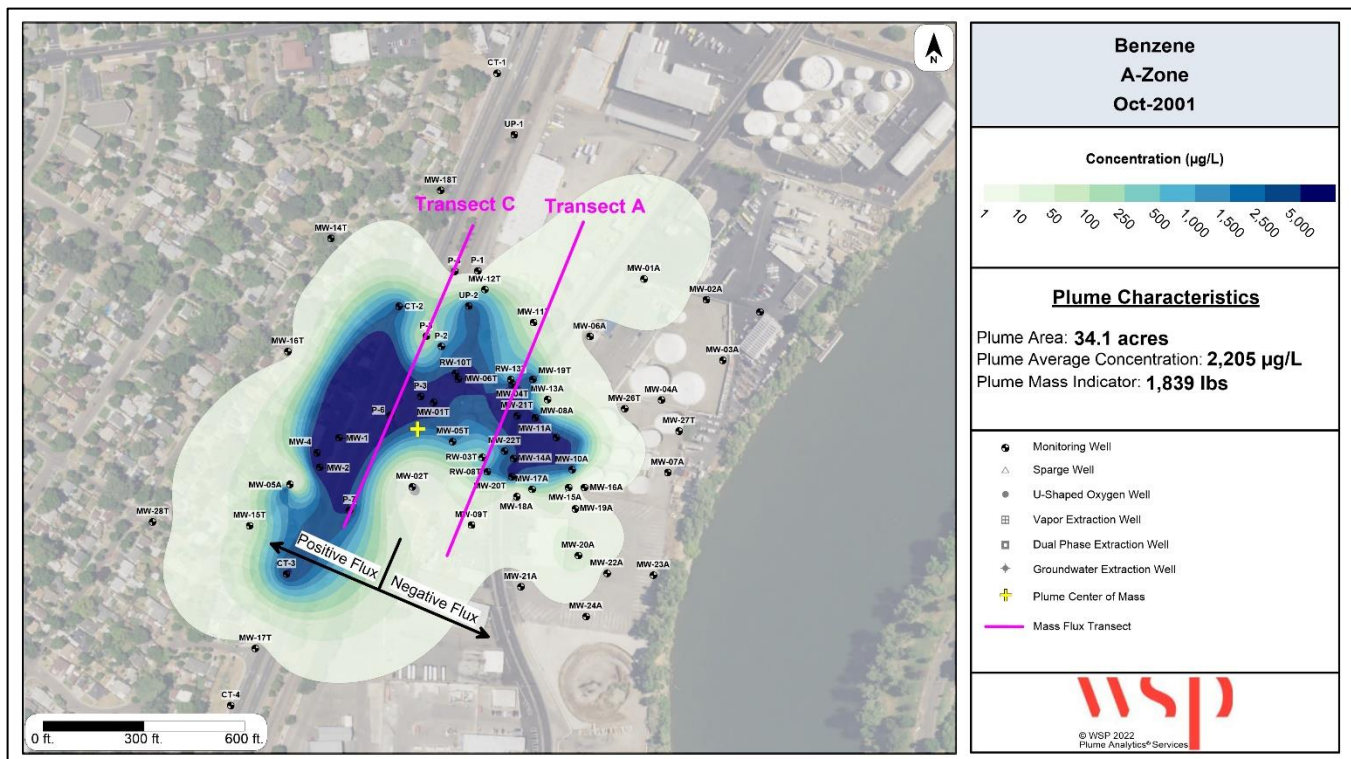
n - number of data points  
 S - sum of comparisons  
 SES - square root of variance  
 Z - Mann-Kendall Statistic



### 4.1.3.3 Mass Flux Analysis

A mass flux analysis in the A-Zone was conducted as part of the initial plume stability assessment in 2019. As defined in ITRC (2010), mass flux combines two key features of a contaminant plume: how much contaminant is in the groundwater and how fast the groundwater is moving through a defined cross-sectional area. In this summary, the term “mass flux” is used to describe mass discharge through a defined cross-sectional area. For the mass flux analysis, two transects were constructed as shown in Figure 4-7. Transect A is generally upgradient closer to the known source area (tank farm) and Transect C is located predominantly downgradient from Transect A to the west.

Figure 4-7: A-Zone Transects

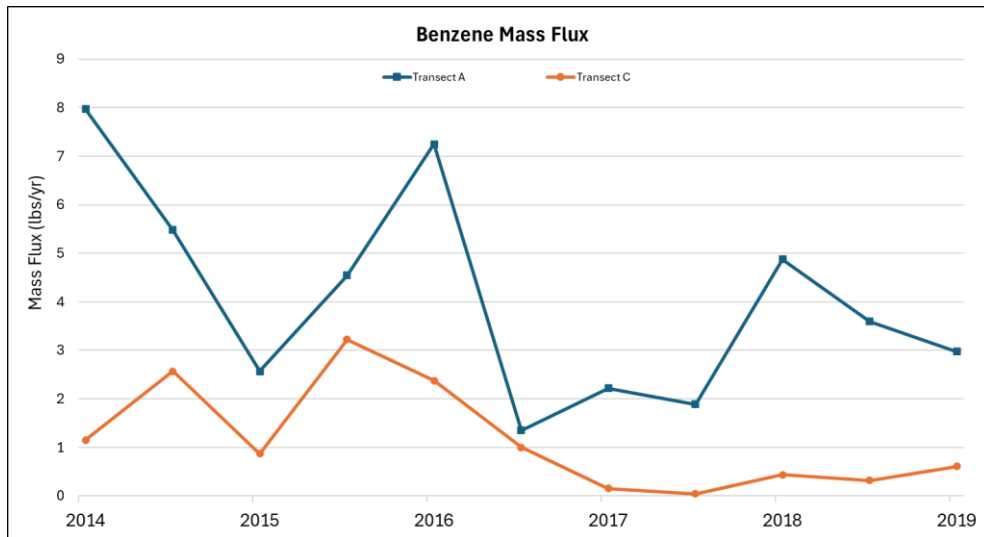


The mass flux for each sampling event was calculated by discretizing the transect line into segments and calculating discrete mass flux values for each segment. The discrete mass flux values are then summed for a net mass flux for each sampling event. Discrete mass flux values are calculated by multiplying a concentration by a groundwater velocity, the plume thickness, and plume segment width at each discrete location along the transect. The width used for each discrete mass flux estimate is based distance between concentration nodes in the contaminant concentration contour. The sum of the segment widths represents the width of the plume at the transect line.

A site-wide average hydraulic conductivity of 1.0 ft/d was used for the mass flux calculations. The hydraulic gradient at each discrete location was determined from groundwater potentiometric surface data for each sample event. The hydraulic gradient used in the calculations is the slope of the groundwater surface at each discrete concentration location along the transect line perpendicular to the transect line. As noted in Figure 4-7, the hydraulic gradient may be positive (indicating flow to the west) or negative (indicating flow to the east).

A summary of the mass flux analysis for Transect A and Transect C is shown in Figure 4-8. As observed in Figure 4-8, the benzene mass flux along Transect A is higher than the mass flux across transect C, indicating that mass is attenuating in the general direction of groundwater flow. It is further observed that the observed mass flux along each transect is decreasing.

**Figure 4-8: Benzene Mass Flux Summary**



#### 4.1.4 Conclusions

The plume stability analysis for the site indicates that the benzene plume exhibits strong decreasing trends in area, average concentration and mass. Multiple remediation systems were idled in 2019 as a result of observed decreasing trends in site COCs. Based on the observed decreasing trends in all COC plumes evaluated in 2019, the monitoring program was revised to change the frequency of sampling from semi-annually to annually. The updated plume stability analysis conducted in 2023 confirmed that the plumes are still attenuating under natural conditions and that annual sampling is adequate for the site.

## 4.2 Chlorinated Solvent Site

### 4.2.1 Background

The conceptual site model for a chlorinated solvent site is a former recycling facility located in Ohio that operated from 1974 to 1980. Following closure of the facility, site investigations determined that facility operations had contaminated the soil beneath the site and groundwater both on- and off-site within the shallow and intermediate horizons of the underlying aquifer. Groundwater beneath the site is typically encountered between 8.0 and 9.0 mbgs. Shallow wells are screened from approximately 9.0 to 15 mbgs; the intermediate wells are set from approximately 15 to 21 mbgs.

A remedy for the site was implemented in the late 1980s that included capping and an extensive on- and off-site groundwater extraction, treatment, and reinjection system. The system, consisting of 25 extraction wells, operated from 1987 through June 2015, at which time the system was shut down as part of a pilot test to evaluate the

efficacy of monitored natural attenuation (MNA) as a final remedial action for the remaining chlorinated volatile organic compound (CVOC) plume. The primary COCs at the site are chlorinated ethenes, with lesser impacts of chlorinated ethanes, chlorinated methanes, and other volatile organic compounds.

The impetus for implementing the MNA pilot test was a comprehensive plume stability assessment conducted in 2014 which suggested that intrinsic processes would be more effective since most of the original dissolved mass in the subsurface had been removed. A subsequent comprehensive plume stability assessment was conducted in 2019 to evaluate the efficacy of natural attenuation as a sole remedy for the site.

This conceptual site model focuses on the 2018 plume stability analysis for chlorinated ethenes at the site, including tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride (VC).

Figure 4-9 shows the site and monitoring well network in 2018.

**Figure 4-9: Chlorinated Volatile Organic Compound Site Well Network**



## 4.2.2 Fate and Transport

COCs for the site consist primarily of CVOCs including chloroethenes (PCE, TCE, and associated breakdown compounds), chloroethanes (1,1,2,2-tetrachloroethane and its associated breakdown compounds), and chloromethanes (carbon tetrachloride and its associated breakdown compounds). Prior to the start of remediation in 1987, the total CVOC plume was approximately 305 m wide, 550 m long, and up to 15 m deep.

The highest groundwater impacts are currently offsite and occupy a much smaller footprint than the original size. Based on the initial plume stability analysis conducted in 2014, engineered remediation at the site resulted in approximately 76% reduction in area and more than 99% reduction in dissolved mass. The current CVOC plume is mostly exhibited by concentrations above cleanup levels in four wells within the main plume which are MW-15, SE-3, SE-6, and SE-7.

## 4.2.3 Plume Stability Analysis

An initial plume stability analysis was conducted in 2014 as part of an effort to evaluate effectiveness of remediation systems and to serve as a basis for cessation of an extraction and treatment system. A subsequent plume stability analysis was conducted in 2018 to evaluate stability of the CVOC plume under natural conditions during the three-year shutdown period. This section discusses the plume stability analysis that was conducted in 2018. The plume stability analysis included temporal trends in individual wells and a whole plume analysis using the Ricker Method®.

Further details of the plume stability analyses are discussed below. Because the site is in Ohio, imperial units are used in the following discussion.

### 4.2.3.1 Temporal Trends in Individual Wells

The remnant CVOC plume at the site is composed mainly of data from four wells. Temporal trends were therefore evaluated in each of the following wells: MW-15, SE-3, SE-6, and SE-7. Table 4-2 shows the trend analysis results for the four key CVOCs in MW-15, as well as the total CVOCs in MW-15 on a molar concentration basis. See Section 1.3 for details on the molar analysis. The trend analyses were conducted using the WSP Mann-Kendall Tool.

**Table 4-2: MW-15 Mann-Kendall Trend Summary**

Data Set ID	n	S	SES	Z	Confidence Factor	Coefficient of Variation	Conclusion	Most Recent Value	Units	All Values Below Screening Level	Most Recent Value Below Screening Level
MW-15 PCE	13	-40	16.33	-2.39	99%	0.46	Decreasing Trend	470	µg/L	N	N
MW-15 TCE	13	-31	16.3	-1.84	97%	0.34	Decreasing Trend	140	µg/L	N	N
MW-15 cis-1,2-DCE	13	37	16.28	2.21	99%	0.48	Increasing Trend	480	µg/L	N	N
MW-15 VC	13	40	16.33	2.39	99%	0.7	Increasing Trend	110	µg/L	N	N
MW-15 Total CVOC	13	-8	16.39	-0.43	67%	0.27	Stable	10.5	µmol/L	N	N

n - number of data points

S - sum of comparisons

SES - square root of variance

Z - Mann-Kendall Statistic

As shown in Table 4-2, decreasing trends are observed for PCE and TCE, and increasing trends are observed for cis-1,2-DCE and VC. This is not an uncommon observation at many CVOC sites and can sometimes lead to misinterpretation of data. For example, observed increasing trends in daughter compounds can sometimes be interpreted as degradation stall, when they may simply be accumulating because the degradation rate of the daughter compound is slower than the degradation rate of the parent compound. One way to assess this phenomenon is evaluate the total CVOC family of compounds on a molar basis. As observed above, the total CVOC trend in MW-15 is stable. Since the total CVOC trend is stable, it would be possible that degradation stall is occurring. That is, based on data from one well, there is evidence of parent compounds decreasing coupled with daughter compounds increasing but no significant change in total concentration. Thus, it appears that parent compounds PCE and TCE are merely breaking down to daughter compounds cis-1,2-DCE and VC. In fact, it was suggested by some project stakeholders that DCE stall was occurring based on the observed increasing trends.

Table 4-3 shows the trend results for the other three wells evaluated.

**Table 4-3: Mann-Kendall Trend Summary for SE-3, SE-6, and SE-7**

Data Set ID	n	S	SES	Z	Confidence Factor	Coefficient of Variation	Conclusion	Most Recent Value	Units	Most Recent Value Below Screening Level
SE-3 PCE	13	-47	16.3	-2.82	>99%	0.21	Decreasing Trend	48	µg/L	N
SE-3 TCE	13	-54	16.33	-3.25	>99%	0.23	Decreasing Trend	18	µg/L	N
SE-3 cis-1,2-DCE	13	-21	16.09	-1.24	89%	0.19	Stable	170	µg/L	N
SE-3 VC	13	-6	16.25	-0.31	62%	0.18	Stable	45	µg/L	N
SE-3 Total CVOC	13	-26	16.39	-1.53	94%	0.16	Decreasing Trend	2.9	µmol/L	--
SE-6 PCE	12	-48	14.58	-3.22	>99%	0.7	Decreasing Trend	110	µg/L	N
SE-6 TCE	12	-52	14.58	-3.5	>99%	0.82	Decreasing Trend	97	µg/L	N
SE-6 cis-1,2-DCE	12	21	14.48	1.38	92%	0.39	Increasing Trend	69	µg/L	N
SE-6 VC	12	10	14.51	0.62	73%	0.64	No Trend	8.7	µg/L	N
SE-6 Total CVOC	12	-26	14.58	-1.71	96%	0.29	Decreasing Trend	2.2	µmol/L	--
SE-7 PCE	13	-61	16.36	-3.67	>99%	0.44	Decreasing Trend	40	µg/L	N
SE-7 TCE	13	-58	16.33	-3.49	>99%	0.41	Decreasing Trend	20	µg/L	N
SE-7 cis-1,2-DCE	13	-32	16.25	-1.91	97%	0.28	Decreasing Trend	34	µg/L	N
SE-7 VC	13	-16	16.39	-0.92	82%	0.48	Stable	1.9	µg/L	Y
SE-7 Total CVOC	13	-46	16.39	-2.75	>99%	0.35	Decreasing Trend	0.77	µmol/L	--

n - number of data points

S - sum of comparisons

SES - square root of variance

Z - Mann-Kendall Statistic

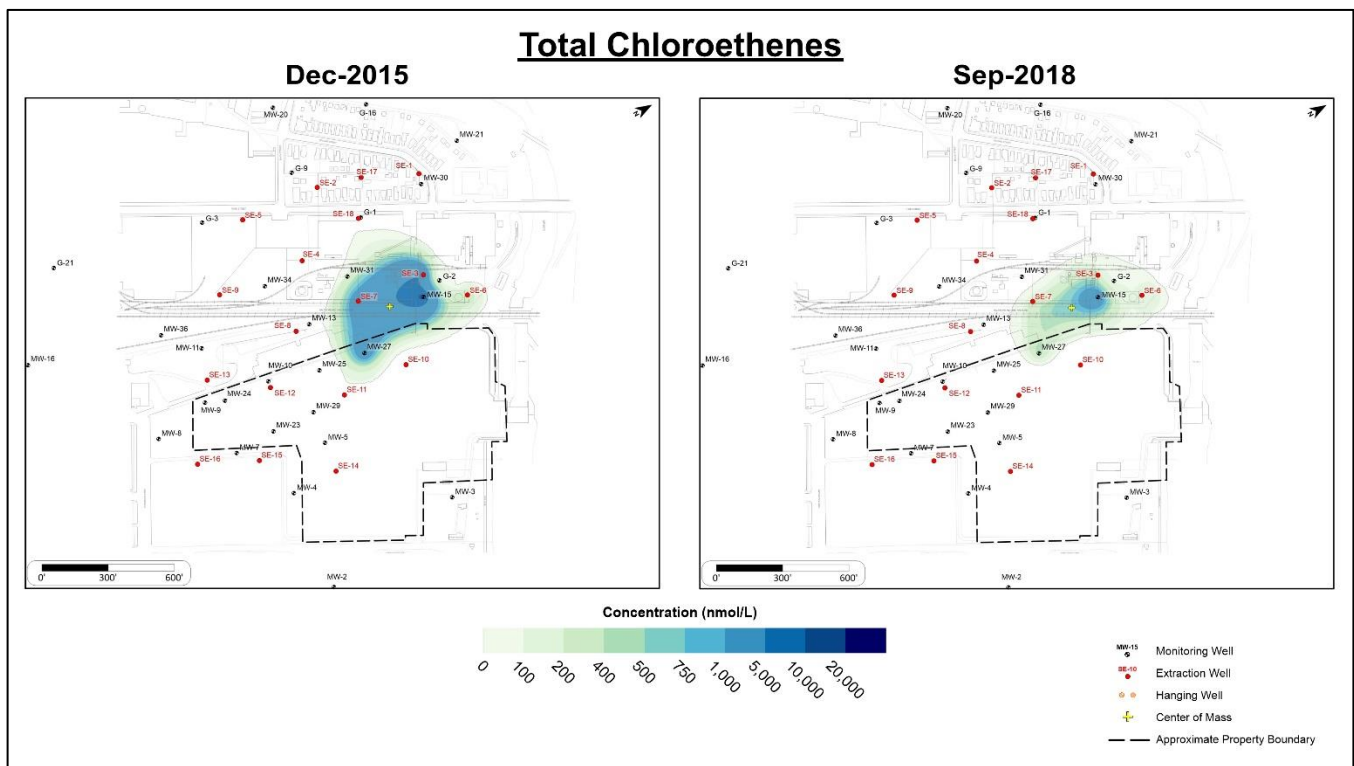
As observed above, SE-6 exhibits an increasing trend for cis-1,2-DCE and no trend for VC. However, the SE-6 total CVOC trend is decreasing. This is an indication that although daughter compounds are accumulating, the degradation is not stalled in SE-6 because there is a net decrease in total CVOCs. SE-3 and SE-7 also exhibit decreasing trends in total CVOCs suggesting that complete degradation is occurring.

Even though three wells exhibit decreasing total CVOC trends, the trend in the highest concentration well (MW-15) is stable. To better assess if the CVOC plume is undergoing complete degradation, plume-based methods that account for total mass within a plume (i.e., control volume) should be employed. Plume mass-based methods are more accurate because they allow an analysis to be conducted within a control volume, thereby allowing for a mass-balance approach.

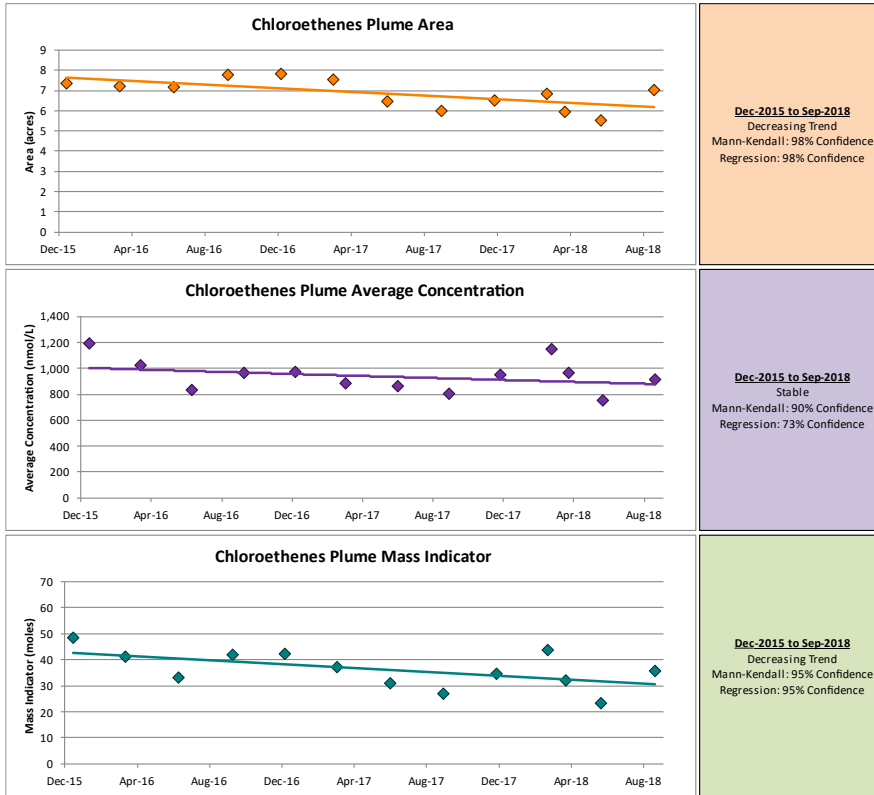
### 4.2.3.2 Ricker Method Analysis

A Ricker Method plume stability analysis was also conducted to evaluate CVOC plume behaviour during the MNA pilot test. Although the analysis was conducted for all CVOCs, this conceptual site model focuses on the total chloroethenes plume (including PCE, TCE, cis-1,2-DCE, and VC), which is historically the largest plume at the site in both concentration and areal extent. The plume stability analysis was conducted for individual chloroethene compounds, as well as for the total chloroethenes plume. Figure 4-10 shows the chloroethenes plume at the start and end of the MNA pilot test, and Figure 4-11 shows the trends in each of the plume stability metrics for the total chloroethenes plume. As observed in Figure 4-11, the trends in total chloroethenes plume area and mass indicator are decreasing and the average concentration is stable.

Figure 4-10: Total Chloroethenes 2015 vs. 2018

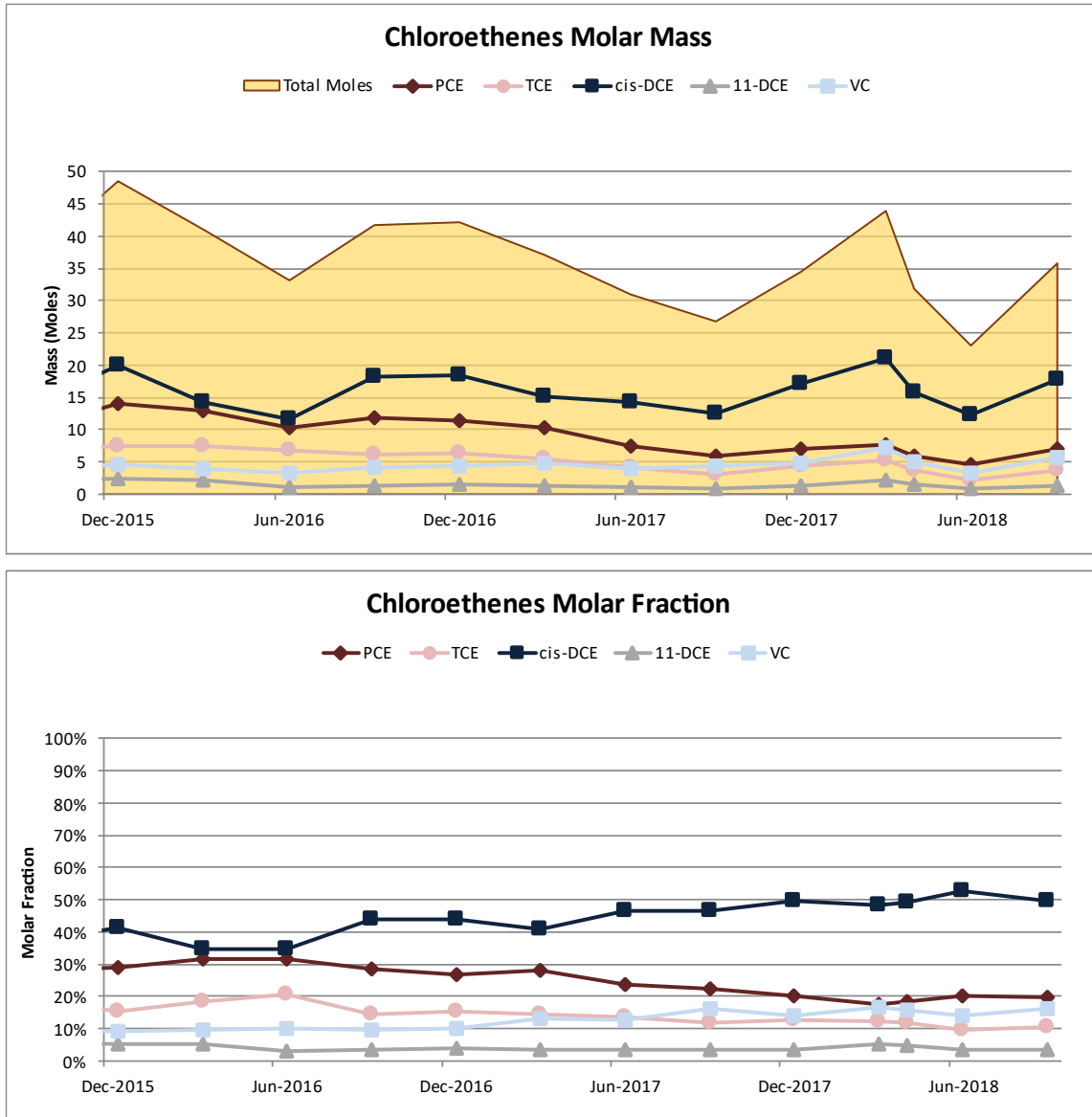


**Figure 4-11: Chloroethenes Ricker Method Plume Stability Trends**



The total chloroethene plume molar mass was calculated by summing the molar mass for each individual chloroethene contaminant plume. Figure 4-12 below shows the total chloroethenes plume molar mass trend, including the relative molar mass of each chloroethene contaminant plume, as well as the molar fraction of each constituent.

**Figure 4-12: Total Chloroethenes Plume Mass Trends**



As observed in Figure 4-11 and Figure 4-12 the total chloroethenes plume mass is decreasing. Moreover, it appears that the parent compounds PCE and TCE are decreasing and the daughter compounds cis-1,2-DCE and VC are stable. Table 4-4 shows the trend analysis results for the molar mass of each of the chloroethene contaminant plumes using the WSP Mann-Kendall Tool.



**Table 4-4: Trend Analysis Summary for Chloroethene Plumes**

Data Set ID	n	S	SES	Z	Confidence Factor	Coefficient of Variation	Conclusion	Units
Total Chloroethenes	13	-28	16.39	-1.65	95%	0.2	Decreasing Trend	moles
PCE	13	-56	16.39	-3.36	>99%	0.3	Decreasing Trend	moles
TCE	13	-58	16.39	-3.48	>99%	0.3	Decreasing Trend	moles
cis-1,2-DCE	13	-2	16.39	-0.06	52%	0.17	Stable	moles
VC	13	24	16.39	1.4	92%	0.23	Increasing Trend	moles

n - number of data points

S - sum of comparisons

SES - square root of variance

Z - Mann-Kendall Statistic

Statistical trend analysis summarized in Table 4-4 reveals that the cis-1,2-DCE plume mass is stable, and the VC plume is increasing in mass. However, because the total chloroethene plume mass is decreasing, there is unequivocal evidence that biodegradation is not stalled. The observed trends in molar fractions in Figure 4-12 provide further evidence that biodegradation is occurring. That is, as the molar mass is decreasing, the fractions of parent compounds are decreasing, and the fractions of daughter compounds are increasing.

#### 4.2.4 Conclusions

The plume stability analysis for the site indicated that natural biodegradation is occurring even three years after cessation of the extraction and treatment system. Whereas the plume stability analysis using trends in individual wells suggested that the plume was decreasing, the Ricker Method plume stability analysis provided unequivocal evidence that natural biodegradation is occurring and supports MNA as a remedy for the Site.

## 5.0 CONSIDERATIONS FOR SITES IN BRITISH COLUMBIA

There are several factors specific to BC that may affect plume stability assessments which practitioners should be aware of. These include common industry practices pertaining to delineation, hydrological effects including freshet (i.e., spring runoff), large precipitation events, and monitoring considerations for tidally influenced sites. These factors are discussed below.

### 5.1 Delineation Practices

Groundwater delineation practices vary from site to site and by practitioner, and this will strongly affect the type of plume stability analysis which is practical at a site. For example, a common practice in BC is to delineate a groundwater plume along its perimeter, as opposed to a coordinate-based approach where monitoring locations are installed in a two-dimensional grid with equidistant spacing. Although a plume perimeter delineation approach may minimize the potential for cross-contamination and unintended creation of subsurface vertical migration pathways in the source zone, it also limits the spatial extent of data being collected (Section 2.1). This type of approach will result in less data being available from the source zone and along the areal extent of the plume, and as a result, the estimation of total contaminant mass over the areal footprint of the plume may be less accurate. In such instances, the plume-based methods may be less suitable, and other plume stability analysis methods (i.e., well-by-well analysis or mass flux estimation) will be more appropriate. In these instances, the practitioner must be cautious of uncertainty in the overall plume stability assessment imposed by the limited dataset.

### 5.2 Tidal Influences

Many contaminated sites in BC are affected by tides, either through direct hydraulic connection to the ocean, or via hydraulic connection to a freshwater body which is affected by tides.

A typical convention for groundwater sampling at tidal sites is to collect samples at or shortly after low tide, when the instantaneous local hydraulic gradient towards the receptor (i.e., water body) is presumed to be at its maximum. Different conventions may apply elsewhere due to practical limitations or site-specific knowledge regarding groundwater flow; however, for the purposes of plume stability monitoring, it is recommended that recurring groundwater sampling efforts always be conducted at the same point in the tidal cycle (e.g., low tide), and ideally at a similar stage (i.e., forecasted tidal height).

At many contaminated sites affected by tides, the hydraulic gradient or direction of groundwater flow may vary at different points in the tidal cycle. In such cases, the effects of dispersion relative to advection are generally amplified, and horizontal (i.e., transverse) plume migration may become more prevalent.

Tidal effects on plume migration in groundwater should be monitored using a network of monitoring wells equipped with transducers for the collection of continuous hydraulic head measurements.

To estimate the hydraulic gradient and direction of groundwater flow at a tidal site, the barometrically compensated hydraulic head dataset must be averaged across the tidal cycle. Serfes (1991) offers a tidal averaging method whereby average hydraulic heads (over 72-hour periods) are estimated using a series of moving averages calculated from the continuous hydraulic head measurements. Although 72 hours of data is the minimum duration required for tidal averaging, longer datasets (if not continuous monitoring), are recommended.

### 5.3 Hydrological Effects

Due to accumulation of snow at high elevations during the winter months, many rivers in BC experience a strong freshet, whereby flow observed during spring runoff may be up to an order of magnitude greater than that observed at baseflow.

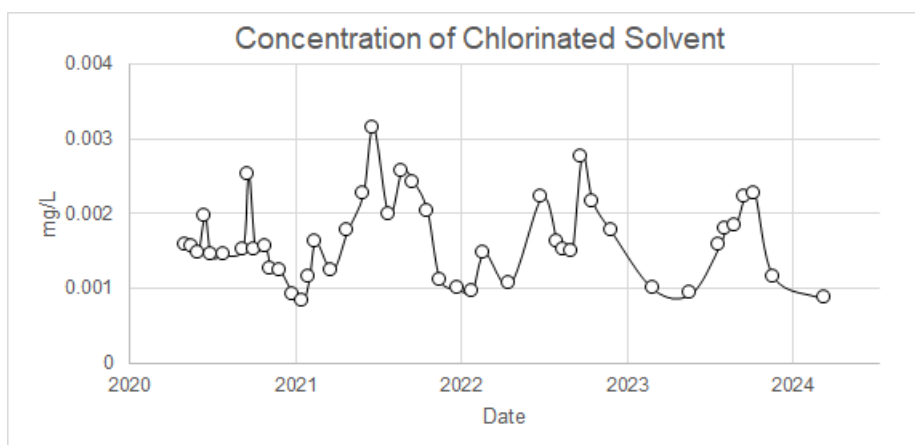
In aquifers which are hydraulically connected to freshet-affected rivers, these changes constitute a dominant seasonal effect which can transform the groundwater flow regime. Freshet-induced changes to hydraulic heads in an aquifer may drastically affect the dominant transport mechanism (i.e., advection/dispersion vs. diffusion).

As groundwater levels rise in unison with a river during freshet, the ambient hydraulic gradient mobilizing mass away from the source zone via advection may weaken significantly, reach zero (i.e., flat gradient), or turn negative (i.e., flow direction reversal). Conversely, freshet may also lead to aquifer recharge and a resulting increase in advection.

If the hydraulic gradient across the site approaches zero, advective transport may become temporarily subdued. At sites with dense non-aqueous phase liquid contamination in underlying aquitards, this may result in diffusion temporarily becoming the dominant transport mechanism (Section 2.1), because contamination back-diffuses upwards in the aquifer, resulting in increased dissolved contaminant concentrations in the short term. During abnormally strong or extended freshets, these effects can be pronounced.

At sites where changes to the dominant transport mechanisms are observed on an annually recurring basis, practitioners must plan monitoring efforts to coincide with anticipated annual maximum concentrations, which may be associated with back-diffusion events. By adequately capturing and characterizing this variability, plume stability analysis can still be successfully conducted. For example, Figure 5-1 provides an example of chlorinated solvent concentrations at a dense non-aqueous phase liquid site which experiences back-diffusion events in the months following freshet. Despite there being strong variability in the observed concentrations each year, the annual maximum concentrations have been observed to be decreasing. Although a trend analysis using the complete dataset may result in a “no trend” output, a similar approach using only the annual maximum concentrations observed would likely result in a “decreasing trend” output (Section 3.2.1).

**Figure 5-1: Concentration of Chlorinated Solvent Following Annual Back-Diffusion Events**

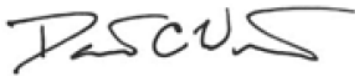


Through continuous monitoring of hydraulic heads using a network of transducers, changes in the groundwater flow regime at a site can be monitored, and the potential effects on contaminant transport can be predicted and iteratively assessed.

## 6.0 CLOSURE

We trust this information is sufficient for your needs at this this time. Should you have any questions or concerns, please do not hesitate to contact the undersigned

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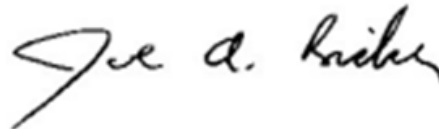


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