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Assessment of Plume Stability in Monitored Natural Attenuation Assessments Using the Center of Mass and Total Plume Mass Approach

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ABSTRACT: Monitored natural attenuation (MNA) is becoming a commonly employed sustainable site remediation strategy for sites with petroleum hydrocarbon groundwater impacts. Natural attenuation is essentially the reduction in contaminant concentration, mass or mobility due to naturally occurring processes within the environment. Aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are common compounds of concern in the context of petroleum hydrocarbon related investigations because of their relative mobility and toxicity characteristics. Despite this, these compounds have historically displayed a strong affinity towards attenuating temporally and spatially away from the source areas. Evaluating plume stability is an important element of evaluating the overall attenuation of groundwater plumes and numerous methods have been developed in order to assess plume stability including graphical and statistical methods. It is often the case however that these analyses focus on single wells in isolation and do not take an integrated approach to evaluate the attenuation of contaminant mass over the entire plume. The authors present a case study where historical trends in plume characteristics have been used to assess overall plume stability. Trends in parameters such as average plume concentration, total plume contaminant mass, plume area and plume center of mass were statistically assessed to determine whether the groundwater plume was expanding, stable, or shrinking. The methods employed in the plume stability analysis were found to be effective tools in demonstrating the occurrence of natural attenuation of contaminant plumes. It is important to note that a good quality dataset is required, in terms of a spatially representative monitoring well network and adequate time series data, in order to conduct analyses that will yield meaningful conclusions.

INTRODUCTION

Natural attenuation (NA) describes the naturally occurring biological and physio-chemical processes that are responsible for the reduction in concentration or mass of contaminants within a particular groundwater bearing unit, or aquifer. Over the past two decades NA has become accepted as a viable cost-effective alternative (under favorable conditions) to sustainably manage the risks posed by groundwater contamination. NA has the potential to greatly reduce contaminant clean-up costs if employed as part of a robust and defensible risk-based approach. As part of the risk-based approach, three main criteria are typically applied to determine the acceptability of NA as a sustainable alternative, these are:

1. The occurrence of NA processes must be demonstrated to an acceptable level of confidence, and these processes can be confidently predicted to meet the remedial objectives within a reasonable timeframe;
2. The intended land uses must not adversely affect the NA processes in the longer term; and
3. Identified receptors will be protected in the short and long term and the risk profile of the plume will remain constant in terms of there being minimal expansion of the plume.

A monitored natural attenuation (MNA) strategy will typically consist of a *screening level* stage, which is focused on determining the overall viability of NA in comparison to other alternatives being considered. This is followed by a *demonstration and assessment* stage which is aimed at providing scientifically defensible evidence to support the implementation of the MNA strategy. Should the assessment confirm the effectiveness of the NA processes, this may then be followed by the *implementation* stage which typically entails a long-term monitoring strategy to demonstrate that the defined remedial objectives are achieved.

MATERIALS AND METHODS

Evaluating plume stability is an important element of the *demonstration and assessment* stage and the *implementation* stage of the MNA strategy. Numerous methods have been developed in order to assess plume stability including graphical methods such as concentration isopleth maps, plotting contaminant concentration vs. distance for several monitoring wells along a flow path, and plotting contaminant concentration vs time for individual monitoring wells (Wiedemeier et al., 2000). Whilst the comparison of concentration isopleth maps over time may provide a visually compelling case for plume stability, the apparent plume size changes over time may not necessarily provide a quantitative assessment of plume mass stability and attenuation.

Other stability assessment methods include statistical evaluations such as regression analysis, Mann-Kendall analysis and the Mann-Whitney U-test. These methods are commonly employed on individual wells in order to determine stability; however individual wells may display varying trends (i.e., increasing, decreasing, no trend) across a plume which may make a plume-wide assessment problematic. Individual well trend analyses are also dependant on the number wells present as well as their location and may bias the overall stability determination in a fashion that is inconsistent with the overall plume movement/behaviour. The total mass and center of mass approaches aim to conduct the assessment of trends on a plume-wide scale in terms of average concentration, average mass and overall plume area, and provide a more integrated approach to determining plume stability as opposed to single point locations within the plume. The total mass and center of mass approach outlined in this paper has been described in detail elsewhere (Ricker, 2008), and a brief summary of the approach is provided below.

For a given site, concentration isopleth maps are generated for a selected compound of potential concern (COPC) for multiple sampling events spanning the lifetime of the monitoring programme. Interpolation and visualisation software (in the case of this paper, Golden Software Surfer®) is then used to calculate the overall plume area, average concentration and plume mass for the selected COPC over the various sampling events. These values can then be statistically assessed to demonstrate whether a plume is expanding/stable/shrinking. In addition to this, the plume center of mass (COM) is also calculated for each sampling event. As a plume expands, the COM will typically move in a down-gradient direction, whilst the COM of a stable plume should be spatially stable. An assessment of the plume COM can thus provide an additional line of evidence of a plume's stability.

Site Description. The subject site for this assessment is a large operating manufacturing facility in Cape Town, South Africa. The site is underlain by loose, moderately well-sorted, medium-to-fine grained Quaternary sediments (sand) of the Sandveld Group down to a depth of 6 m below ground level. This is in turn underlain by a residual clay horizon, representing the weathered bedrock of the regional Malmesbury Group shale. Groundwater levels range between 1 m and 2 m below ground level and groundwater flow was estimated to be in a westerly direction. The Sandveld Group sand unit is considered to be the target aquifer under consideration whilst the clay of the weathered Malmesbury Group forms a regional aquitard. A site diagram is shown in FIGURE 1.

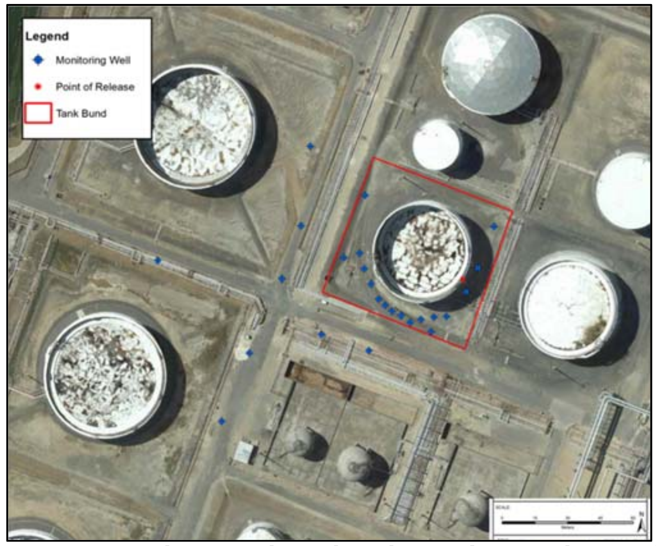

FIGURE 1. Site location showing spill location and surrounds.

In January 2011 a large surface spill of gasoline occurred within one of the storage tank farms due to a faulty pipe flange. Subsequent to the spill, a site investigation programme was initiated which included plume delineation through monitoring well installation, product recovery, well installation and passive skimming, and groundwater monitoring of the plume and surrounding area. Following cessation of product recovery in September 2012, an MNA programme was commenced with bi-annual monitoring of wells within the plume core, the down-gradient portion of the plume and in sentinel wells surrounding the plume to assess for plume stability.

RESULTS AND DISCUSSION

As part of the stability analysis, a COPC was selected as an indicator compound. Due to the product type (gasoline), benzene was selected as the indicator compound as it is typically the primary risk driver for gasoline releases due to its relative toxicity and mobility. Benzene concentration isopleth maps were generated for biannual sampling of the monitoring well network from 2013 through to the end of 2016, and were delineated to a concentration of 3.5 µg/L (the laboratory LOD) which for the purposes of the assessment was considered to be the plume boundary. Wells which yielded

FIGURE 2. Site concentration isopleths for the April 2013 event.

concentrations below detection limits were assigned a value of 1.75 µg/L (0.5*LOD) for interpolation purposes. Grid files were generated based upon well coordinate data (X and Y values) and benzene concentration data (Z values), and isopleth maps were generated from the grid file outputs. FIGURE 2 displays the post recovery monitoring phase contour isopleth maps of the April 2013 sampling event (although isopleth maps were generated for biannual events from 2013 through 2016 for the plume stability calculations).

Plume Area and Mass Calculations. Following the generation of the grid files, the plume average concentration, plume mass and plume area were calculated for each sampling event. The respective isopleth maps were generated as three-dimensional surfaces within Surfer (as shown in FIGURE 3) and the grid volume function within Surfer was used to calculate the planar area of the surface after having set the lower surface threshold to 3.5 µg/L (i.e., the plume boundary). The grid volume function also provided the positive grid volume from the 3.5 µg/L "cut" up to the maximum concentrations. The grid volume with units of $\mu g/L \cdot m^2$ would then be divided by the planar area to calculate the average plume concentration. Since the calculated concentration is the average concentration above the 3.5 µg/L plume boundary, this value would be added to the average concentration to yield the actual average concentration. The calculations described above are summarised in Table 1.

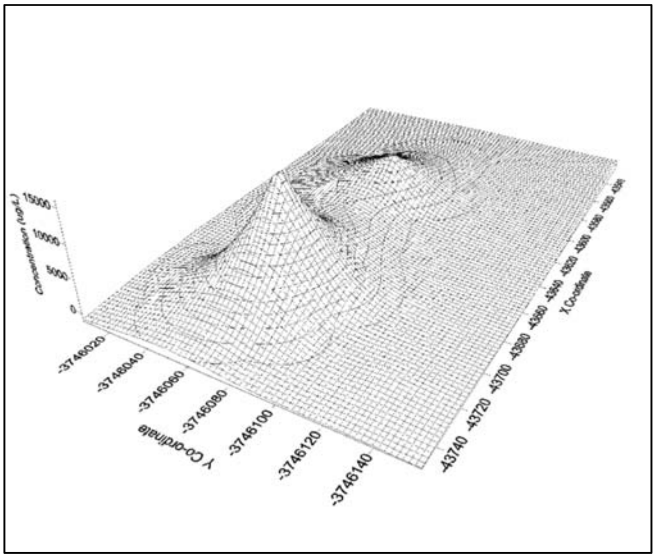

FIGURE 3. Wireframe three-dimensional surface of the April 2013 sampling event data.

TABLE 1. Summary of benzene plume characteristics.

Sample Event (Month-Yr)	Plume Area (m^2)	Average Concentration (µg/L)	Actual Average Concentration (µg/L)	Plume Mass (kg)
Apr-2013	26,131	2,821	2,825	110
Oct-2013	25,969	2,691	2,695	104
Apr-2014	26,279	1,578	1,582	62
Oct-2014	26,152	1,971	1,975	77
Apr-2015	11,894	599	602	11
Oct-2015	9,188	861	865	12
Oct-2016	6,521	300	304	3

Following calculation of the average plumes concentrations, site specific data for aquifer thickness (observed to be 5 m from soil logging observations) and assumed values for effective porosities (30%, based upon literature values) were used to estimate plume mass. As noted by Ricker (2008), the mass calculations may not provide truly accurate estimates of actual mass, however the method provides a means to combine area and concentration related variables into a single mass based variable whose relative changes over time provide meaningful insights into the stability of the plume. The mass values are summarised in Table 1. The time series for the calculated values for average concentration, plume mass and planar area were plotted in Figures 4, 5 and 6. From the figures, a clear decreasing trend is notable (i.e. plume attenuation is occurring).

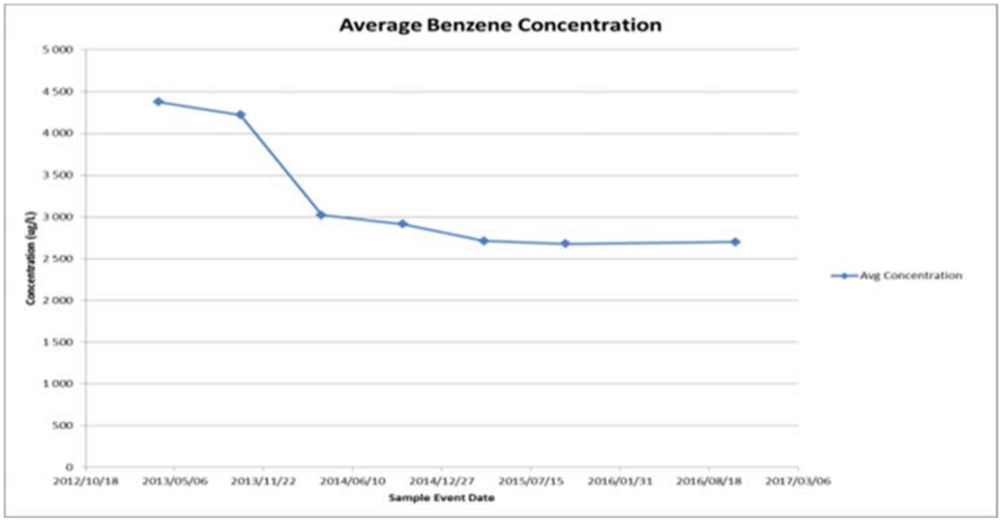

FIGURE 4. Time series data for the average benzene concentration from 2013 to 2016.

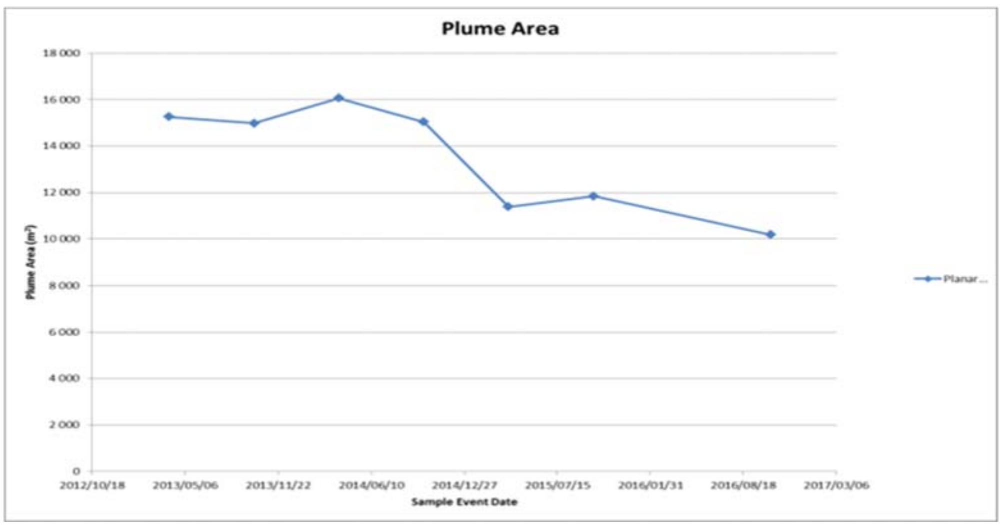

FIGURE 5. Time series data for the benzene plume planar area from 2013 to 2016.

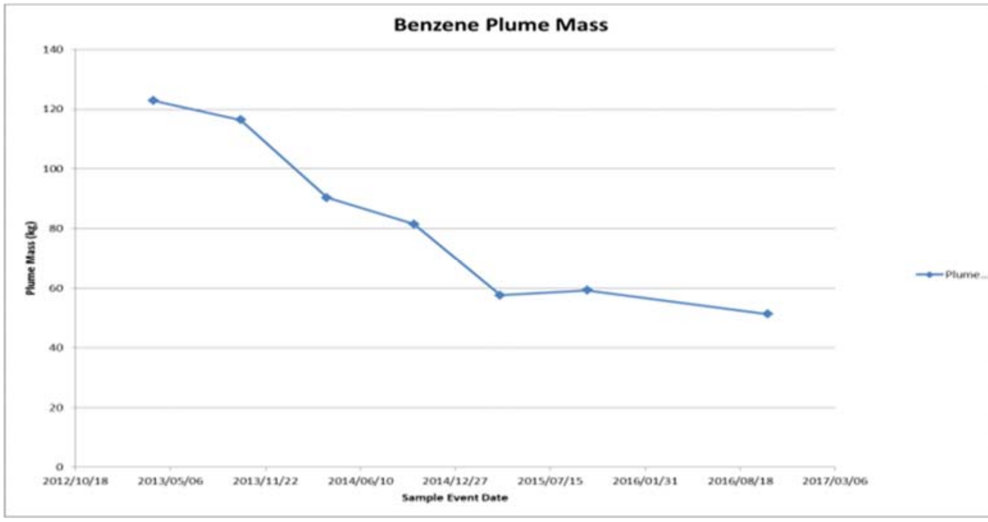

FIGURE 6. Time series data for the benzene plume mass from 2013 to 2016.

Statistical Analysis. In order to provide a more quantitative assessment of the plume trend data, a linear regression trend analysis using a 95% confidence level was performed using Microsoft® Excel as per US EPA (1992) guidelines:

- No trend is discernible when the calculated confidence level of the regression line slope contains 0; or
- A significantly increasing or decreasing trend can be concluded when the calculated confidence level of the regression line slope contains only positive values (increasing trend) or negative values (decreasing trend).

The regression analysis results are summarised in TABLE 2 and in all three cases, a decreasing trend was confirmed. Based upon the plume concentration, area and mass analysis, it is evident that at the very least, the plume is stable, and that appreciable natural attenuation is most likely occurring within the plume.

TABLE 2. Linear regression trend analysis.

Parameter	R^2	Regression Line Slope	95% Lower Confidence Limit	95% Upper Confidence Limit	Trend Analysis Conclusion
Concentration	0.69	-1.3	-2.44	-0.32	Decreasing
Mass	0.88	-0.06	-0.08	-0.04	Decreasing
Area	0.77	-4.6	-7.47	-1.72	Decreasing

Plume Center of Mass Calculations. The plume center of mass (COM) is essentially the geometric center (or centroid) of the plume as defined by the generated grid files. Where sufficient time series data exists, plotting the COM can provide insights into the general stability of the plume under consideration. In the case of an expanding plume, the COM will generally migrate in a down-gradient direction; a stable plume would generally display a stable COM while a shrinking plume would display a receding COM back towards the original source area. In order to calculate the center of mass the grid file must be filtered to remove all node points with concentrations (Z values) less than the defined plume boundary concentration (i.e., 3.5 µg/L). The center of mass X (and Y) co-ordinate is then calculated from the remaining grid nodes, and is the weighted average of the respective X (or Y) coordinate using the interpolated concentration value (Z value) at that grid node as the weighting factor:

Center of mass X co-ordinate, $\mathrm{X} = \frac{\sum_{1}^{n} \mathrm{X} \times \mathrm{Z}}{\sum_{1}^{n} \mathrm{Z}}$

Center of mass Y co-ordinate, $\mathrm{Y} = \frac{\sum_{1}^{n} \mathrm{Y} \times \mathrm{Z}}{\sum_{1}^{n} \mathrm{Z}}$

The center of mass coordinates are then plotted on a site map and an assessment of the stability of the plume center of mass can be made. The calculated plume center of mass points for the site are plotted on FIGURE 7. From the image it can be seen that the plume COM has remained relatively stable over the monitoring period from 2013 to 2016. These observations coupled with the plume mass calculations provide strong evidence that the plume is shrinking or at the very least is stable.

FIGURE 7. Plume center of mass movement from 2013 to 2016.

CONCLUSIONS

The total plume mass and center of mass approaches described in this paper have provided strong evidence that natural attenuation is occurring within the plume under consideration and that the plume is in a stable state or possible shrinking state. In terms of the overall MNA strategy and the required criteria, the decreasing trends observed through the methods are useful in demonstrating that NA processes are occurring and that further expansion of the plume is unlikely. The generated data supports the notion that an MNA strategy is an appropriate and sustainable approach to employ within the site-specific context in order to bring the site to closure in a risk-based manner.

It should be noted that the method may not be applicable in complex hydrogeological settings such as fractured bedrock, and relies on the monitoring well network providing sufficient coverage of the plume in order for the interpolation calculations to provide meaningful approximations in terms of contaminant mass distribution across the plume under consideration.

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