University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
May 2015

Analysis of Air Sparging of Contaminated Springs on Trichloroethene and Cis-1,2-Dichloroethene Content in Surface Streams.

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Abstract

Trichloroethene (TCE) and its degradation product (via microbial action) cis-1,2-dichloroethene (DCE) are contaminants found at the CTS of Asheville, Inc, a former electroplating facility. Due to high levels of the contaminants, the site became an Environmental Protection Agency (EPA) superfund site. Contamination is also found at property neighboring CTS of Asheville and an air sparging system was installed in 2014 to reduce TCE air levels. For this study, stream samples were collected and analyzed for TCE and DCE using Gas Chromatography Mass Spectrometry from the property adjacent to the superfund site for a span of 2 years (prior to, during and after the air sparging system installation). TCE and DCE contamination concentration and volatilization rates downstream were determined. During system installation, TCE contamination in the stream decreased to less than a third of prior values and DCE increased by about a factor of 3. The combined amount of TCE and DCE remained the same, indicating that the contamination remained constant but TCE had degraded more readily into DCE during installation. After system installation was completed, the TCE concentration began increasing and DCE concentration decreasing.

1. Introduction

TCE (trichloroethene), a colorless, odorless liquid used as a solvent for metal degreasing is the most common contaminant in groundwater in the US.[1, 2, 3, 4, 5, 6] TCE's widespread use and inadequate disposal from medical, industry, military and general public uses make it one of the most common contaminants listed by the EPA (Environmental Protection Agency).[7] TCE is found dissolved in water but quickly volatilizes from surface water and can often be detected in the air. When exposed to UV radiation, TCE can be photo-oxidized and completely mineralized into trichloroethanol, trichloroacetic acid, dichloracetic acid, and carbon dioxide using oxygen from the air as the oxidant.[3,4,8] Under anaerobic conditions it degrades into other toxic chemicals such as DCE (cis-1,2-dichloroethene) and VC (vinyl chloride).[4] DCE and VC can be monitored to evaluate TCE degradation. DCE and VC both volatilize at a faster rate than TCE.[6] Exposure to TCE through the air, water, and food can cause impaired heart function, unconsciousness, central nervous system depression, hepatotoxicity and nephrotoxicity.[5] Recent studies indicate its potential carcinogenic effects.[4] It has been termed a likely carcinogen by EPA and a probable carcinogen by WHO (World Health Organization).[9] The negative effects, and especially the danger of carcinogenic effects of TCE create an immediate need for remediation. Many current technologies are labor and financial intensive and therefore are not feasible for large-scale cleanup.

The site of research, called the Adjacent Property, is neighboring an EPA superfund site. The superfund site is the property of the company CTS of Asheville, Inc., a former electronics components manufacturer off Mills Gap Road in Asheville, N.C.[10] The EPA deemed this site hazardous because the levels of TCE in the water greatly exceed the 5ppb allowed for drinking water.[7] It was discovered in the 1990s that the soil and water in the areas surrounding the plant are contaminated with TCE.[10] Preliminary remediation of the site, neighboring the CTS superfund site, included a soil vapor extraction system through a process that involves mechanized machines to aerate the soil and release TCE into the atmosphere.[10] TCE levels in the shallow soils did decrease due to this method however TCE is a dense non aqueous phase liquid more dense than water so most of the contaminant percolated into deep soil below the water table and onto the bedrock.[11] Measurements at the most concentrated source are 1.2 million ppb, almost pure TCE.[9]

Due to trespassing restrictions, the CTS site itself cannot be used in this research but the Adjacent Property adjacent to the site will be used with permission from the landowners. The Adjacent property, shown in Figure 1, is down slope from the CTS site and has an area where springs come out of the ground. This area is fenced in because TCE contamination was found in the springs. There is also a stream that flows out of the fence from the springs that is also contaminated.

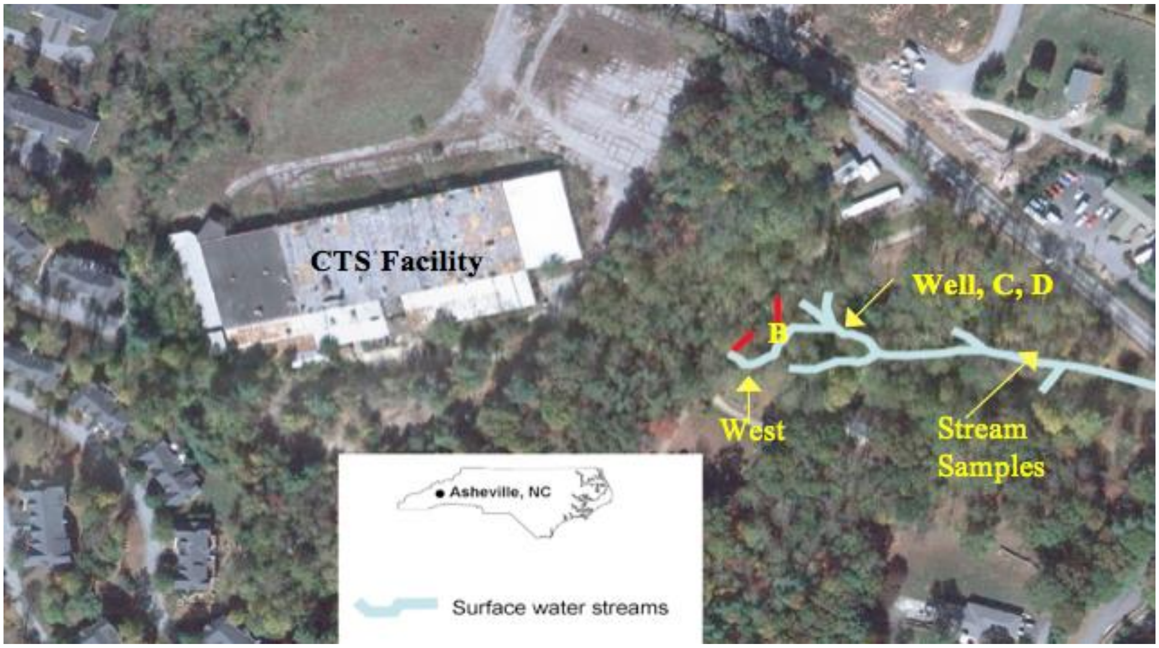

Figure 1. Arial view of the CTS site and adjacent property.

Preliminary research done by Jeffrey Wilcox of UNC Asheville at the Adjacent Property indicated that the water flowing from the CTS site onto the Adjacent Property fenced in area has TCE concentrations of 15,000-21,000ppb. Tree core samples were also taken from about 80 year old poplars in different locations on the Adjacent Property and TCE was detected in 16 of the 31 trees tested by a tree-coring sampling method. The trees located near the streams contaminated with TCE were the ones that had detections for TCE. The tree coring sampling method involves allowing the plant tissues to come to equilibrium in a solution of pure water in order to inject the aqueous sample. [9]

Research conducted by Georgia Tryon working on the Adjacent Property showed that the geochemistry of the streams within a two-mile radius is variable. The orange colored sediment on the site was analyzed and the metals in question (Pb, Cr, and Cu) were not significantly higher than literature and EPA standards.[12]

Although the springs and streams are known to be contaminated, families continue to live on the Adjacent Property. TCE levels in the air were sampled by EPA in 2014 and found to be higher than safe for humans so the families next to the fenced stream were relocated off site.

There are several options for reducing TCE and DCE contamination at both the contamination source and the springs down slope subsequently cleaning the air near the springs on the Adjacent Property. The widespread method is the pump-and-treat technology, which ranges from decades to centuries for expected treatment time. Methods include pumping the water to the surface where it can be treated atmospherically, by chemical or microbial attack or sorbed into activated carbon.[4] When treated atmospherically, the contaminated water is allowed to aerate because exposure to ultraviolet radiation causes photo-oxidation using oxygen from the air, completely mineralizing TCE.[8] Chemical and microbial attack involves adding solutions of chemicals or microbes in order to allow degradation of TCE. Generally the mechanism for chemical attack is using photo catalysis with oxygenated chemicals.[4,8] In an experiment conducted by Maria et al., titanium dioxide was used as a chemical oxidizing agent of TCE and a maximum particle size of 7nm was found to be successful in degradation of TCE.[8] When being sorbed into activated carbon, the contaminant is absorbed by the carbon through its small pores.[4] Some methods require toxic chemicals, which can create chemical contamination.

Phytoremediation is a proposed solution for cleaning contaminated sites. It involves using plants that accumulate the contaminant within their tissues and then metabolize the contaminant into benign byproducts. Hybrid poplars, a tree indigenous to North America, have been extensively researched to be accumulators of TCE.[1,4,13,14] Trees and other shrubs prove to be good phytoremediators of TCE because they uptake the contaminant from ground water and soil and transpire the contaminant, ultimately releasing it into the atmosphere and allowing photo-oxidation to occur.[3] Hybrid poplars are commonly used because they grow fast and uptake large amounts of water.[13] In a studies done by Ma and Burken Researchers at the University of Missouri-Rolla found that TCE is removed from soil and groundwater by volatizing from the stem into the atmosphere through diffusion because and minimal TCE was measured on the leaves in comparison to stems.[3,4]

Another method was experimented by Shen and Wilson using permeable reactive barrier (PBR). The PBR was made with 40 percent shredded tree mulch, 10 percent cotton gin trash and 40 percent sand. Columns were constructed with the PBR that allowed continuous water flow. TCE laced water was flushed through the system. The amount of DCE leaving the PBR was higher than the amount of TCE, concluding that TCE was degraded into DCE by the PBR.[6]

Another form of remediation and currently the most popular is air sparging, often coupled with soil vapor extraction.[11] This method was developed in the late 1980s to treat dissolved VOCs in water.[15] Non aqueous phase liquids (NAPL) are problematic in subsurface pollution because they percolate deep into the soil due to gravity until the water table is reached. Light NAPL (LNAPL) float on the surface of the water and dense NAPL (DNAPL) continue below the water table and can be long term contaminates for ground water.[11] Air sparging works through interphase mass transfer. Air is injected into soil saturated with contamination and the NAPL will volatilize into the gas and rise with the air to the surface. The air is then released into the atmosphere or treated by a soil vapor extraction system. [16] The soil vapor extraction system treats the volatilized contaminant and releases air. A simulation done by McCray and Falta had nearly 90 percent removal of TCE above the air sparging point in permeable soils. They concluded that air sparging is most effective for more permeable soils.[11] Bass et al. found that higher sparge well density covering the entire source area were more effective. They also found that rebound was likely and success depended on the concentration of rebound. More successful sites had negligible amount of rebound.[15] Studies done by Adams and Reddy concluded that removal of TCE was similar to LNAPL, lower ranges of injection benefited from increased injection flow rate but did not make a difference in higher ranges of air injection and increased initial concentrations did not lead to increased rate of removal.[16]

Air sparging as a form of potential remediation will be investigated. Remediation attempts were developed in order to lower the TCE concentrations in the air on the Adjacent Property. An air sparging system was implemented. The surface streams in the fenced in area on the Adjacent Property were covered with a layer impermeable to gases. Air was pumped into the soil then back into the atmosphere to prevent volatilization at the springs. Although the springs have been covered with an impermeable layer, the stream remains flowing out of the fenced-in area.

TCE and DCE contamination in surface streams on the Adjacent Property affected by air sparging will be analyzed using Gas Chromatography Mass Spectrometry (GCMS). Gas chromatography (GC) is the most common separation method in the literature because of the volatility of TCE and DCE; however different detectors are used for quantification. Mass spectrometry (MS) is the most common detection method for quantification of both water and tissue samples and will be used in this study. Other studies in the literature employing MS detection include Zhang et al. analyzing uptake of VOCs by willows, Shen et al. analyzing efficacy of permeable reactive barriers, Wilcox analyzing TCE uptake by poplars, and a water and soil contamination report by Dorian.[5,6,9,10] Newman et al. analyzed VOCs in plant tissue using a solid-phase micro extraction fiber detector,[4] whereas Liu et al. analyzed water and plant tissue samples and Adams and Reddy analyzed the effect of air sparging on TCE using GC with flame ionization detection.[13,16] Orchard el al. and Burken et al. used GC with an electron capture detector to analyze water samples.[1,14] High Performance Liquid Chromatography (HPLC) is also a method for VOC separation analysis.[4,17] And other studies used measurements of physical properties for quantification: McCray and Falta used changes in head pressure to determine plume size and the radius of influence in an TCE air sparging simulation and Bass et al. used degree of contact between soil and air to determine efficacy of sparging.[11,15]

The objective of this research is to investigate how the air sparging system, installed at the springs to prevent localized TCE and DCE volatilization into the air, impacts TCE and DCE content in surface streams emanating from the springs. Water samples were analyzed periodically increasing sampling frequency during air spraging site activity in order to compare TCE to DCE concentrations and relative concentration ratios before, during and after air sparging site activity. In addition, TCE and DCE volatilization down the stream will be measured.

2. Instrumentation

The method of quantification was gas chromatography mass spectrometry (GCMS) analytical instrumentation, Schimadzu model GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer with a Teledyne Tekmar Stratum Purge and Trap. This instrument required the user to set up the system with the EPA method 524.2 for analyzing volatile organic compounds in water.[18] Before injection into the GCMS, volatile compounds are extracted from liquids by bubbling helium through a 5mL amount of the sample and 10µL of the 15ppm internal standards (IS) in the purge and trap inlet. The sample is then qualified by the gas chromatograph and quantified by the mass spectrometer. The compounds of the sample are separated by interaction with the GC capillary column and are detected as a function of time based on their mass-to-charge ratio.

The dynamic range for the instrument is 0.24ppb to 50ppb due to standard error for the instrument and the upper limit of the calibration curve. Samples were analyzed based on ratios of the peak area of the analyte to the peak area of an internal standard (IS). There are seven internal standards injected into the sample before analyzation: pentrafluorobenzene, 1,4 difluorobenzene, chlorobenzene-d5, 1,4 dichlorobenzene-d4, and toluene-d8. TCE and DCE ratios were compared to 1,4 difluorobenzene as the IS. The example calibration curves for TCE and DCE are shown in Figures 2 and 3; but were updated semesterly. For example, the slope for the TCE calibration curve for Fall 2014 was 0.011±0.00024 and the y-intercept was 0.00067±0.0066. The limit of detection based on the calibration curve was 1.9ppb and the limit of quantification was 6.0ppb. The slope for the Fall 2014 DCE calibration curve was 0.013±0.00021 and the y-intercept was -0.00024±0.0060. The limit of detection based on the calibration curve was 1.5ppb and the limit of quantification was 4.6ppb. For quality control, a standard check was analyzed every other day using a VOC standard for TCE and field blanks (vials with ultra pure water) were carried when collecting field samples.[18]

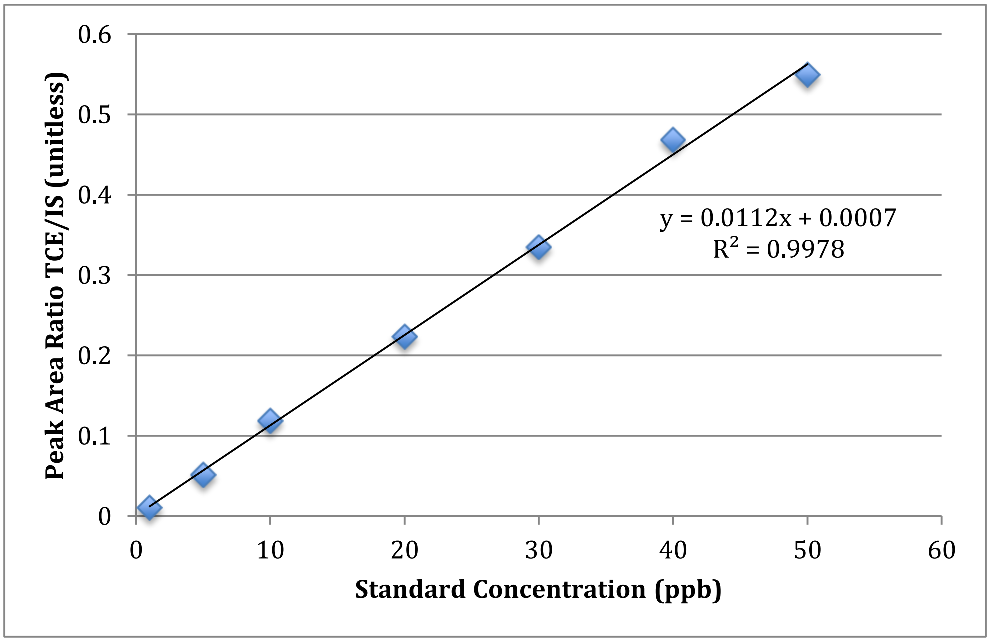

Figure 2. Calibration curve for TCE Fall 2014.

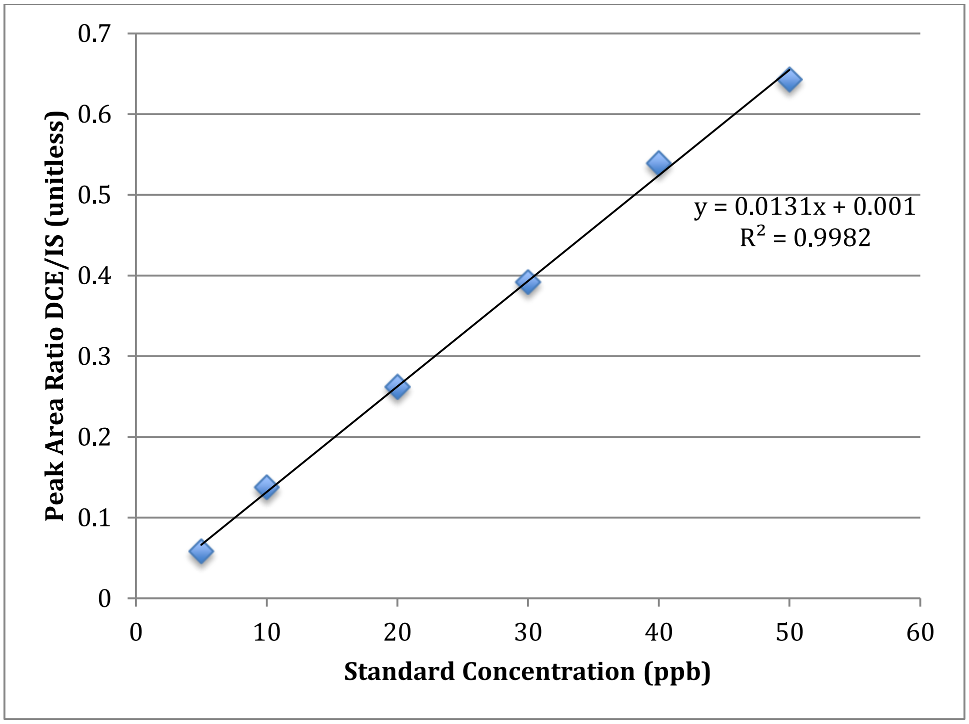

Figure 3. Calibration curve for Fall 2014 DCE.

3. Experimental Methods

Water samples were collected from the steam at the fence line, at locations inside the fence and downstream samples occasionally for the duration of 2 years. The fence line stream sample was sampled more frequently (bi-weekly then weekly) during air sparging site activity in order to get the TCE to DCE ratios before, during and after air sparing activity. Samples were also taken every 20 feet down the stream a couple times to ensure the usage of an exponential regression but more often only sampled 40 feet downstream (at the bridge) and 134 feet downstream (at the pole) from the fence line. Samples were also collected from springs in the fenced in area prior to air sparging and burial of the springs for reference and knowledge of the TCE levels for the stream.

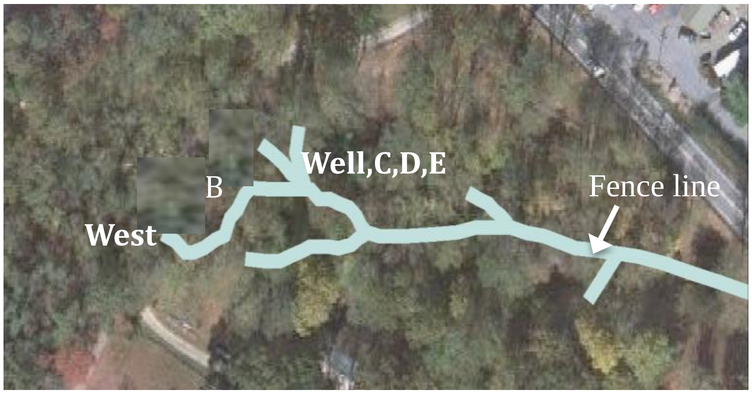

Figure 4. Arial view of surface streams.

When stream samples were collected, a drop of concentrated hydrochloric acid was added to prevent microbial growth and closed with no air space. The water samples could be analyzed immediately for TCE content or refrigerated for up to two weeks according to EPA 524.2 method.[18]

3. Results and Discussion

Air sparging activity at the springs on TCE and DCE content in the surface streams was investigated before, during and after installation. Water samples were analyzed periodically increasing sampling frequency during site activity. Samples were also taken from springs in the fenced in area for reference of TCE levels. In addition, TCE and DCE concentrations were measured at intervals downstream from the fence line to determine the rate of volatilization.. All samples were analyzed using gas chromatography mass spectrometry (GCMS) analytical instrumentation, using EPA method 524.2.[18]

3.1 Surface Stream Samples

Water samples were collected from the steam at the fence line for the duration of 2 years. The steam water was sampled every week during the summer of 2012 and TCE and DCE concentrations are plotted as a function of date in Figure 5. TCE and DCE were analyzed more frequently before, during and after air sparing installation. Figure 5 shows that TCE and DCE levels changed due to environmental condition but overall remained fairly consistent.

Samples collected from surface level streams inside the fenced area are shown in Table 1. These streams originate from springs and are the source for the remaining stream. These springs have much higher concentrations of TCE because the water source contains the concentrated underground plume of TCE the springs are downslope from the source of contamination (CTS site). The air was tested unsafe for breathing due to volatilization from the high concentration of water contamination. For this reason the air sparging system was implemented to reduce TCE levels in the air by burying the springs. Although the springs were buried, the stream outside the fence still flows.

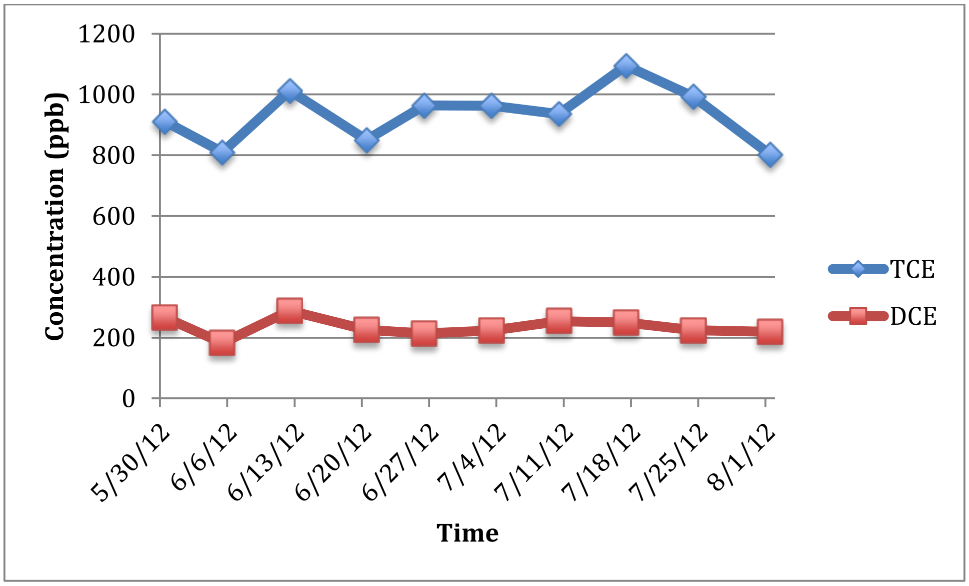

Figure 5. TCE (ppb) and DCE (ppb) for fence line stream in the duration of Summer 2012.

Table 1. TCE and DCE concentrations (ppb) for surface water in fenced area

Name	**TCE (ppb)**	**DCE (ppb)**
West Spring [a]	130	160
West Spring[a]	36	50
Spring B[b]	6800	1500

Spring C[c]	8400	2200
Spring C.2[c]	11000	170
Well[c]	1680	70
Spring D[c]	57	3.7
Spring C[c]	5400	N/A
Spring E[c]	570	N/A

[a] Near fence by first driveway: West Spring: collected 5/30/12, 7/17/12

[b] Near yellow jackets (middle): Spring B: collected 5/30/12

[c] Multiple spring system: Spring C: by well, collected 5/30/12, 7/17/12, 6/11/13, Well: round concrete structure, collected 7/17/12, Spring D: new spring by spring C, collected 8/2/12, Spring E: Spring downstream from well, collected 6/11/13. Refer to Figure 4 for location of the springs.

Water samples were collected from the steam at the fence line (where the springs converge to form a stream) and downstream from the fence line. The data at the fence line has been consistent since the start of the project, however during air sparging installation, the concentrations changed, confirmed by a t-test. Figure 6 shows the concentrations of TCE and DCE before, during and after site activity. The concentration of TCE historically has been was on average 1000ppb±150ppb and the concentration for DCE 200ppb±70ppb. There is a high standard deviation because TCE and DCE concentrations fluctuate due to environmental conditions such as rainfall and temperature. At the start of implementation of air sparging, the concentrations changed dramatically: TCE declined sharply and DCE inclined sharply. Figure 7 shows only the TCE and DCE concentrations after air sparging activity. After the sharp change in concentrations, TCE and DCE continue to change but more slowly. The air sparging system has been running for the "After" samples since the second week of November. Concentrations seem to slowly be balancing back to original concentrations. TCE is increasing while DCE is decreasing. This change in concentration cannot specifically be attributed to the air sparging system because it could also be the stream reaching a new equilibrium after the activity or a contribution of both equilibrium and air sparging. More time and analysis is needed to get more information about the effect of the air sparging system being turned on.

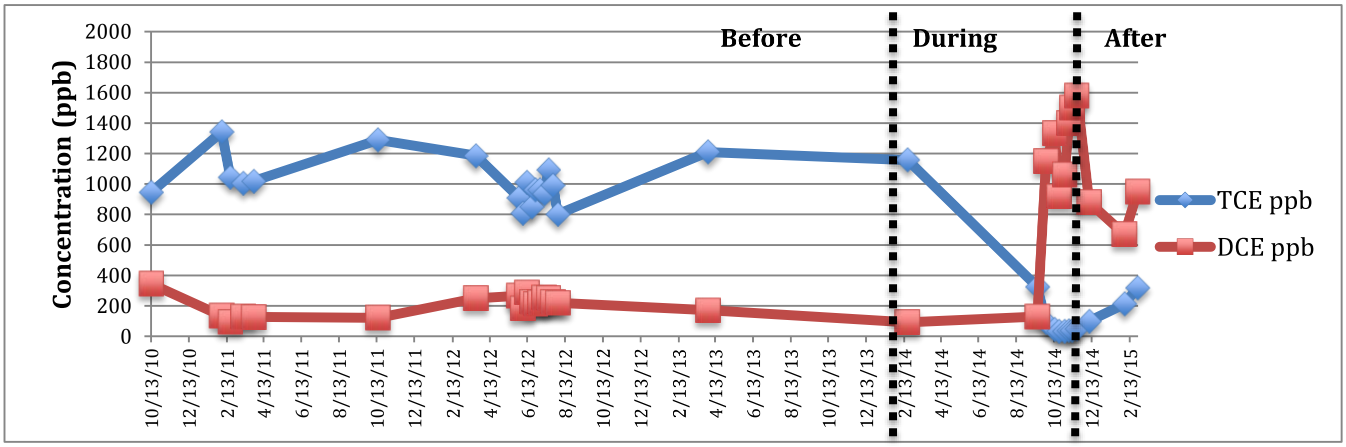

Figure 6. TCE (ppb) for fence line stream and DCE (ppb) in the duration of site activity.

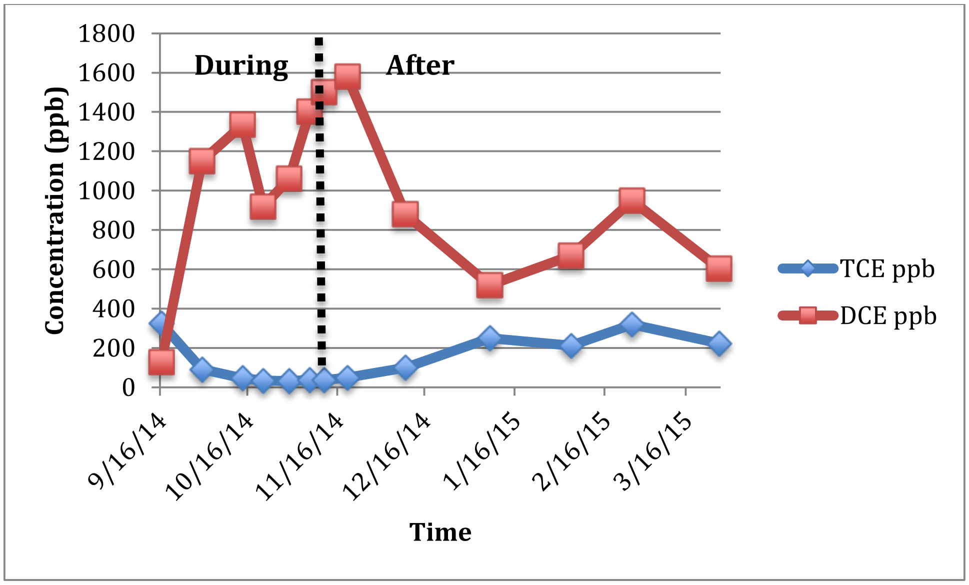

Figure 7. TCE (ppb) for fence line stream and DCE (ppb) in the duration of soil-vapor extraction remediation project.

At the start of air sparging installation, TCE went down to less than a third of historical values and DCE went up by about a factor of 3. However, the molar ratio of TCE +DCE still remained the same. When adding the average value of TCE and the averge value of DCE then converted to moles per liter the amount prior to site activity was 9.7E-06 moles/L and after site activity it is 10E-06 moles/L. The average amount during site activity is still similar to historical values when added together. This means that the amount of contamination is still about the same but due to recent activity, TCE has been degraded into DCE making DCE levels higher than TCE. TCE degradation is likely due to churning of the soil in order to bury the springs, which increases microbial action therefore degrading TCE into DCE. Thus far, it appears that there is no change in total contamination in the surface water during and after air sparging is taking place.

3.2 Volatilization down the Stream

The rate of volatilization of TCE and DCE in the stream was measured. Data is shown below for the rate before, during and after air sparging implementation in Table 2 for TCE and Table 3 for DCE. An exponential regression, shown in Figure 8, was fitted to the data to find the rate of volatilization to help compare data. Sampling number 1 was before air sparging activity. Sampling numbers 2 through 4 were during air sparging activities and sampling numbers 7 and 8 were after implementation of air sparging. Sampling numbers 7 and 8 were sampled every 20 feet down the stream from the fenceline and the rest were sampled at the fenceline, 40 feet downstream and 134 feet downstream.

Henry's law shows that TCE will volatilize out of water due to the partial pressure of TCE on top of the water. Because volatile organic compounds (VOC) disperse into the atmostphere as soon as they volailize, this fundamental can be used to create an equation to determine the concentration of a VOC in a stream due to exponential decay of the original concentration taking into accound the water velocity and distance downstream.[19]

$$C=C_0e^{(-Kv)(1.16E-5)(L/U)} \tag{1}$$

In Equation 1 K_v=volatilization coefficient (day^{-1}) C_0=initial concentration L=distance (m) U=water velocity (m/s) 1.6E-5=day to second conversion factor.[19] This equation is used to understand the exponential regression for the volatilization of TCE and DCE downstream. In Tables 2 and 3 there is information on the volaitization for different samping times. The initial concentration changed after air sparging activity started. Initial concentration for TCE was similar to the initial concentration DCE was historically and DCE was at the concentration TCE was historically. The coefficient of the exponent is equivalent to the volatilization coefficient multiplied by a constant and the water velocity. The volatization coefficient currently is consistent for TCE before air sparging activity and after implementation. DCE likewise is similar to historic values because the volitalization coefficient is a constant. The slight variance in the exponential cofficient can be attributed to water velocity. Water velocity is highly dependent on environmental conditions, such as rain fall, which are variable.

Comparing the mole per liter value of TCE added to DCE the average amount during site activity is still similar to historical values. This means that the amount of contamination is still about the same except that due to recent activity, TCE has been degraded into DCE.

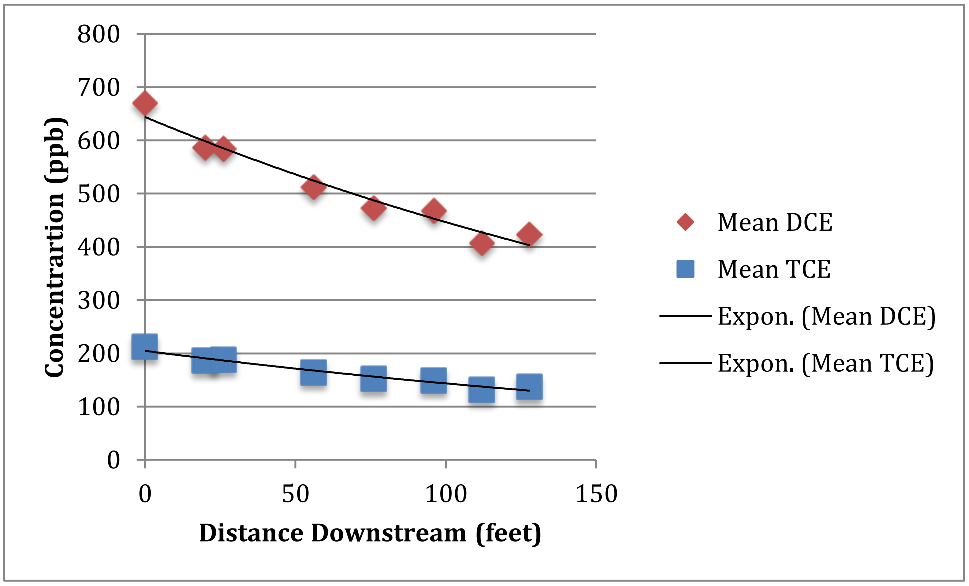

Figure 8. TCE and DCE (ppb/foot) volatilization downstream for sampling number 5.

Table 2. TCE (ppb/foot) volatilization downstream

Sampling Number	**Date**	**Equation (TCE volatilization)**	**R^2 Value**
1	**04/01/2013**	**$y = 1{,}200e^{-0.00424x}$**	**$R^2 = 0.936$**
2	**09/30/2014**	**$y = 86e^{-0.00454x}$**	**$R^2 = 0.948$**
3	**10/14/2014**	**$y = 44e^{-0.00353x}$**	**$R^2 = 0.973$**
4	**10/21/2014**	**$y = 34e^{-0.00530x}$**	**$R^2 = 1.00$**
5	**02/04/2015**	**$y = 200e^{-0.00355x}$**	**$R^2 = 0.955$**
6	**02/25/2015**	**$y = 300e^{-0.00310x}$**	**$R^2 = 0.943$**

Table 3. DCE (ppb/foot) volatilization downstream

Sampling Number	**Date**	**Equation (DCE volatilization)**	**R^2 Value**
1	**04/01/2013**	**$y = 260e^{-0.00810x}$**	**$R^2 = 0.968$**
2	**09/30/2014**	**$y = 1{,}100e^{-0.00433x}$**	**$R^2 = 0.982$**
3	**10/14/2014**	**$y = 1{,}300e^{-0.00336x}$**	**$R^2 = 0.988$**
4	**10/21/2014**	**$y = 910e^{-0.00487x}$**	**$R^2 = 0.999$**
5	**02/04/2015**	**$y = 640e^{-0.00366x}$**	**$R^2 = 0.957$**
6	**02/25/2015**	**$y = 900e^{-0.00293x}$**	**$R^2 = 0.928$**

4. Conclusion

This research analyzed the effect of air sparging on TCE and DCE concentrations in surface streams using GCMS. Due to high levels of TCE in the air, the springs inside the fenced in area on the Adjacent Property were covered and an air sparging system was put into place to reduce localized TCE and DCE volatilization. The stream outside the fenced area remained flowing and was sampled at the fence line to quantify TCE and DCE concentrations and compare TCE-to-DCE concentration ratios before, during and after the air sparging system was installed. Water samples were collected from the steam at the fence line periodically for 4 years. The steam water was sampled more frequently (bi-weekly then weekly) during sparging site activity. Due to air sparging activity, TCE and DCE levels in the stream changed significantly. TCE initially decreased to less than a third of historical values and DCE increased by a factor of 3. However, the molar ratio of TCE+DCE remained unchanged, concluding that total stream contamination was not affected by the air sparging system. After installation was completed, TCE and DCE concentrations continued to change. TCE began gradually increasing while DCE gradually decreased. A new TCE and DCE stream contamination equilibrium has yet to be established.

Because DCE is a degradation product of TCE, the influence of the air sparging system on stream contamination has been to facilitate TCE degradation into DCE, making DCE levels higher during and after site activity with decreased TCE concentrations. This degradation of TCE is most likely due to heightened levels of microbial action from churning of the soil in order to cover the springs during system installation. However, because the combined molar ratios of TCE and DCE are the same before and after air sparging installation, it is concluded that the system has no impact on total stream contamination at this time and has only impacted microbial TCE degradation.

The rate of volatilization was analyzed by sampling at different intervals downstream from the fence line. The rate of volatilization for TCE after installation was similar to the before air sparging activity volatilization rate for DCE. Similarly, the rate of volatilization for DCE after installation was similar to the before rate for TCE. Only the initial contaminant concentrations have changed and the molar ratio of combined TCE and DCE volatilization was very similar to before air sparging installation, further concluding that the amount of VOC contamination is consistent before, during and after air sparging installation. The variance in the exponential coefficient in the volatilization models is due to water velocity, which is reliant on environmental factors.

Further research on this project includes continuing to monitor TCE and DCE concentrations in the stream to establish a new TCE and DCE contaminant concentration equilibrium and the long-term efficacy of air sparging on TCE and DCE stream contamination.

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