



RESEARCH & DEVELOPMENT

Field Evaluation of Hardening Methods for Subsurface Utilities and Drainage Pipes

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16. Abstract A new field monitoring approach in the form of metallic capsules is developed to evaluate Benzene and PCE diffusion through concrete pipe gaskets. The capsules are developed and tested with three gasket materials: Neoprene, Buna-N, and Viton. To validate the monitoring approach and develop field retrieval protocol, capsules were deployed in three contaminated sites: (i) Nash county maintenance depot in Nashville, NC (gasoline contaminated site), (ii) A maintenance facility yard in Newton, NC (gasoline contaminated site), and (iii) Triangle Laundromat in Durham, NC (chlorinated solvent contaminated site, PCE). The tensile strength of gasket materials, integrated with the deployed field capsules, is evaluated with time. In addition to testing under field conditions, tensile strength testing is also performed under controlled conditions in the laboratory to establish material degradation model. Computational modeling is used to simulate the site conditions of the installed capsules considering test sites' hydraulic gradient, soil properties and plume concentration and the influence of such parameters on the rate of breakthrough within the installed capsules. The hydraulic parameters of gaskets were calibrated using field measurements and data from a series of experimental studies under controlled condition. Results indicated nonlinear power relationship for the mass breakthrough of benzene and PCE with time. Compared to chlorinated solvent, benzene has higher diffusivity among gasket materials (Neoprene, Buna-N, Viton). Viton showed the highest resistance to the diffusion of benzene and PCE. Viton and Neoprene showed the lowest and highest tensile strength degradation, respectively, once exposed to gasoline or chlorinated solvent contamination. Based on modeling results, benzene concentration breaking through the Neoprene and Buna-N will reach more than 70% and 60% of the monitoring well concentration, respectively, after 4 months. Benzene breakthrough reaches 85% to 90% of monitoring well concentration after 6 months. Results from the experimental and modeling studies are synthesized and a protocol is proposed for installing/retrieval of capsules to monitor PCE and benzene breakthrough rates into pipe materials.			
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EXECUTIVE SUMMARY

A new monitoring approach in the form of metallic capsules is developed to measure Benzene and PCE diffusion through concrete pipe gaskets in the field. The development of the new monitoring approach utilized data from field studies and modeling. The capsules are proposed for assessing the performance of various gasket materials at sites contaminated with gasoline and chlorinated solvents. The proposed capsules were deployed in three contaminated sites: (i) Nash County maintenance depot in Nashville, NC (gasoline contaminated site), (ii) A maintenance facility yard in Newton, NC (gasoline contaminated site), and (iii) Triangle Laundromat in Durham, NC (chlorinated solvent contaminated site, PCE). Data obtained from the field study show that benzene, compared to PCE, has higher diffusion rate through gasket materials used in the project (Neoprene, Buna-N, Viton). Both benzene and PCE had the lowest diffusion rate in Viton, among the three gasket materials. A similar trend was observed for tensile strength of gasket materials exposed to the contaminated water under field conditions. In this respect, Viton and Neoprene showed the lowest and highest tensile strength degradation, respectively, once exposed to gasoline or chlorinated solvent contamination.

In addition, data generated herein are utilized to assess the suitability of a proposed model for predicting tensile strength of gasket materials, aged under controlled conditions at the laboratory. The predictions from the analytical model (presented in previous project: PR #2017-08) that estimate the tensile strength of gasket materials exposed to different contaminants are compared to the experimental results obtained herein. The measured tensile strength of gasket samples aged in the field differed from the model predictions by 0-23% depending on the type of contaminant and gasket materials. This finding supports the use of the model to provide a reasonable estimate of the degradation in gasket materials. Qualitative assessment of such results is summarized in the Table S1.

Table S1. Comparative performance of gasket materials exposed to water contaminated by gasoline or chlorinated solvent under field conditions.

Contamination cause	Major contaminant	Diffusivity		Tensile strength	
		Lowest	Highest	Lowest	Highest
Gasoline	Benzene	Viton	Neoprene	Neoprene	Viton
Chlorinated solvent	PCE	Viton	Neoprene	Neoprene	Viton

Computational 3D numerical modeling is used to simulate the site conditions of the installed capsules considering test sites' hydraulic gradient, soil properties, plume concentration and the influence of such parameters on the rate of breakthrough within the installed capsules. The hydraulic parameters of gaskets are calibrated using field measurements and data from a series of laboratory experimental studies under controlled conditions. Calibrated parameters were then used in the numerical simulations to predict the rate of breakthrough. The benzene mass breakthrough rate through Neoprene showed the highest value among the three gasket materials tested and is estimated at 0.002-0.0025 mg/d at the steady state condition after 3-4 months of deployment. The results show PCE needs more than four months to reach steady state condition. A protocol is

developed and recommended for installing/retrieval of the capsules to monitor PCE and/or benzene breakthrough rates, depending on the type of gasket and contaminant, as shown in Table S2. The percent of contaminant detected in the monitoring capsule in this case is normalized with respect to monitoring well concentration. The results are presented as a function of monitoring duration (month). Results are not shown for Viton since no discernible breakthrough concentration was estimated.

Table S2. Recommended protocol for installing/retrieving capsules to monitor benzene and PCE breakthrough rates.

Benzene and PCE breakthrough concentration normalized with respect to monitoring well concentration (%) (C_c/C_{wi})- predicted by numerical simulations of field conditions				
	Sample/time	2 months	4 months	6 months
Benzene	Neoprene	50	69	90
	Buna-N	43	64	85
PCE	Neoprene	42	59	64
	Buna-N	42	59	64

According to the proposed capsules' deployment protocol, the benzene concentrations that diffuse through Neoprene and Buna-N are more than 70% and 60%, respectively, of the concentration in the monitoring well after 4 months. PCE breakthrough after 4 months is 60% for both the Neoprene and Buna-N. Results indicated nonlinear power relationship between the mass breakthrough of both benzene and PCE and time.

The recommended protocol for deployment duration of the monitoring capsules is summarized as follows:

- i. If there is a contaminated site with known high concentrations of benzene or PCE such that a 40% to 50% breakthrough concentration will pose an environmental risk downstream, then a 2 months monitoring period is recommended.
- ii. If the site has a known lower contamination level where 70% level of such contamination is not a high risk, then the period of deployment can be extended based on protocol and diagrams of contaminant breakthrough presented in this study.

For example, in this study, two gasoline-contaminated sites were examined; Nashville with 19,400 $\mu\text{g/l}$ and Newton with 350 $\mu\text{g/l}$ detected before first deployment. The significant differences of the contamination level between these two sites can lead us to pick different schedules for capsule deployment/retrievals because 50% of contamination level at Nashville is much more than at Newton. That conclusion can be extended to the other future sites with different initial detected contamination levels.

The feasibility of deploying capsules to assess the performance of gasket materials exposed to contamination under field condition is demonstrated using the experimental and modeling data obtained herein. The experimental and computational results obtained in this project, indicates that these capsules can effectively be used to assess the performance of different gasket types in a short period.

TABLE OF CONTENTS

1. Introduction	11
2. Research Approach	12
3. Experimental Methods	18
4. Model Development	18
5. Results and Discussion	18
5.1. Field Investigation.....	18
5.1.1. Measurement of diffusion coefficient of VOCs in gasket materials.....	18
5.1.2. Degradation of tensile strength: gasket materials	20
5.2. Modeling of Contaminant transport	22
5.2.1. Benzene-contaminated sites	22
5.2.2. PCE Contaminated Sites.....	29
5.2.3. Mass breakthrough rate of Benzene and PCE	32
6. Findings and Recommendations.....	34
7. References.....	36
Appendix A: Literature review	40
Appendix B: Field sites.....	43
B.1. Nashville gasoline contaminated site	43
B.2. Newton gasoline contaminated site	44
B.3. Durham chlorinated solvent contaminated site	45
Appendix C: Experimental part 1	48
C.1. General information.....	48
C.2. Materials and tools.....	48
C.2.1. Gasket materials	48
C.2.2. Capsules for VOCs diffusivity quantification in the field.....	49
C.3. Methods	50
C.3.1. Deployment and retrieval protocols for capsules and gasket samples	50
C.3.2. Sampling from the capsules after retrieval	54
C.3.3. Measurement of tensile strength of gasket samples	55
C.3.4. Estimation of tensile strength degradation of gasket materials	55
Appendix D: Experimental part 2.....	57

D.1. General information	57
D.2. Concentration of VOCs in the monitoring wells.....	57
D.3. Concentration of VOCs in the capsules	59
D.4. Calculation of saturation dependence constant factor (β)	60
Appendix E: Modeling part	61
E.1. Model development	61
E.1.1. Nashville gasoline contaminated site.....	61
E.1.2. Newton gasoline contaminated site	64
E.1.3. Durham chlorinated solvent contaminated site.....	67

1. Introduction

North Carolina Department of Transportation (NCDOT) installs a large number of subsurface utilities including drainage pipes every year. In many instances these subsurface structures are installed in profiles with known contamination, or where contamination occurs after installation, and therefore appropriate pipe materials need to be adopted. The majority of contamination incidents in the US are caused by compounds derived from fuel hydrocarbons or dry-cleaning solvents. These contaminants may ingress into the subsurface utilities, resulting in the contamination of water inside such pipes, and potentially the transfer of contaminants to other downstream locations. Although many laboratory-scale studies have been carried out to quantify the effect of various types of contaminants on the permeability and mechanical performances of pipe materials, with the exception of work performed in the past by the research team, no documented study is available in literature to address the ingress potential of contaminants in the field.

Work herein aims at addressing such knowledge gap and providing quantitative measures of the field performance of three gasket materials (Neoprene, Buna-N, and Viton) commonly used as a hardening method to reduce the contamination ingress into concrete pipes at the pipe joints. In addition, as benzene and tetrachloroethylene (PCE) possess the highest concentrations in the gasoline- and chlorinated solvent-contaminated plumes in North Carolina (as reported by North Carolina Department of Environmental Quality), respectively, these two chemicals are the focus of interest herein. A new monitoring approach in the form of metallic capsules is developed to monitor Benzene and PCE diffusion through concrete pipe gasket materials in the field. Development of the new monitoring approach utilized data from field studies and modeling and advances the monitoring approach based on the idea of passive samplers to evaluate the mass transport through gasket materials.

The conventional discrete grab sampling from monitoring wells provides a snapshot of pollutants only at the specific time and place of sampling, which is inadequate for providing data on episodic contamination events. Integrative sampling is an alternative to discrete-sampling for identifying a wide range of volatile and semi-volatile micropollutants over extended timeframes, from hours to months (Vrana et al. 2001). Integrative samplers relying on the subsurface advection to transfer the contaminant-bearing phase to the sampling phase are referred to as ‘active’, while those relying on diffusion are termed ‘passive’ (Roll and Halden 2016, Lohmann et al., 2012, Vrana et al. 2001, 2005). The capsule design herein was developed based on the idea of passive integrative sampling. A comprehensive literature review is presented in Appendix A.

The objectives of the laboratory and field testing, and modeling work carried out in this project were as follows:

1. Designing an approach by which monitoring capsules are deployed and retrieved to obtain field data characterizing the level of gasoline and chlorinated solvents contamination at pipes’ installation sites.

2. Deployment of the proposed monitoring capsules at three contaminated field sites and correlating data from monitoring wells, using conventional sampling approach, to contaminant concentrations obtained using the proposed capsules.
3. Developing 3D field-domain numerical models for the test sites of study to assess rate of breakthrough considering contamination fluctuations under field conditions. The modeling will enable the calibration of hydraulic parameters of gasket materials (diffusion and equivalent hydraulic conductivity) with the progress of benzene and PCE transport.
4. Through field measurements and modeling, quantifying concentration and mass breakthrough rates of benzene and PCE with time through the three gasket materials of Neoprene, Buna-N, Viton. Then, proposing a protocol for installation and retrieval of the capsules for field evaluation of contamination levels.
5. Quantifying degradation in the tensile strength of gasket materials under field condition. In addition, assessing the capability of tensile strength degradation model developed in a previous project (report #2017-08, Hosseini et al., 2019; Hosseini et al., 2020) under laboratory conditions, to predict tensile strength degradation of gasket materials exposed to contamination in the field.

2. Research Approach

Each of the objectives mentioned above have been addressed through a systematic study. A brief description of the approaches and results used to achieve the research objectives is summarized herein.

Site selection and exposure duration for field study

Three contaminated sites in North Carolina were selected for deployment of the proposed monitoring capsules and modeling, after consultation with our colleagues at NCDOT. One of these sites, located in Durham is contaminated with chlorinated solvents while the other two are located in Newton and Nashville, and are contaminated with gasoline. These test sites were selected to represent the Physiographic regions of North Carolina with various depths of water table. In this regard, sites in Newton and Durham are in the Piedmont while Nashville is located in coastal plain region. Additionally, exposure period for gasket samples deployed at each site was chosen to capture variation in water table elevations, and contamination levels, during various seasons in a year. Table 1 summarizes information related to the selected sites and the exposure periods of gasket samples for each site. The description of each test site is presented in Appendix B. Note that to avoid difficulties in deployment and retrieval of capsules and gasket samples in the field, all materials were installed in monitoring wells located at each of the test sites.

Table 1. Selected sites information.

Name	Location	Type of contamination	Exposure durations (month)
Nash County maintenance depot	Nashville	Gasoline	4 and 7
NCDOT maintenance facility	Newton	Gasoline	2 and 9
Triangle Laundromat	Durham	Chlorinated solvent	6 and 9

Capsules for field evaluation of contamination

To evaluate the diffusivity of benzene and PCE through the study gasket materials (Neoprene, Buna-N, Viton,) a specific type of capsule was designed and tested in the laboratory. Each capsule consists of a cap that accommodates a piece of gasket material and a non-reactive metallic cup to have pure water (with no detectable quantity of contaminants) as a receiving medium. Contaminates migrate through the gasket material, installed within the cap of the capsule, and accumulate in the metallic cup. Accumulation of contaminant of interest in the pure water occurs after exposure of gasket material to the contamination via diffusion of contaminant through gaskets. As such, by measuring the concentration of contaminants in the pure water in the cup, after a specific exposure time, one can estimate the diffusion coefficient of contaminants through the gasket materials with the results allowing for comparative assessment between the performance of different gasket materials in the field.

To reduce cost of capsule preparation and avoid corrosion of capsules for their reuse, aluminum was selected as the capsule material. Moreover, mineral clean water was used as pure water within the cup. Note that deionized distilled water was not used as receiving medium due to its corrosive nature for metals. Mineral water was acidified with maleic and ascorbic acids (5 and 0.625 g/L, respectively), following EPA method 524.3 (Prakash et al., 2009).

Deployment and measurement approach

To facilitate installation and retrieval of the capsules, they were deployed in groundwater within existing monitoring wells at the contaminated areas. Such wells are used to perform discrete sampling to detect contamination in groundwater. Deploying capsules in groundwater in monitoring wells for specific durations is beneficial for assessing diffusivity of contaminants in gasket materials as the concentration of contaminants outside the capsule, which is required for calculation purposes, can be readily obtained. Also deploying capsules in wells eliminates the need for additional excavation, placement, and backfilling at contaminant sites. Accordingly, capsules were designed to fit into monitoring wells.

For each of the three gasket materials, three capsules were prepared. Three blank capsules were also prepared without any gasket materials to evaluate the sealability of capsules deployed in monitoring wells during the exposure period. Capsules were hung in the monitoring well using a stainless-steel wire in a way such that the water table was at least 4-5 feet above the top capsule

of the deployed sequence. Capsules were kept in monitoring wells for specific periods of time to evaluate the effect of exposure time on diffusivity of benzene and PCE through gasket materials.

After each specific exposure time, capsules were retrieved from monitoring wells, their outside carefully cleansed with deionized water on site, and placed in a cooler with ice packs to prevent degradation of volatile organic compounds (VOCs) within the capsules during transportation. Capsules were transported to the laboratory and immediately transferred to a fridge until sampling from within each capsule was performed (which occurred within 24 hours after capsule retrieval event).

Degradation in the tensile strength of gasket materials exposed to field condition

Tensile strength of gasket materials is an important indicator in determining their stability in contaminated areas. Fast degradation of gasket materials would result in higher diffusion of VOCs into the pipe and thus higher contamination would be expected. Also, gasket materials can swell once exposed to VOCs such as benzene leading to instability of pipes due to deterioration of gasket materials at the joints. This issue would lead to new pathways for contamination to enter the pipe. Since tensile strength is one of the major mechanical properties of rubbers, assessing degradation of tensile strength of gasket materials provides an indication of how well these materials can perform when placed in contaminated environments.

Rubber gasket specimens were cut from commercially available rubber sheets of three materials: Neoprene, Buna-N, and Viton, using a press die with the dimensions specified for Type C dumbbell specimens according to ASTM D412. The thickness of sheets was 0.125" and the specimens were 4.5" long. Separate gasket samples were deployed in the monitoring well during deployment of capsules and retrieved at the same time when the capsules were retrieved. After retrieval, gasket samples were dried at $104 \pm 3^\circ\text{F}$ for 24 hours in an electric oven before performing tensile strength measurements. Drying samples would minimize the effect of liquids such as water and VOCs on the tensile strength. Specimens were considered "dry" when less than 0.1% change in the weight of specimen was measured within an hour. The tensile strength measurements were then normalized to the tensile strength of "unaged" samples to characterize the rate of degradation of tensile strength during the exposure period.

Applicability of tensile strength degradation model previously developed (Hosseini et al., 2020)

To reduce the effort required for deployment and retrieval of gasket materials in the field, an attempt was made to assess the appropriateness of the tensile strength degradation models developed under lab conditions in a previous project for NCDOT (Hosseini et al., 2019.) The model was developed using data from laboratory testing to predict tensile strength degradation of gasket materials. For the models developed based on the laboratory data, the main variable was the concentration of contaminant which was kept at its solubility limit in water. However, in field contamination incidents there are other variables such as fluctuations in the temperature and in the concentration of contaminants. These effects can only be captured by having data from the field investigation. Therefore, the degradation of tensile strength of gasket materials exposed to benzene and PCE with field concentrations was computed using the model by Hosseini et al., (2019.) The

model data were then compared with tensile strength measurements conducted for the samples retrieved from the field. The percentage of difference between experimental measurements and model predictions was reported.

Development of 3D numerical model of field domain

A 3-dimensional (3D) numerical model of the domains at the field test sites was developed for each site using finite difference method incorporated in GMS transient mass-transport computer program. The model domains were selected based on the extent of benzene or PCE plume. For example, the Nashville site was simulated with dimensions 30 m × 15 m × 5 m (98.4 ft × 49.2 ft × 16.4 ft). The dimensions were chosen to capture the field area with groundwater plume concentrations more than 50 ppb. The total number of grids depends on model domain and the mesh size is 0.25-0.5 m becoming as fine as 0.002 m towards the monitoring well where the capsules have been deployed. The hydraulic gradient in the domain was simulated with constant head boundaries. The fluctuation in monitoring well's concentration has been applied using transient functions.

The distribution of the initial soil and groundwater contamination was assigned based on information from field measurements of monitoring wells and retrieved soil samples from borings (Wood Inc. 2019, Pace analytical services report 2020, 2021). Similar to field deployment, a capsule with 2.54 cm diameter and 7.8 cm height was simulated at 75 cm below the water table level in a monitoring well having 5.0 cm diameter. The gasket sample located on the top of the capsule has 3.2 mm thickness and an initial concentration of zero was assumed inside the capsule. The water table level and plume concentration are not constant with seasonal changes.

The model flow and transport parameters were assigned with advection, dispersion/diffusion, chemical reaction/adsorption, and degradation processes considered in the analyses. The diffusion coefficient (D) and equivalent hydraulic conductivity (k_e) of the gasket samples are unknown and will be calibrated using the results from numerical simulations and measurements. As a part of the modeling contaminant transport toward the monitoring wells (where the capsules were located) adsorption of the organic chemical onto the solid-phase is defined by linear equilibrium-controlled sorption isotherm and the soil-water partition coefficient (K_d). The partitioning of chemicals onto the soil particles is a function of the organic carbon fraction (f_{oc}) present in the soil that is defined based on site assessment and soil sampling reports illustrated in field sites description. The first-order reaction rate of dissolved phase (K_1) and sorbed phase (K_2) were employed to account for the decay or degradation of the contaminant due to natural biochemical attenuation. The diffusion coefficient, adsorption/degradation parameters of benzene, as well as the rational for dispersivity have been described in previous studies (Faelli et al. 2020, 2021). Different adsorption and degradation parameters have been considered for the Durham site which has PCE contamination versus the two other sites with benzene from gasoline contamination (Aronson and Howard 1997). The diffusion coefficient values of benzene and PCE in water (D) were assigned as $9.5 \times 10^{-5} \text{ m}^2/\text{d}$ ($1.1 \times 10^{-9} \text{ m}^2/\text{s}$) and $8.8 \times 10^{-5} \text{ m}^2/\text{d}$ ($1.0 \times 10^{-9} \text{ m}^2/\text{s}$), respectively (GSI Environmental 2014). The longitudinal dispersivity parameter (α_x) was estimated, based on Neuman (1990) as $\alpha_x = 0.0175 \times L^{1.46}$, and L is domain size in the x-direction. The transverse (α_y) and vertical dispersivity (α_z) have been assumed as 30% and 5% of α_x , respectively, as recommended per ASTM, 1994.

Quantifying hydraulic parameters of gasket materials (diffusion and equivalent hydraulic conductivity)

To compute the diffusivity of benzene and PCE in gasket materials, Fick's second law was employed assuming 1-D diffusion (see Equation 1).

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (1)$$

$$C(x, 0) = 0, \quad 0 < x \leq L \quad (\text{Initial condition})$$

$$C(0, t) = C_o, \quad 0 \leq t \quad (\text{Boundary condition})$$

where $C(x,t)$ is the concentration diffused through the gasket sample (mg/m^3) as estimated by sampling from the liquid in the capsule cup over time; x is the distance within the sample in the diffusion direction (m); L is the sample thickness (m); D is the diffusivity of VOCs or PCE in gasket material (m^2/s), and C_o is the concentration of the VOC at $x = 0$ obtained by measuring the concentration of the VOC in the monitoring well at the time of capsule retrieval, t .

According to equation 1, and to find the diffusivity of benzene and PCE in gasket materials, concentration of the VOCs in both capsule and monitoring well at the time of retrieval are measured. This was done by sampling from the monitoring well at the time of capsules retrieval and measuring the concentration of VOCs in the capsule by sampling from within the capsule cup.

The 3-D numerical simulations have been used to calibrate the hydraulic parameters of gasket materials (D , k_c) after each measurement during the retrieval. The initial diffusion coefficient (D) was assigned based on 1-D diffusion equation 1 and was verified with a set of sensitivity analyses assuming field parameters. The equivalent hydraulic conductivity of samples was calibrated such that the contamination level inside the capsule is consistent with measurement after each field retrieval. Figure 1 shows a flowchart explaining the procedure of calibration. The average or best estimates based on field conditions were presented as hydraulic parameters of each gasket material. The data used in the study included site material properties, plume distribution, as well as the capsule concentration measurements (C_c) at the retrievals and monitoring well concentrations (C_w) per deployment/retrieval.

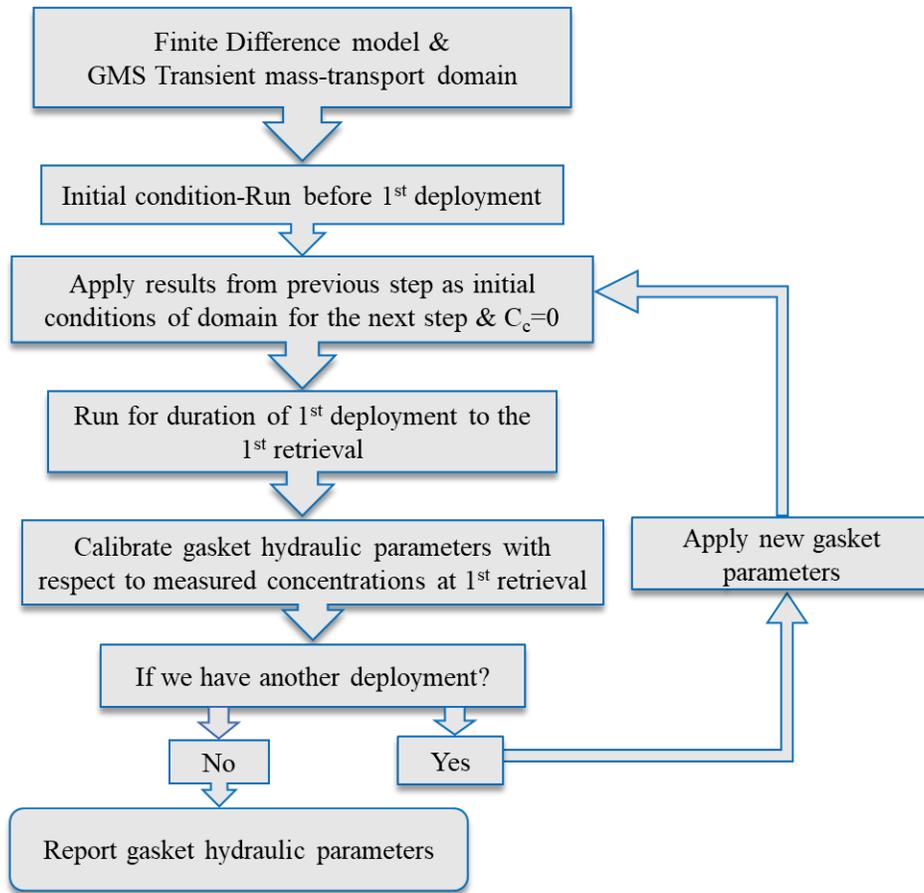


Figure 1. Calibration flowchart (Cc: capsule, measurement).

Concentration and mass breakthrough rates of benzene and PCE with time through gaskets

Benzene and PCE breakthrough in gasket materials installed within the deployed capsules have been determined per each time increment from the numerical modeling results. The calibrated parameters are used in the developed model of each site to predict the benzene and PCE breaking through gasket materials with time. The domain concentrations at the end of first retrieval are used as the initial conditions for the second deployment. The concentrations calculated inside the capsules at each time increment were normalized with respect to maximum concentration of the monitoring well groundwater sample during deployments (C_{wmax}) and the monitoring well groundwater sample concentrations calculated at each time step (C_{wi}). The concentrations inside the capsule from simulations were compared with measurements at each of the three test sites.

The mass breakthrough rates of benzene and PCE were obtained. A power relationship of “mass breakthrough rate with time” was obtained for each deployment period at each study site. Such relationship is characterized as follows (Equation 2)

$$M_{bt} = a 0.1^b t^b \quad (2)$$

Where M_{bt} is mass breakthrough rate (mg/d), t is the time elapsed since the deployment, a and b are constants. The constants, a and b , as well as R squared parameters of mass breakthrough rate fitting curve are calculated and presented for each site.

Protocol for installation and retrieval of field capsules.

The measured field data and numerical simulation results indicated the breakthrough of contaminant for each gasket material depends on the contaminant fluctuation within the field. The comparison between concentrations at each time duration, comparison between the rates of breakthrough at two deployment sites as well as comparison between the sites have been used to develop the protocols for installation and retrieval of capsules to monitor PCE and benzene breakthrough rates.

3. Experimental Methods

Materials and methods employed in the experimental investigation part of the project are discussed in detail in Appendices C and D.

4. Model Development

Model development and simulation process using finite difference method incorporated in GMS are discussed in detail in Appendix E.

5. Results and Discussion

5.1. Field Investigation

5.1.1. Measurement of diffusion coefficient of VOCs in gasket materials

Using concentrations measured in the monitoring wells within the capsules for each gasket material (Tables D1 and D2 in Appendix D) and employing Equation 1, diffusivities of benzene and PCE were obtained under various exposure durations. The results are summarized in Table 2.

Table 2. Diffusivity of benzene and PCE within the gasket materials under field condition; results based on data from deployed capsules

Gasket material	Site location	Contaminant	Exposure duration (month)	Diffusivity ($10^{-13} \text{ m}^2/\text{s}$)
Neoprene	Newton	Benzene	2	12.32 ± 0.21
			9	ND*
	Nashville	Benzene	4	3.90 ± 0.08
			7	3.78 ± 0.15
			6	ND*
			9	1.22 ± 0.01
Buna-N	Newton	Benzene	2	4.54 ± 0.16
			9	ND*
	Nashville	Benzene	4	2.12 ± 0.03
			7	ND*
			6	ND*
			9	1.32 ± 0.06
Viton	Newton	Benzene	2	ND**
			9	0.40 ± 0.02
	Nashville	Benzene	4	0.34 ± 0.02
			7	ND**
			6	0.15 ± 0.02
			9	ND**

* Not Determined due to higher concentration of VOC of interest in the capsule compared to level detected in the monitoring well.

** Not Detected as the concentration of VOC of interest was below the detection limit of the GC-MS ($< 5 \mu\text{g/L}$).

According to data in Table 2, and regardless of exposure time, Viton showed the lowest diffusivity among all gasket materials in both gasoline and PCE contaminated sites. This is due to the high chemical degradation resistance of Viton rubber (Hosseini et al., 2019). In addition, diffusivity of PCE in Viton is less than that of benzene indicating benzene molecules have greater detrimental effect on Viton. Similar performance trend was observed for benzene in Neoprene and Buna-N gasket materials as higher diffusivity for benzene was obtained compared to PCE.

Based on the data obtained for both Newton and Nashville sites, Buna-N showed higher resistance to benzene diffusion as reflected in lower diffusivity of benzene in Buna-N than Neoprene. This finding is consistent with data from the previous study conducted for NCDOT (Hosseini et al., 2019). However, according to the data from Durham site, and after 9 months of exposure, Neoprene and Buna-N performed similarly considering the statistical sensitivity of the results. Nevertheless, according to data in Table D3 (Appendix D), lower concentration of PCE was detected within the capsule with Buna-N after 6 months of exposure. Such observation can be

related to the existence and interaction of various variables such as temperature, availability of other diffusing species, fluctuations in the concentration of VOC of interest during the exposure time, and seasonal rate of rainfall infiltration. As such, and in general, Buna-N exhibits higher resistance, albeit slightly, to benzene and PCE compared to Neoprene,

In some cases, the concentration of VOCs (benzene or PCE) within the capsules was higher than their concentration in the monitoring wells preventing computing diffusivity in gasket materials. This is because we can only monitor the level of contaminants in the monitoring well during the deployment/retrieval events which cannot capture the fluctuations in the concentration of VOCs during the exposure period. However, the results shown in Table 2 indicate that we can comparatively assess the performance of gasket materials in a real contamination situation and assess the suitability of various materials as a hardening measure.

Highlights:

- Viton showed the highest resistance against both benzene and PCE among the three gasket materials studied in this project. See Table 2 for estimated values; the authors were not able to find such values reported in literature.
- In general, Buna-N outperforms Neoprene in gasoline and PCE contamination environment.
- Application of the proposed monitoring capsules in the field showed the approach to be a reliable method for comparatively evaluating the performance of the gasket materials.

5.1.2. Degradation of tensile strength: gasket materials

The results of tensile strength measurements on gasket samples deployed in the monitoring wells at the three selected test sites are presented in Table 3. Note that data were normalized with respect to the original, or unaged, tensile strength of gasket materials (all results are reported in Table C1 in appendix C) to better characterize the tensile strength loss due to the polymer chain degradation by VOCs.

As shown from data in Table 3, increasing exposure time resulted in greater loss of tensile strength for all three types of gasket materials. Neoprene showed the highest tensile strength loss among all gasket materials while Viton was the most resistant gasket material against tensile strength degradation under both gasoline and chlorinated solvent contaminations. These results are consistent with data from diffusivity measurements in section 5.1.1 and previous study (Hosseini et al., 2019).

As presented in Table 3, benzene is more detrimental than PCE with respect to tensile strength degradation for all gasket materials. The degradation rate is increased by increasing exposure time due to the cumulative adverse effect on the polymeric matrix of the synthetic rubber material.

Table 3. Tensile strength of the aged samples at the selected sites and the estimated values of tensile strength using model proposed by Hosseini et al. (2020)

Gasket material	Site location	Contaminant	Exposure duration (month)	Normalized measured tensile strength (%)	Estimated tensile strength* using model by Hosseini et al., (2020) (%)	
					Linear model for β	Nonlinear model for β
Neoprene	Newton	Benzene	2	85 ± 10	86	86
			9	81 ± 4	86	86
	Nashville	Benzene	4	79 ± 3	86	85
			7	70 ± 1	86	81
	Durham	PCE	6	86 ± 2	90	84
			9	72 ± 2	88	79
Buna-N	Newton	Benzene	2	92 ± 5	73	73
			9	77 ± 4	73	73
	Nashville	Benzene	4	80 ± 4	73	73
			7	75 ± 3	73	70
	Durham	PCE	6	88 ± 3	86	83
			9	87 ± 1	85	80
Viton	Newton	Benzene	2	92 ± 6	89	89
			9	92 ± 5	89	89
	Nashville	Benzene	4	94 ± 3	89	88
			7	89 ± 9	89	85
	Durham	PCE	6	98 ± 1	89	86
			9	94 ± 4	88	83

* Data are normalized to the tensile strength of original samples.

Using Equation C1 (Appendix C), and data in Tables C2 (Appendix C), D2 (Appendix D), and D4 (Appendix D), tensile strength of the gasket samples exposed to contaminated water at the test sites was estimated and presented in Table 3. Note that two models (i.e., linear, and nonlinear) were used to account for the lower concentration of VOCs in water observed in the monitoring wells, as compared to the solubility limit. The influence of the lower concentrations is included through the use of saturation-dependence parameter (β) (Table D4 – Appendix D).

According to data in Table 3, the percentage difference between the normalized measured and computed tensile strength of gasket materials falls within a range of 0-23% when the linear model is used for calculating β , while this range is 1-21% when the nonlinear model is used for calculating β . Specifically, in the case of using the linear model for estimating β , average percentage difference between measured and computed values for Neoprene, Buna-N, and Viton is 11%, 7%, and 5%, respectively, while this value is 7%, 9%, 7%, respectively when the nonlinear model is used to estimate β . Also, expect for Neoprene, using both models for β show lower tensile

strength indicating that the proposed model by Hosseini et al. (2020) provides conservative estimates.

Highlights:

- Viton and Neoprene had the highest and lowest tensile strength, respectively, once exposed to VOC contamination at the three test sites.
- Compared to PCE, Benzene showed to have more detrimental effect on the tensile strength of the three gasket materials.
- Model proposed by Hosseini et al. (2019 and 2020) predicts the tensile strength of the aged gasket samples in the field with an error range of 0-23% depending on the type of gasket material and the model used for calculation of saturation-dependence parameter (β).

5.2. Modeling of Contaminant transport

5.2.1. Benzene-contaminated sites

The hydraulic parameters of gasket materials (D , k_e) were calibrated after capsules' retrievals and contaminant-level measurements, as indicated in Table 4. The average, or best estimate, of the hydraulic parameters of each gasket material is presented in Table 5. The data used in the study included subsurface soil properties, plume distribution, as well as the capsule concentration measurements (C_c) at the retrieval periods and the monitoring well groundwater concentrations (C_w) at deployment/retrievals. The calibrated parameters are used to develop the numerical groundwater and contaminant transport model of each test site to predict the benzene and PCE breaking through gasket materials with time.

Table 4. Calibrated hydraulic parameters of gasket samples (D and k_e) for each site and after each deployment/retrieval

Site	Analyte	Sample	Exposure duration	D	k_e	Exposure duration	D	k_e
			(mo.)	(m ² /s)	(m/s)	(mo.)	(m ² /s)	(m/s)
Nashville	Benzene	Neoprene	4.5	3.89×10^{-13}	4.55×10^{-11}	7	3.78×10^{-13}	1.10×10^{-11}
		Buna-N		2.12×10^{-13}	1.00×10^{-12}		ND	3.70×10^{-11}
		Viton		3.40×10^{-14}	ND		ND	ND
Newton	Benzene	Neoprene	9	ND	1.40×10^{-11}	2	1.23×10^{-12}	4.50×10^{-11}
		Buna-N		ND	1.30×10^{-12}		4.54×10^{-13}	7.00×10^{-12}
		Viton		4.04×10^{-14}	ND		ND	ND
Durham	PCE	Neoprene	6	ND	ND	9	1.22×10^{-13}	9.0×10^{-12}
		Buna-N		ND	ND		1.32×10^{-13}	1.1×10^{-11}
		Viton		1.45×10^{-14}	ND		ND	ND

Table 5. Calibrated hydraulic parameters of gasket samples (D and k_e) for benzene and PCE used in prediction studies.

Analyte	Sample	k_e	D
		(m/s)	(m ² /s)
Benzene	Neoprene	2.89x(10 ⁻¹¹)	3.85x(10 ⁻¹³)
	Buna-N	1.45x(10 ⁻¹¹)	2.12x(10 ⁻¹³)
	Viton	ND	3.40x(10 ⁻¹⁴)
PCE	Neoprene	9.0x(10 ⁻¹²)	1.22x(10 ⁻¹³)
	Buna-N	1.1x(10 ⁻¹¹)	1.32x(10 ⁻¹³)
	Viton	ND	1.45x(10 ⁻¹⁴)

Benzene breakthrough of the gasket samples installed within capsules are determined per each time increment. Results are shown in Figure 2 for Neoprene (as an example,) after one, two, three, and four months at the Nashville test site.

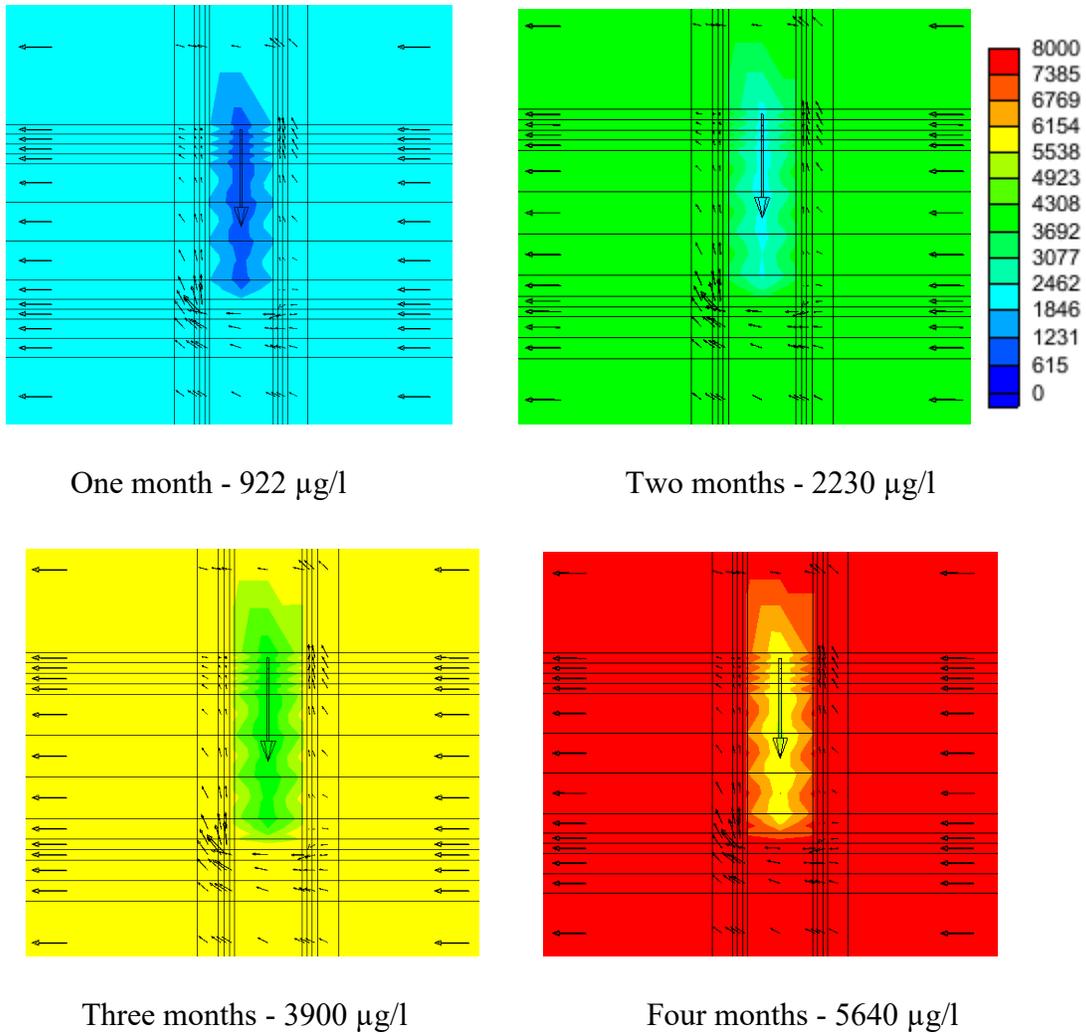
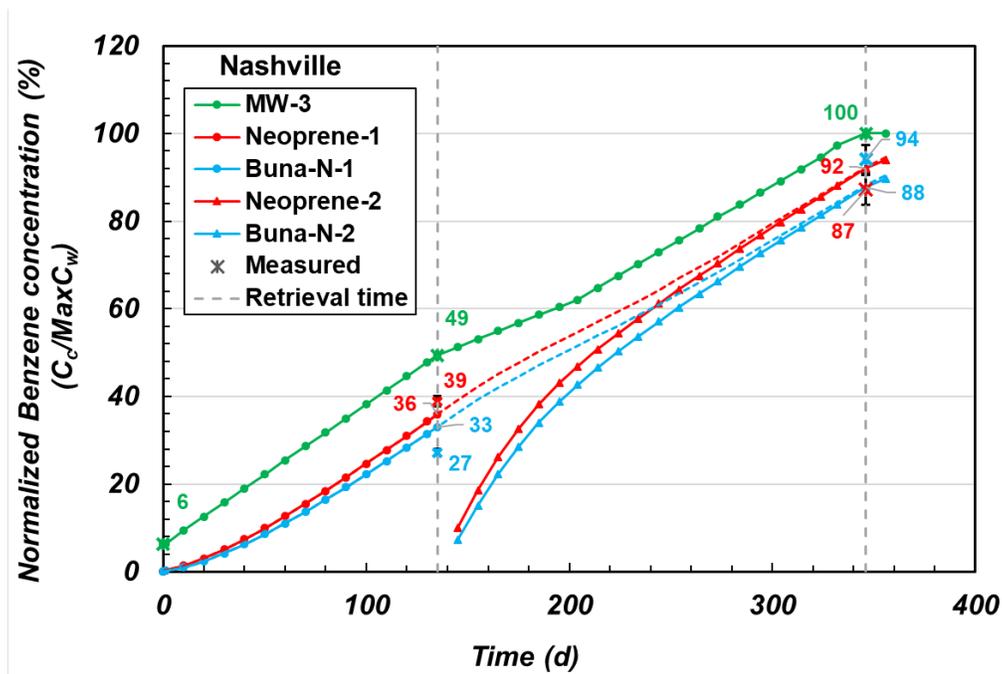
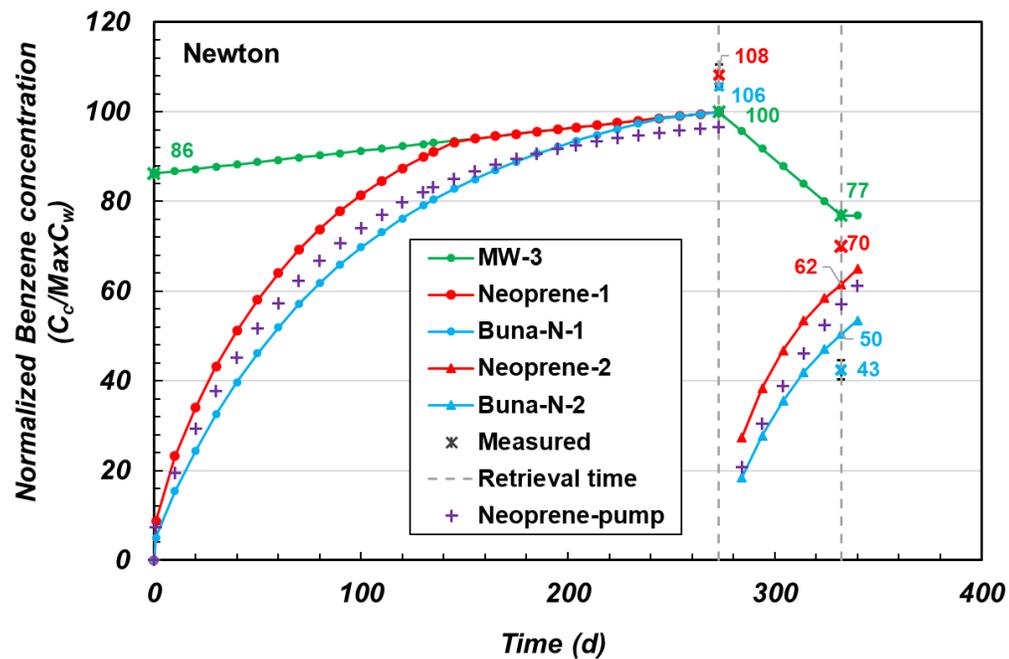


Figure 1. Benzene breakthrough of the sample (Neoprene) installed at the top of the capsule after one, two, three, and four months at Nashville site. The direction and relative magnitude of velocity vectors are shown.

Figure 3(a), 3(b) show plots of benzene concentration normalized with respect to maximum contaminant concentration in monitoring well groundwater at the Nashville and Newton sites.



(a) Nashville site



(b) Newton site

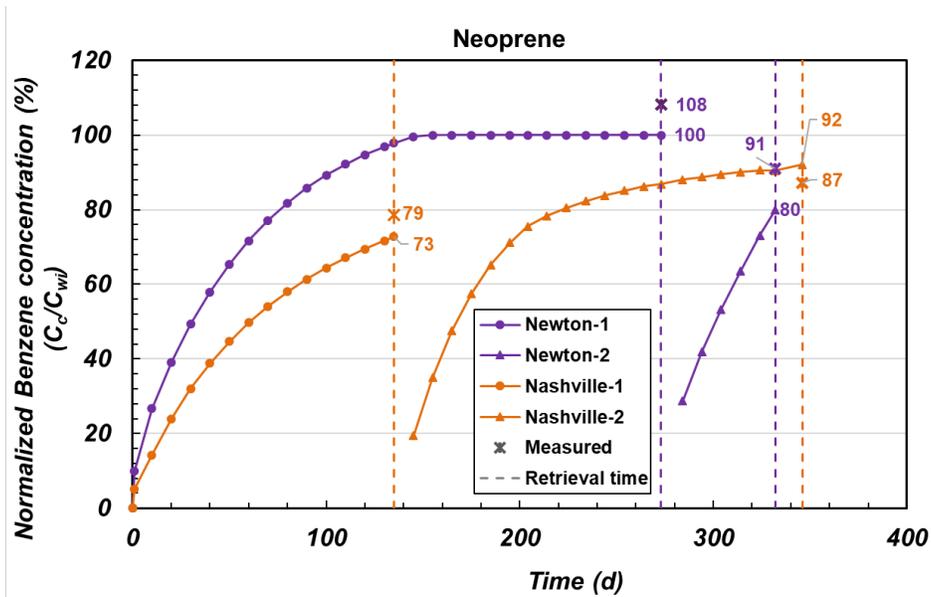
Figure 2. Normalized benzene breakthrough concentration (normalized with respect to maximum detected well concentration) using calibrated parameters of both gasoline contaminated sites (a) Nashville site (b) Newton site.

The measured concentrations from field groundwater samples (denoted as star symbols) have been compared with the simulation results in Figure 3(a) at each retrieval period. The simulated data are obtained using the calibrated model parameters in Table 5. The comparison shows good agreement between results from the model and measurements. At the Nashville site, the simulation run time was continued past the time of the first retrieval (dashed lines) and the results have been compared with the results of the second deployment and field measurements. The rate of breakthrough at the Nashville site was higher at the beginning of the second deployment, compared to the rate of breakthrough at the beginning of the first deployment, due to higher concentrations present within the monitoring well during the second deployment (see Figure 3(a)).

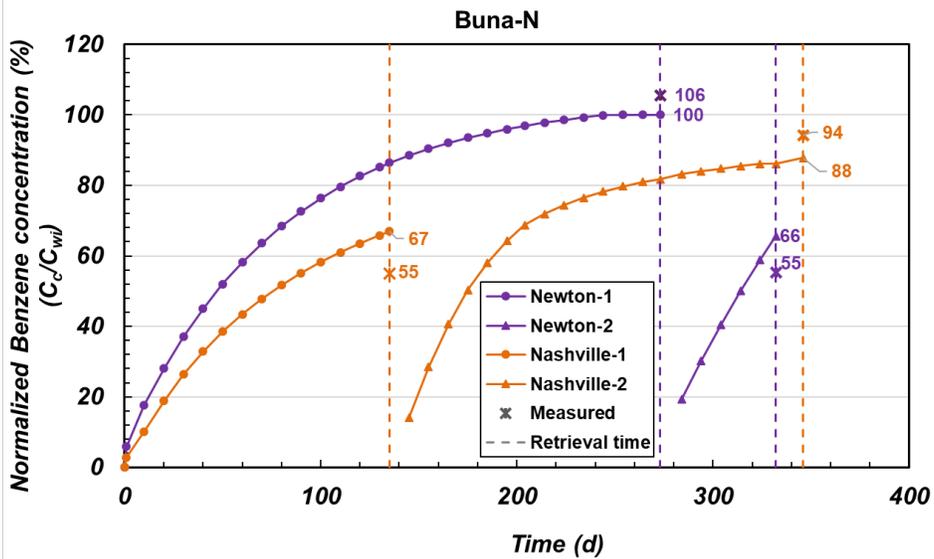
At the Newton site, results from modeling the first deployment indicate that both Neoprene and Buna-N show 100% breakthrough after 9 months, while Neoprene has higher breakthrough rate compared to Buna-N. The model results from the second deployment show that even though the concentration in well MW-3 decreases, the breakthrough will be 50-62% of monitoring well concentration, after two months which is similar to the breakthrough after first two months of the first deployment (2% differences). These results indicate the average magnitude of the fluctuated concentrations in monitoring wells affects more the breakthrough rate and concentration inside the capsules compared to the rate of rise or fall of chemical concentration in monitoring well. At the Nashville site, the rate of breakthrough was higher at the beginning of the second deployment and then decreases with the decreasing monitoring well concentrations. The rate of breakthrough was lower at the beginning of the first deployment and then increases within first two months. However, two months after both first and second deployments, the rate of benzene breakthrough would be constant, per using the average concentration of monitoring well during a two months period (Figure 3(b)). As explained in the description of Newton contaminated site, an extraction pump has been installed in MW-6 as a remediation method. A pumping rate of 0.7 liter/day was estimated according to the remediation system data. When the pump is operated the maximum reduction in normalized concentration is 9% (ex. C_c/C_{wmax} decreases from 93 to 84) as shown in Figure 3(b) with “purple markers.”

The concentrations have been normalized with respect to the monitoring well concentrations at each time interval in order to develop and propose a protocol for installation/retrieval of the capsules (Figure 4(a), 4(b)). The field measurement data and simulation results indicated the breakthrough of contaminant for each gasket material depends on the VOCs concentration and fluctuation at the deployment sites. Table 6 provides the error estimation of the calibrated model, indicating good agreements between model predictions and field measurements with an average error of 10%. Data from minimum normalized concentrations at each time interval, and data from the two sites of Nashville and Newton as well as comparison between the rates of breakthrough at each deployment, have been used to develop the protocol proposed in Table 7. The model predicts benzene breaking through the Neoprene and Buna-N will reach more than 69% and 64%, respectively, of the monitoring well concentration after 4 months. Since the capsules

were installed in the monitoring wells while assuming constant hydraulic gradient across each site, the obtained results represent the upper bound values, or the “worst case scenario.”



(a) Neoprene



(b) Buna-N

Figure 3. Benzene breakthrough rate for Neoprene and Buna-N normalized with well concentration at each time slot, comparing two sites and two deployment/retrieval (C_{wi} ; concentration measured in monitoring well at each time slot) (a) Neoprene (b) Buna-N

Table 6. Error estimation of calibrated model.

Site	Sample	Normalized Measured 1 st retrieval	Normalized Predicted 1 st retrieval	Normalized Measured 2 nd retrieval	Normalized Predicted 2 nd retrieval	Error 1 st retrieval (%)	Error 2 nd retrieval (%)	Average Error (%)
Nashville	Neoprene	79	73	87	92	7	5	10
	Buna-N	55	67	94	88	18	7	
Newton	Neoprene	108	100	91	80	8	12	
	Buna-N	106	100	55	66	5	16	

Table 7. Recommended protocol for installing/retrieval of gasket-capsules to monitor benzene breakthrough rate.

Normalized benzene breakthrough concentration with monitoring well concentration (%) (C_c/C_{wi})- predicted by field simulation				
	Sample/time	2 months	4 months	6 months
Minimum 2 sites	Neoprene	50	69	90
	Buna-N	43	64	85

Highlights:

- Numerical models have been developed to simulate conditions at the three field sites of study and results are used to calibrate hydraulic parameters of the proposed monitoring capsules (k_e , D) and predict breakthrough rates under field conditions.
- The diffusion coefficient (D) and equivalent hydraulic conductivities (k_e) of Neoprene and Buna-N were calibrated for benzene contamination. Very low breakthrough values were considered for the diffusion coefficient of benzene through Viton. Both gasket materials of Neoprene and Buna-N showed a higher rate of breakthrough compared to Viton.
- The numerical modeling shows breakthrough of contaminant for each gasket material depends on the field conditions and contaminant fluctuation within the domain. Results indicate benzene concentration breaking through the Neoprene and Buna-N gasket materials will reach more than 70% and 60% of the monitoring well concentration after 4 months, respectively.
- A protocol has been developed and proposed for deployment/retrieval of capsules to monitor breakthrough rates of VOC in the field.
- A summary of such protocol is as follows: if there is a contaminated site with known high concentrations of benzene so that 50% breakthrough of the background contamination level can be a risk to utilities based on a pre-described criteria, then 2 months or less is recommended for capsules installation/retrieval. If the site has lower known contamination level where a 70% breakthrough of the background contamination

level do not pose high risk, then the period of deployment can be extended based on the recommended protocol. A diagram of contaminant breakthrough presented in this study can guide such deployment.

5.2.2. PCE Contaminated Sites

Figure 5 shows PCE concentration normalized with respect to maximum concentration in the monitoring well groundwater sample (15,400 $\mu\text{g/l}$) at the Durham site. Since the measured concentrations within the capsules at first retrieval (17,920 and 13,970 $\mu\text{g/l}$) were higher than monitoring well groundwater sample concentration (9,900 $\mu\text{g/l}$) at the same time, it is hypothesized the contaminant concentration within the monitoring well fluctuated with time. It is noted that the purging processes during groundwater sample collection from monitoring wells yield aquifer concentration only at the time of capsule retrieval, and do not reflect concentration fluctuations in prior months (while data from sampling capsules will reflect such fluctuations.) The fluctuation of concentrations in monitoring well can be due to seasonal rainfall and changes in groundwater level. Furthermore, the spatially and temporally varying hydrologic conditions in heterogeneous sites pose significant variations to contaminant fluxes with time. For modeling purposes, it is assumed that both Neoprene and Buna-N gained 100% of monitoring well concentration at first retrieval, accordingly, the k_e was obtained to be 4.3×10^{-11} m/s for both materials at first retrieval. The results from the 3D numerical modeling of the contaminated site in Durham have been updated by incorporating the data from the second retrieval. Lower values were calibrated for k_e and D of Neoprene and Buna during the 9 months exposure of the second deployment, as presented in Table 4. Due to the lower concentration detected in capsule with Neoprene, the k_e and D of Neoprene are slightly smaller than the corresponding values for Buna-N. However, this slightly less concentration can be due to environmental conditions such as seasonal rainfall, temperature fluctuation, as well as multi-species diffusion, or even accuracy of the measured lab analyses of the water samples. Thus, the results herein should be viewed with caution as these do not necessarily reflect a better performance of Neoprene over Buna-N. The calibrated parameters are used in the numerical model to predict the PCE breaking through gasket materials with time, as a part of the development of deployment protocol. Figure 5 confirms similar trends of contaminant breakthrough with time for both Neoprene and Buna using calibrated parameters.

Figure 6 shows PCE breakthrough the gasket materials with time, normalized with respect to monitoring well concentration. The minimum normalized concentrations at each time step for Neoprene and Buna, as well as comparison between the rates of breakthrough at each deployment, have been used to develop the protocol presented in Table 8. The model predicts PCE breaking through the Neoprene and Buna-N will reach approximately 59% of the monitoring well concentration after 4 months. Due to the similar performance of Neoprene and Buna, the same protocol for installing/retrieval of both materials is proposed. It is noted that due to small concentrations detected in capsule with Viton (not detected), the parameters of this gasket type

were not well calibrated, however, the results indicate Viton performance against PCE and benzene significantly surpasses that of Neoprene and Buna-N.

The Peclet number is a parameter that is used to determine the dominant mode of transport (i.e., diffusion versus advection). Hatfield et al. (2004) indicated one order of magnitude relative difference between advective and diffusive transport processes (i.e. Peclet number=10) is needed to ensure advective dominated flux transport. Permeation-based samplers are typically used to directly measure contaminant mass flux (Verreydt et al. 2010). Hatfield et al. (2004) used a passive flux meter (PFM) to quantify cumulative contaminant mass flux. The Peclet numbers in experiments of PFM ranged from 43 to 415, hence indicating advective dominated transport. The Peclet number herein is calculated in the range of 24 -to- 50 as shown in Table 9. Such range of values, indicate in the simulation approach used to calibrate the capsules, advective transport dominates diffusive flux. Therefore, the simulation results are sensitive to the groundwater flow rate, hydraulic gradient and equivalent hydraulic conductivities of pipe samples.

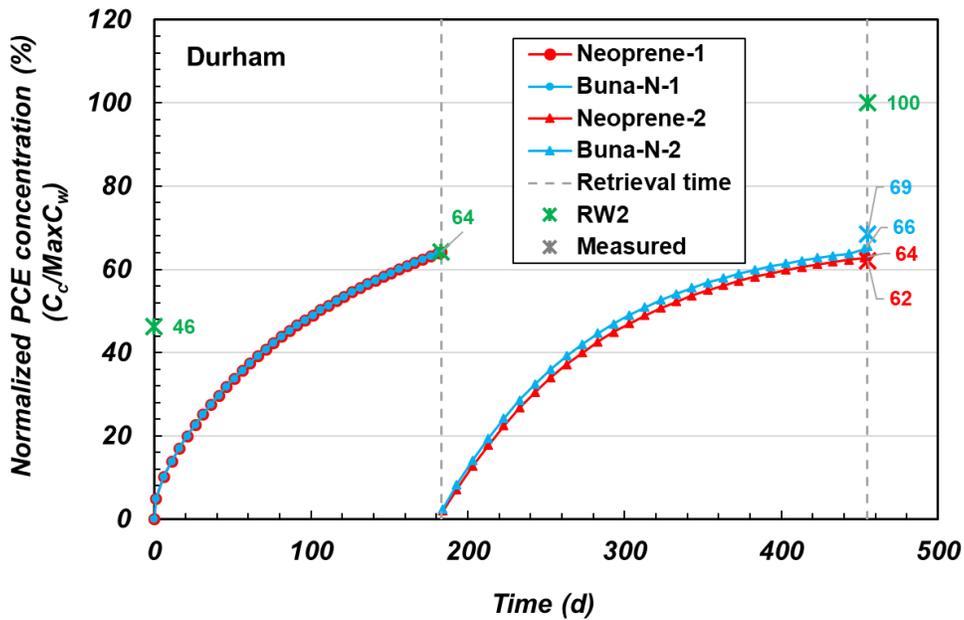


Figure 4. Normalized PCE breakthrough concentration with maximum detected well concentration in Durham site using calibrated parameters of PCE for contaminated site.

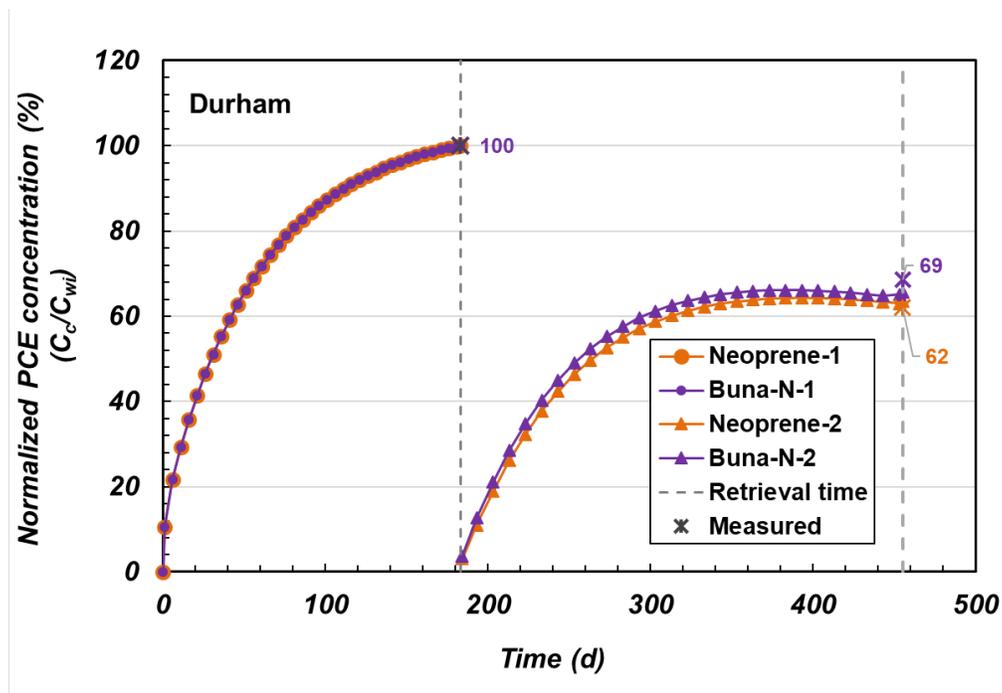


Figure 5. PCE breakthrough rate for Neoprene and Buna-N normalized with well concentration at each time slot comparing two deployment/retrieval (C_{wi} : concentration measured in monitoring well at each time slot).

Table 8. Recommended protocol for installing/retrieval of gasket-capsules to monitor PCE breakthrough rate.

Normalized PCE breakthrough concentration with monitoring well concentration (%) (C_c/C_{wi})- predicted by field simulation				
	Sample/time	2 months	4 months	6 months
Durham	Neoprene	42	59	64
	Buna-N	42	59	64

Table 9. Calculated Peclet number for benzene and PCE breakthrough in the gasket materials installed in capsule.

Peclet Number			
Sample/Site	Newton	Nashville	Durham
Neoprene	26.14	36.30	49.73
Buna-N	23.83	33.89	27.38

Highlights:

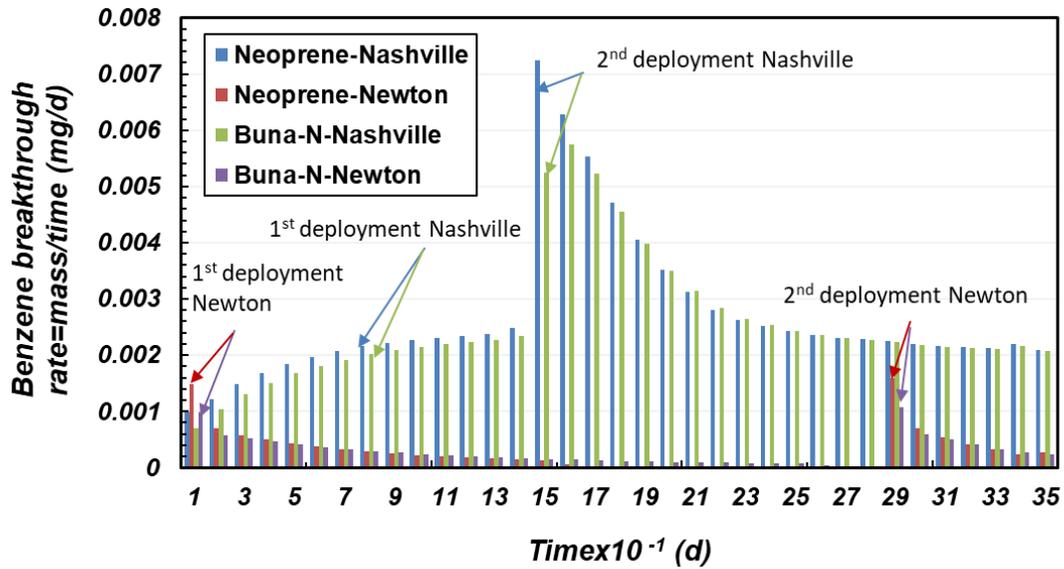
- Results from the contaminant transport numerical model indicate that PCE concentration breaking through Neoprene and Buna-N will reach around 60% of the monitoring well concentration after 4 months.
- A protocol has been proposed for installing/retrieval of capsules to monitor breakthrough rate of PCE.
- According to the recommended protocol, if there is a contaminated site with known high concentrations of PCE such that 40% breakthrough concentration poses a risk to utilities (PCE MCL is 5 µg/l, EPA 2002), then 2 months is recommended for install/retrieval of the monitoring capsules. If the site has known lower contamination level where 60% breakthrough concentration is not a high risk, then the period of deployment/retrieval can be extended based on the recommended protocol and diagrams of contaminant breakthrough presented in this study. The concentration level at Durham site was 7,120 µg/l during first deployment, so installation duration more than two months is not recommended for this site.

5.2.3. Mass breakthrough rate of Benzene and PCE

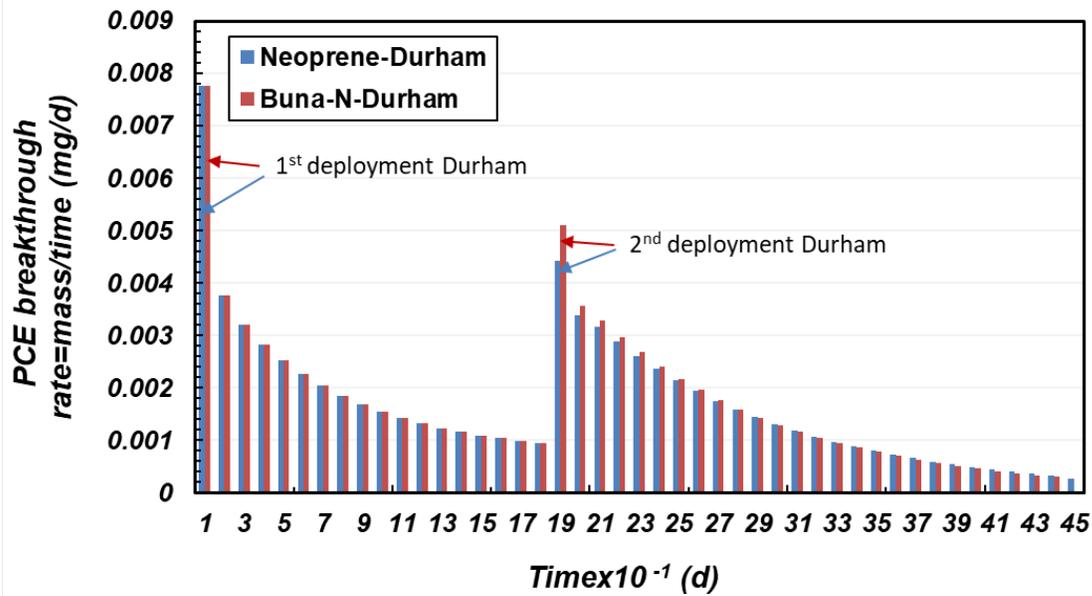
The numerical analyses showed gasket materials of Neoprene and Buna-N have approximately similar performances with a higher rate of contaminant breakthrough compared to Viton. The mass breakthrough rates of benzene at Nashville and Newton sites were obtained for Neoprene and Buna-N as shown in Figure 7(a). The data show the trend and variation of breakthrough rates with time at different study sites. A power relationship of “mass breakthrough rate with time” was obtained for each deployment period per study site (Equation 2).

The results indicate that despite considering linear relationship for monitoring well concentrations between deployment and retrievals, the mass breakthrough rate relationship shows nonlinearity with time which is not simply predictable, and varies from site to site, and at each deployment period. The mass breakthrough rate can be increasing with time (e.g., first deployment at Nashville), or can be decreasing (ex. second deployment at Nashville). The nonlinear relationships are also shown for mass breakthrough rates of PCE at Durham site obtained for Neoprene and Buna-N. The results are presented in Figure 7(b) and the relationship parameters are indicated in Table 10. As shown in Figure 7(a), (b) and Table 10, there is no unique relationship for mass breakthrough rate, however, the results of benzene breakthrough at two sites, show after a certain amount of time, the concentration exchanges between capsules and monitoring wells reach steady state and mass breakthrough rates follow an approximately constant trend with time. As an example, the mass breakthrough rate for Neoprene at Nashville site reached steady state (0.0023-0.0025 mg/d) after three months since first deployment, and reached 0.0020-0.0023 mg/d after four months from second deployment. The mass breakthrough rate at Newton site reached

steady state after maximum four months since first deployment, however, the mass breakthrough rate at steady state was as low as 10^{-4} mg/d due to lower concentration detected at this site. The results show PCE needs more time than four months to reach steady state condition.



(a) Benzene



(b) PCE

Figure 6. Mass breakthrough rate with time (a) Benzene, (b) PCE.

Table 10. Mass breakthrough rate parameters.

Site	Analyte	Gasket Material	1 st deployment			2 nd deployment		
			a	b	R ²	a	b	R ²
Nashville	Benzene	Neoprene	0.001	0.354	0.99	0.0081	-0.468	0.96
		Buna-N	0.0008	0.448	0.98	0.0068	-0.404	0.92
Newton	Benzene	Neoprene	0.0031	-1.37	0.87	0.0015	-0.94	0.98
		Buna-N	0.0017	-0.96	0.86	0.0011	-0.745	0.99
Durham	PCE	Neoprene	0.0073	-0.688	0.99	0.0088	-0.88	0.86
		Buna-N	0.0073	-0.688	0.99	0.0094	-0.903	0.88

Highlights:

- Nonlinear power relationships have been calibrated for mass breakthrough rate of the contaminant soluble phase with time. At the two benzene-contaminated test sites, the mass breakthrough rate reached steady state condition after three to four months from deployment.
- Results indicated in the case of PCE that more than four months is needed to reach steady state flux of the soluble phase within the monitoring capsules.

6. Findings and Recommendations

Based on the data of experimental and modeling results presented herein, the following conclusions and recommendations are advanced:

- A new monitoring approach was designed and tested to evaluate volatile organic compounds (VOCs) breaking through three gasket material types used by NCDOT at pipe joints: Neoprene, Buna-N, and Viton. This monitoring tool, in the form of metallic capsules can be of considerable value in providing data for assessment and management of subsurface utility materials potentially located in contaminated areas.
- Benzene showed higher diffusivity than PCE in all three gasket materials (Neoprene, Buna-N, and Viton) aged under field condition.
- Regardless of type of contamination, Viton had the highest resistance to the diffusion of VOCs studied in this project (benzene and PCE). Neoprene showed the lowest resistance to the diffusion of VOCs (benzene and PCE).

- The proposed monitoring capsules could successfully be used in assessing the performance of various gasket materials as a concrete pipe hardening method in contaminated areas.
- Viton had the lowest tensile strength loss while Neoprene showed the highest loss of strength. The tensile strength of gasket materials exposed to contamination under field condition was further reduced with increasing exposure time.
- Results of tensile strength measurements are in concert with the results of diffusivity quantification for both benzene and PCE and gasket materials used in this project (Neoprene, Buna-N, and Viton).
- Tensile strength model proposed based on the lab results was demonstrated to predict the tensile strength of gasket materials aged under field condition with an error range of 0-23%. The magnitude of error is reduced when a parameter accounting for the contamination concentration level is introduced into the predictive equation.
- Results from 3D numerical developed for the sites of study are used to calibrate hydraulic parameters of the monitoring capsules (k_e , D). The diffusion coefficient (D) and equivalent hydraulic conductivities (k_e) of Neoprene and Buna-N were calibrated against benzene and PCE; such values, not reported in literature, are valuable to have in future prediction models. A very low value was calibrated for diffusion coefficient of Viton. Both gasket materials of Neoprene and Buna-N showed a higher rate of contaminant breakthrough compared to Viton.
- The model predicts benzene concentration breaking through the Neoprene and Buna-N will reach more than 70% and 60% of the monitoring well concentration after 4 months, respectively. Benzene breakthrough reaches 85% to 90% of monitoring well concentration after 6 months.
- The model predicts PCE concentration breaking through the Neoprene and Buna-N will reach 59% of the monitoring well concentration after 4 months. PCE breakthrough reaches 64% of monitoring well concentration after 6 months.
- A protocol has been proposed for installation/retrieval of capsules to monitor VOC breakthrough rates. According to the recommended protocol, if there is a contaminated site with known high concentrations of PCE such that 40% breakthrough concentration poses a risk to utilities, then 2 months is recommended for installation/retrieval of the monitoring capsules. If the site has known lower contamination level where 60% breakthrough concentration is not a high risk, then the period of deployment/retrieval can be extended based on the recommended protocol and diagrams of contaminant breakthrough presented in this study.

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Appendix A: Literature review

In this appendix, the existing knowledge on the effect of soil and groundwater contamination on the performance of subsurface utilities such as pipes and gaskets is presented.

This new idea of capsule development for pipe material monitoring can be related to passive integrative samplers in groundwater studies. They are similar in components but different in application. The conventional time-discrete grab sampling provides a snapshot of pollutants only at the time and place of sampling, failing to account for episodic contamination events. Integrative sampling is introduced as an alternative to discrete-sampling for identifying a wide range of volatile and semi-volatile micropollutants over extended timeframes, from hours to months (Vrana et al. 2001).

Integrative samplers requiring mechanical work on the environment to transfer the contaminant-bearing phase to the sampling phase are referred to as ‘active’, while those relying on diffusion or environmental advection are termed ‘passive’ (Roll and Halden 2016, Lohmann et al., 2012, Vrana et al. 2001, 2005).

Previous studies have shown continuous active samplers can successfully detect analytes in water (Ellis et al., 2009, Coes et al. 2014, Roll and Halden 2016). Coes et al. (2014) used a continuous low-level aquatic monitoring (CLAM) sampler consisting of a nylon body containing a low-flow pump and two extraction disks that continuously draws water through solid-phase extraction media. The active samples were deployed four times for a duration of 19-23 hours with a period of 7 days between deployments. The passive samplers, consisting of solid-phase sorbent contained between two sheets of polyethersulfone membrane, were submerged for the duration of 29-day deployment period. By comparing continuous active sampling method, continuous passive, and discrete sampling methods for the sampling of trace organic compounds (TOCs) in water, Coes et al. (2014) found a greater number of TOCs detected in active samplers, but lower concentrations than the other methods. The variability in the results between the three methods was affected by variability in stream discharge and possibly constituent loading. Roll and Halden (2016) suggested that active samplers have the potential to reduce more sampling rate and analyte uptake errors, by applying high-precision mechanical pumps, instead passive samplers can increase the number of replicates due to much lower cost, thereby increase spatial coverage of environmental monitoring. Furthermore, some studies reported that peak concentrations pass the monitoring well may not be noticed in active sampling because this kind of monitoring is not continuous (Verreydt et al. 2010).

Passive sampling methods have shown to be a promising tool for measuring aqueous concentrations of a wide range of priority pollutants. Depending on sampler design, the mass of pollutant accumulated by a sampler can reflect either the in-situ concentration with which the tool is at equilibrium or yield time-weighted averages of concentrations in water over the period of

deployment. Passive tools have been invented for monitoring air quality since the early 1970s. Later, the principles were applied in monitoring in aqueous environments (Vrana et al. 2005). The passive samplers are low-cost and suitable to use at remote sites without vandalism (Vrana et al. 2001).

Passive samplers, generally, consist of a receiving phase enclosed within a permeable housing or membrane bag which are used to measure dissolved gases and volatile organic compounds (VOCs) in groundwater at contaminated sites (Hatfield et al. 2004, Namiesnik et al. 2005). The receiving phase can be solvents, solid-phase extraction sorbent, chemical reagent or even distilled water (Verreydt et al. 2010). Passive samplers in some other design approaches consist of a sealed container with a semipermeable membrane material at the top (Divine and McCray 2004, Ma et al., 2013). Vrana et al. (2001) used a passive sampler consisting of a stir bar coated with poly dimethylsiloxane (PDMS) enclosed in a membrane bag that acts as a receiving organic phase. Upon exposure to solution with constant concentrations, Vrana et al. (2001) derived sampling rate of system using an overall mass-transfer coefficient, membrane surface area, and porosity. They correlated mass-transfer coefficient to diffusion coefficient, thickness of membrane and sampler-water partition coefficients. Divine and McCray (2004) employed passive samplers to estimate equilibration times for several dissolved gas and common VOCs. To predict equilibration times, diffusion coefficients (D_m) of low-density polyethylene membranes (LDPE) employed in samplers were estimated analytically and experimentally. Additionally, a numerical model was developed to evaluate the “lag time” for conditions in which in situ concentrations are temporally variable. Studies have shown that trace organic compounds (TOCs) detected by passive samplers are strongly controlled by sampling rate for the TOC, which can be difficult to define because of many variables, including water velocity, water temperature, and biofouling (Alvarez 2010, Morin et al. 2012, Coes et al. 2014). The passive samplers can be classified as i) diffusion-based passive samplers in which the transport of the contaminants through the housing membrane of the sampler is diffusion-limited and advective transport through the housing is inhibited, and ii) permeation-based passive samplers in which the groundwater flow gradient is the driving force that induces the advective transport of the contaminant through the housing (KotWasik et al. 2007). Using diffusion-based samplers, Fick’s first law is used to calculate uptake rate, while variations in water level and groundwater flow rate can still influence the uptake rate and may not be considered using Fick’s first law.

In situ concentration measurements can vary substantially because of the spatial and temporal variability of the source mass, natural gradient, the pathway patterns of biogeochemical processes, degradation, sorption, desorption, dissolution, as well as human activities (Verreydt et al., 2010). Ma et al., (2013) used a passive diffusion bag (PDB) sampler filled with deionized water in low-density polyethylene (LDPE) tubes to evaluate equilibration time and partitioning of VOCs between the sampler and the water sample. They compared the VOC soluble phase from PDB samplers after 14 days. They measured diffusion coefficient of sampler (D_m) by using time required to reach 90% equilibration of sampling ($t_{90\%}$) in the laboratory. The diffusion coefficient

of benzene through LDPE membrane with 100 μm thickness was measured to be $2.84\text{-}8.34 \times 10^{-10}$ cm^2/s .

In the present study, the monitoring capsules are developed based on the idea of passive samplers to evaluate the mass transport properties of pipe materials. A sample of pipe gasket was installed at the top of a sealed aluminum capsule, and then was deployed in monitoring wells located in contaminated sites with chlorinated solvents (from dry cleaning operations) and gasoline (at gas stations) for specific periods. The resident analytes flow from the surrounding media and break through across the pipe material during the sampling period. Afterwards, the capsules are retrieved and the analytes of benzene and PCE inside the capsules were measured. The potential differences between concentrations of two constituents inside the capsule and monitoring well, as well as hydraulic gradient in site prompt the rate of breakthrough in the pipe materials. Modeling approaches were used to simulate site condition of installed capsules. The capsules were calibrated using the measurement data and the hydraulic parameters of pipe materials. Next, the calibrated parameters were used in simulations to predict the rate of breakthrough and a protocol was recommended for installation/retrieval of capsules to monitor PCE and benzene breakthrough rate.

Appendix B: Field sites

Three sites have been identified for field evaluation of capsules; i. Nash county maintenance depot in Nashville, NC (gasoline contaminated site), ii. NCDOT maintenance facility project in Newton, NC (gasoline contaminated site), and iii. Triangle Laundromat in Durham, NC (chlorinated solvent contaminated site). Benzene and Tetrachloroethylene (PCE) have been assessed as the dominant concentrations in the gasoline and chlorinated solvent contaminated sites, respectively.

B.1. Nashville gasoline contaminated site

Figure B1 shows a plan view of the Nashville site map including monitoring well locations and benzene plume distribution (Wood Inc., 2019). The subject site includes vehicle and equipment storage, maintenance, and vehicle fueling station. The gradient of groundwater flow is to the southwest of the site with an approximate average hydraulic gradient of 0.01 ft/ft. Historical data show fluctuations in groundwater elevation over time, and the largest fluctuation was observed in MW-12 at approximately 7.8 ft (Wood Inc. 2019). Several geological borings were advanced to a depth of 16 ft bgs to investigate soil types and properties. According to geologic cross-sections (ATEC Inc. 2012) and soil sampling reports (AMEC Inc. 2013) native soils generally consisted of red to brown clayey silt, sand and sandy silt at the impacted site.

The soil contamination was observed for the first time in 1990, when seven 1,000 to 10,000-gal capacity gasoline and diesel underground storage tanks (USTs) were removed from a fueling pavilion at the site. Accordingly, between 1991 to 2016, 17 monitoring wells (MW-1-17) were installed and screened to a maximum depth of 35 ft below ground surface (bgs) (Wood Inc. 2019). Benzene, toluene, ethylbenzene, xylenes (BTEX), methyl-tert-butyl-ether (MTBE), and diisopropyl ether (DPE) concentrations were detected in groundwater samples in excess of the North Carolina groundwater quality standards (2L Standards). Benzene has been the dominant contaminant with the highest detected concentration in MW-3, thereby the capsules were deployed in this monitoring well in March 2020. Table B1 indicates MW-3 characteristics and gathered data during capsule first deployment. Three in situ chemical oxidation (ISCO) pilot tests were performed by Wood Inc. in 2016, 2018 and, 2019 which reduced concentrations significantly, however, concentrations remained in excess of the gross contamination levels (GCLs) in some of impacted monitoring wells (Wood Inc. 2019).

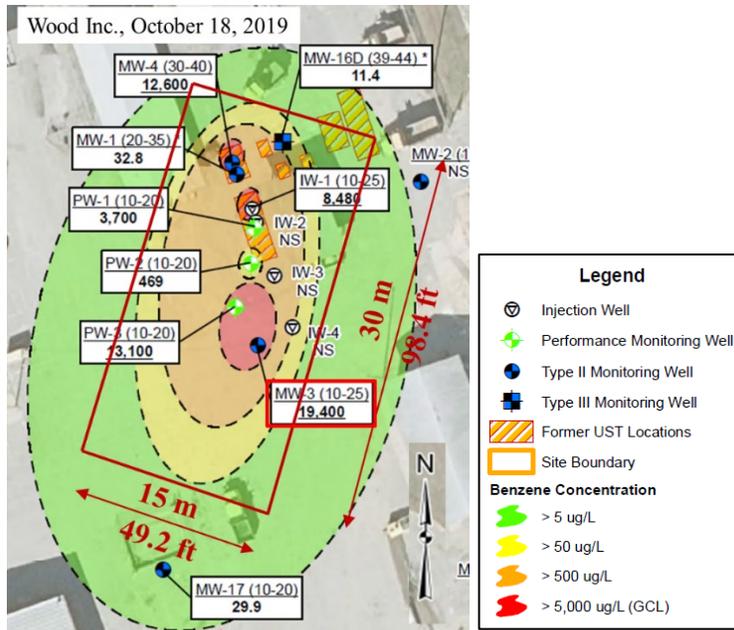


Figure B1 Nashville site map and model domain (after Wood, 2019).

B.2. Newton gasoline contaminated site

The Newton site map, including the location of monitoring wells, the extent of benzene plume and the model domain is shown in Figure B2. The subject site is used as a maintenance and equipment facility yard for NCDOT. The site is placed within the Piedmont area of North Carolina. The soil layers consist of sandy to silty clay fill from the surface to a depth of 5 to 10 ft. The fill soils are generally underlain by sandy silts to a depth of approximately 60 ft, where the partially weathered rock was encountered. Results from the slug test indicated hydraulic conductivity at the site ranging from approximately 0.005 ft/d to 0.35 ft/d with an average hydraulic conductivity of 0.06 ft/d (2×10^{-7} m/s). The horizontal gradient is 0.01 ft/ft to the northwest, and based on the hydraulic conductivity of 0.06 ft/d, and assumed porosity of 0.25, the groundwater seepage velocity is estimated to be approximately 0.88 ft/yr. The hydraulic gradient in the domain is 1% toward the west. The capsules were installed in MW-3. The source area is mainly located around MW-6 where the former gasoline USTs and dispensers have been installed.

According to Hart & Hickman, PC. (2018), contaminated soils were detected in 2003 due to gasoline release from the former UST system in the area. Free gasoline product was observed in MW-6 (Figure B2) with groundwater sampling revealing VOC contamination. The detected contamination included benzene at concentrations up to 35,000 $\mu\text{g/l}$. Benzene was detected in shallow groundwater at concentrations up to 35,000 $\mu\text{g/l}$, which exceeded the groundwater standard of 1 $\mu\text{g/l}$ and the Gross Contamination Level (GCL) of 5,000 $\mu\text{g/l}$. Ethylene dibromide (EDB) and 1,2-dichloroethane (DCA) were also detected at concentrations exceeding GCLs (50,

400 µg/l). Free product recovery and soil treatment systems were initiated from 2004 by using soil vapor extraction remediation system (SVE) (2004), a free product recovery system (2008), in-well aeration system (IWS) (2011), and re-installation of a free product removal pump in MW-6 (2012). The remediation system is currently active.

Sampling of monitoring wells commenced in 2013 and continues to the present time. Free product thickness at MW-6 was measured as rebounding to 0.6 ft in 2018 while it had decreased to 0.01 ft in thickness during product recovery in previous years. Petroleum-impacted groundwater extends from the previous UST domain (around MW-6) primarily to the west, and slightly to the north. The highest concentrations were detected in monitoring well MW-3, which is located down-gradient of the source area. In March 2020, the groundwater level and concentrations were measured in MW-3 immediately before capsule installation. The results are shown in Table B1.

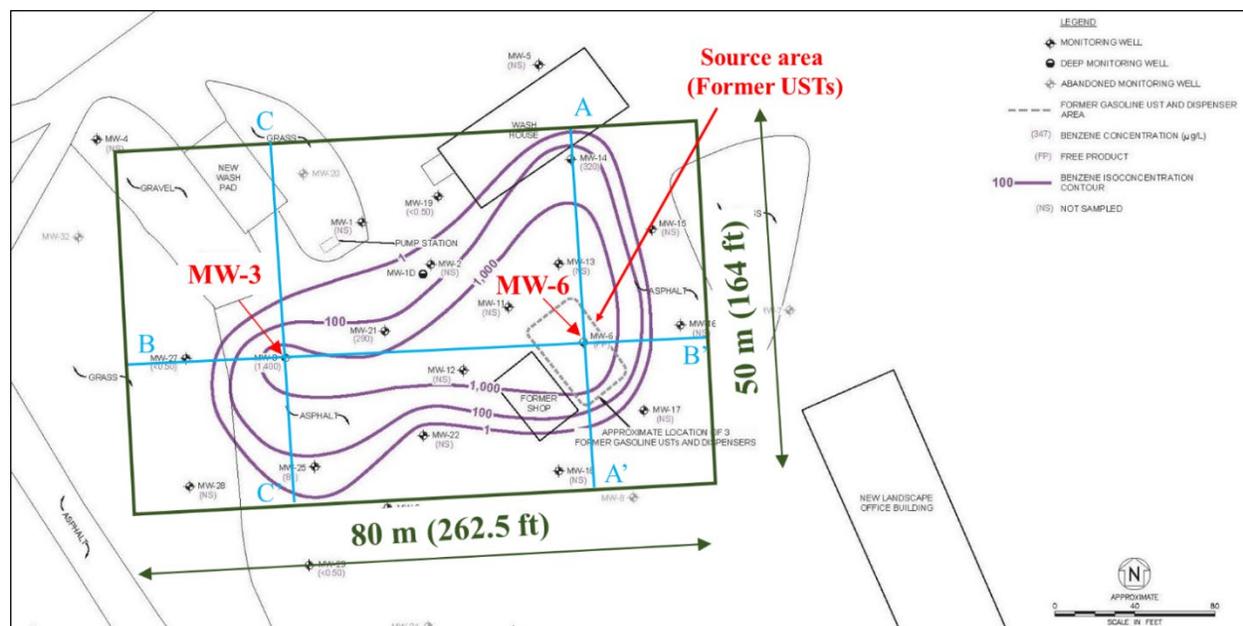


Figure B2 Newton site map and model domain (after Hart & Hickman 2018, Pace analytical services report 2020).

B.3. Durham chlorinated solvent contaminated site

Figure B3 shows a plan view of Durham site map which indicates the extent of chlorinated solvent distribution from sampling events from 2008 to 2010, and monitoring well locations. The subject site includes dry cleaning facility and laundromat which has utilized PCE in its dry cleaning operations since its inception in 1984 (URS 2015). The site stratigraphy, hydrogeology and aquifer characterization data from preliminary site assessment reports have been gathered in the site assessment reported by URS Corporation (2015). The soil layers consist of dark red to reddish-brown silty clay to a depth of 27 ft which gradually transitioned to sandstone/mudstone at 27 to 65

ft. The flow direction is toward south-southeast with a very low hydraulic gradient (<1%). The average hydraulic conductivity from slug test data is 125.5 cm/yr (4×10^{-8} m/s). The depth to groundwater level ranges from 0.5 to 26.8 ft bgs (URS 2015).

PCE, Trichloroethylene (TCE), and 1,2-dichloroethylene (1,2-DCE) were detected at monitoring wells and PCE was at the highest levels above the North Carolina 2L Standard of 0.7 $\mu\text{g/l}$ and GCL 700 $\mu\text{g/l}$. The GCLs for TCE, and 1,2-DCE are 3,000, and 60,000 $\mu\text{g/l}$, respectively. Among the monitoring wells in the vicinity of dry cleaner facility, RW-2 was chosen to deploy capsules. PCE was the dominant contamination with 88,000 $\mu\text{g/l}$ detected in RW-2 in 2008. The monitoring well concentrations were updated during capsule deployments as indicated in Table B1.

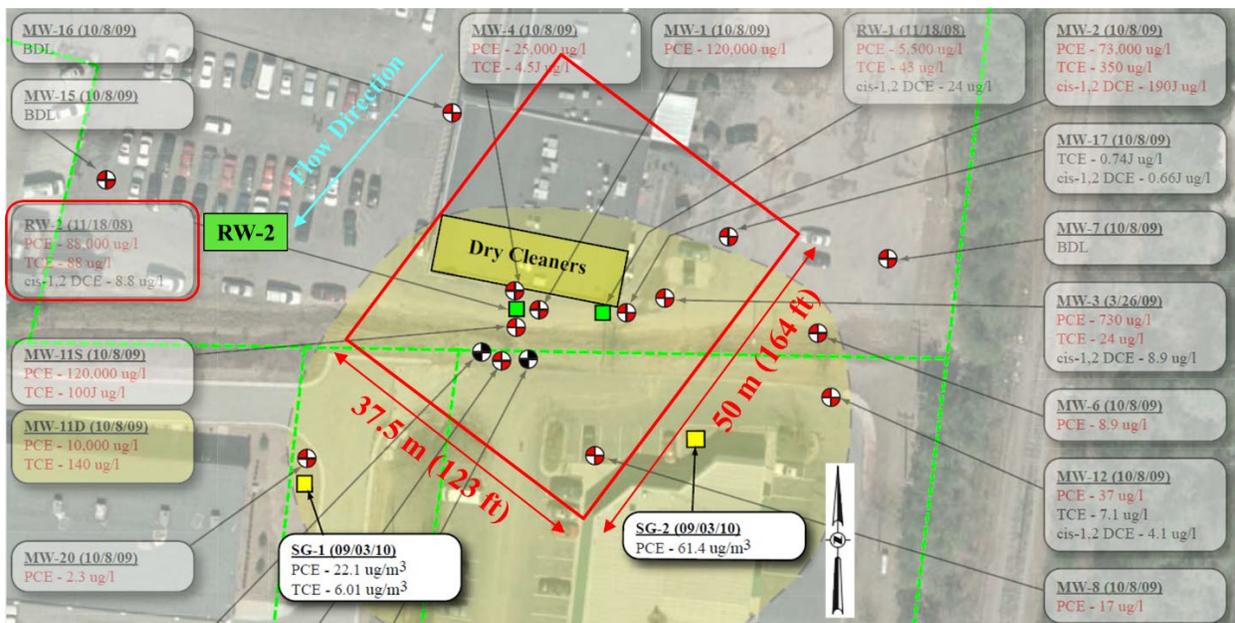


Figure B3 Durham site map and model domain (After URS 2015).

Table B1 Monitoring well characteristics and detected VOC concentration before and during capsule deployment.

Site	Nashville	Newton	Durham
Monitoring well ID (capsule location)	MW-3	MW-3	RW-2
Depth (m)	6.30	10.60	7.60
Depth to groundwater (m)	4.47	6.55	1.70
Analyte	Benzene	Benzene	PCE
Well concentration before 1 st deployment (ppb) in 2019	19,400	350	88,000*
Well concentration at 1 st deployment (ppb) in 2020	506	1,380	7,120
Well concentration at 2 nd deployment/1 st retrieval (ppb) in 2020	8,990	1,600	9,900
Well concentration at 2 nd retrieval (ppb) in 2021	18,200	1,230	15,400

* The last reported concentration for this well before study commencement in 2020 was on Nov. 2008.

Appendix C: Experimental part 1

C.1. General information

In this section, first, the properties of materials and tools used in the field investigation are provided. Next, protocols for deployment and retrieval of the capsules and gasket samples for tensile strength degradation measurements are discussed. In addition, sampling method from the capsules and preparation of aged gasket samples for quantification of tensile strength degradation are presented. Finally, the models used for estimating tensile strength degradation of gasket materials exposed to water contaminated with benzene and PCE are introduced and explained.

C.2. Materials and tools

C.2.1. Gasket materials

Three commercially available types of rubber sheets i.e., Neoprene, Buna-N, and Viton® were purchased and the specimens for tensile strength measurements were prepared manually using a die with the dimensions specified for type C dumbbell specimens according to ASTM D412 (Figure C1). The thickness of sheets was 0.125" as stated in ASTM D412. After preparing gasket samples, tensile strength of gasket materials in their original or unaged condition (i.e., before exposure to any solution) was obtained based on ASTM D412 and the results are presented in Table C1.

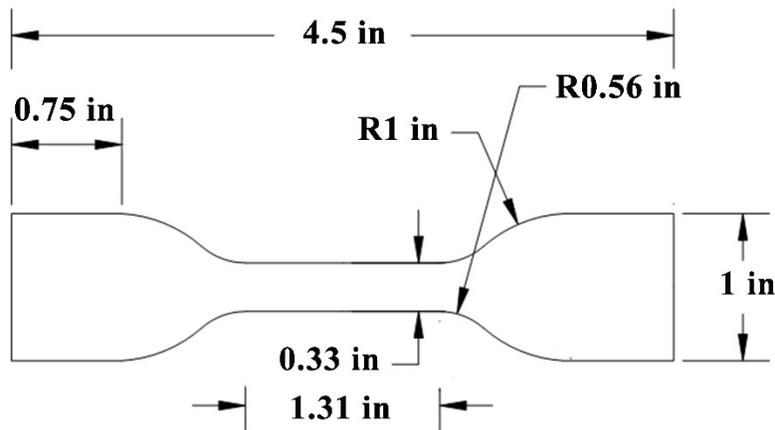


Figure C1. Dimensions of rubber gasket samples for tensile strength measurements.

Table C1. Tensile strength of gasket materials on original materials (unaged condition).

Property	Neoprene	Buna-N	Viton
Tensile strength (psi)	425 ± 5	875 ± 15	900 ± 40

C.2.2. Capsules for VOCs diffusivity quantification in the field

Aluminum capsules were prepared to quantify the diffusivity of benzene and PCE at the contaminated sites. It consists of a lid which can accommodate a gasket sample and a cup that is filled with clean water (e.g., mineral water) as a receiving medium (Figure C2). VOCs available in the monitoring well diffuse through the gasket sample placed in the capsule's cap and accumulate in clean water in the capsule's cup. Note that using aluminum to prepare capsules makes them an economical and light weight choice for assessing the performance of pipe materials and materials used for hardening purposes.



Figure C2. Capsule prepared for field investigation in this project.

To prepare capsules for deployment at the selected sites, cups were filled fully with clean water (mineral water) to achieve headspace-free capsules. Capsules were sealed using Teflon tape as shown in Figure C3. Also, mineral water was acidified with maleic and ascorbic acids (5 and 0.625 g/L, respectively), following EPA method 524.3 (Prakash et al., 2009) to avoid losing diffused VOCs due to bacterial growth in the capsules during the exposure period in the field. Three capsules for each gasket materials were prepared and deployed at each site for each specific exposure period.

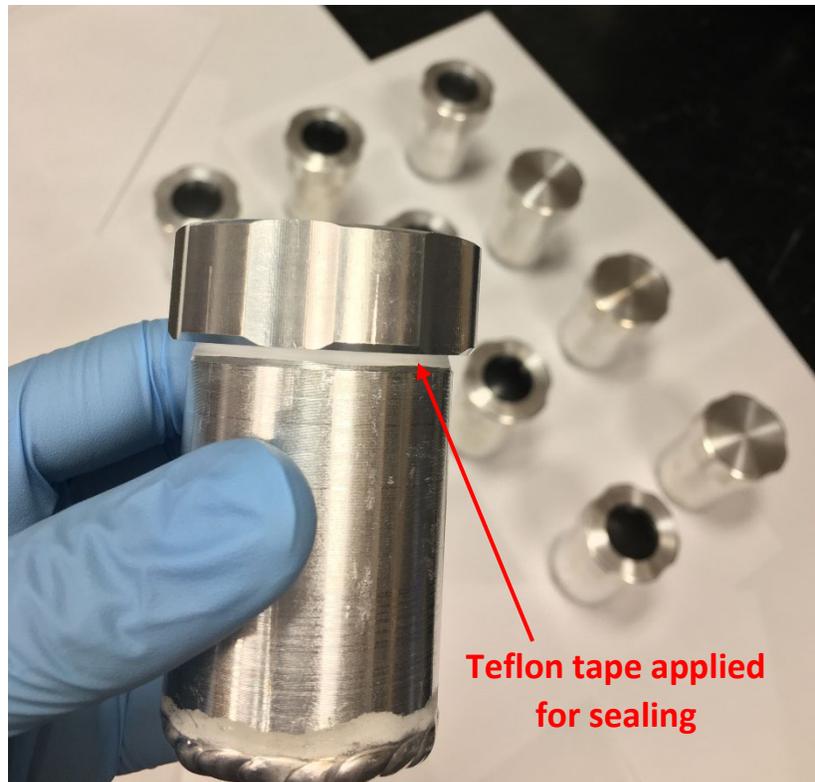


Figure C3. Sealing the capsule by applying Teflon tape between the cap and cup.

C.3. Methods

C.3.1. Deployment and retrieval protocols for capsules and gasket samples

After preparing capsules and gasket samples for tensile strength degradation measurements, they were transported to the selected sites and deployed in the monitoring wells. Capsules were tied up using stainless steel wire and hung in the well from the well's cap (Figures C4 and C5). In addition, gasket samples were installed in the monitoring wells following the same method employed for capsules (Figure C6 and C7).



Figure C4. Capsules tied up with stainless steel wire for deployment in the monitoring well.



Figure C5. Installation of capsules in the well. Capsules are hung from the well's cap.

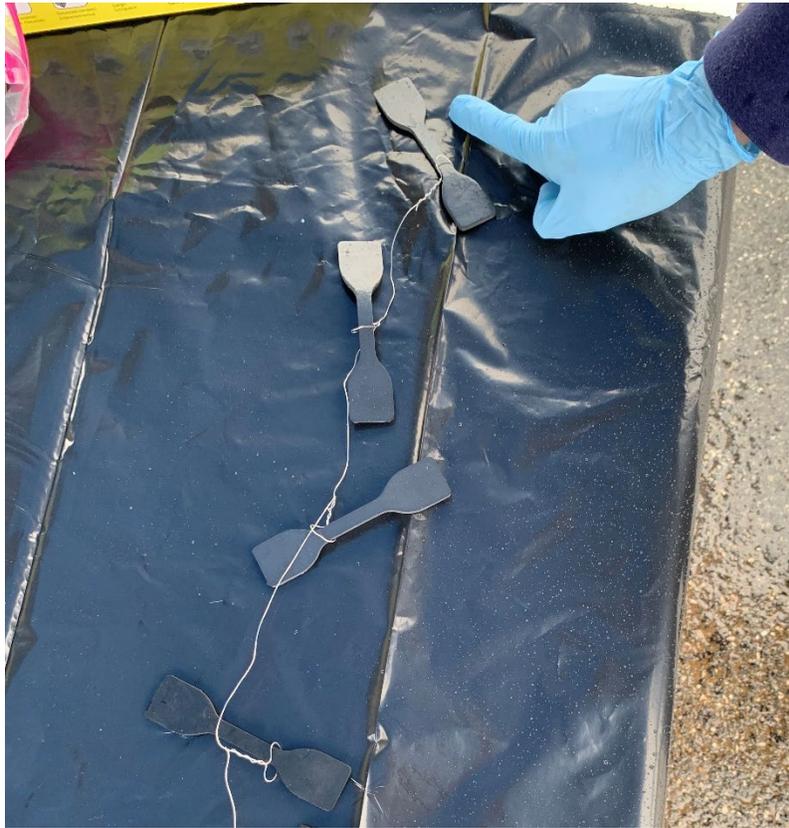


Figure C6. Gasket samples for measuring tensile strength degradation tied together before deployment in the monitoring well.



Figure C7. Deployment of gasket samples in the monitoring well.

Capsules and gasket samples were kept in the monitoring wells until the selected exposure times for each site. After exposure duration, capsules and gasket samples were retrieved from the monitoring well and washed with deionized water on site (Figure C8). Capsules were then surface dried using paper towels and placed in a cooler with ice packs for transportation to the lab. Upon arrival at the lab, capsules were immediately transferred to a fridge to avoid any VOCs degradation. Also, gasket samples were dried with paper towels and transferred to the lab for tensile strength measurements.



Figure C8. After retrieval from the monitoring wells, capsules and gasket samples were washed on site before transportation to the lab.

C.3.2. Sampling from the capsules after retrieval

Once retrieved, capsules were transported to the lab at NC State University and immediately placed in a fridge kept at $39 \pm 0.5^\circ\text{F}$. Within 24 hours after retrieval, sampling from capsules were performed. Using a Hamilton gastight® syringe, two samples ($500 \mu\text{L}$ for benzene measurement, $1000 \mu\text{L}$ for PCE measurement) were taken from each capsule and then diluted to a total volume of 42.7 mL with deionized distilled water (ASTM type II water) previously acidified with ascorbic and maleic acids (5 and 0.625 g/L , respectively, following EPA method 524.3 by Prakash et al., 2009). The resulting headspace-free vials were gently turned upside down three times to ensure a well-mixed solution. Next, samples were kept in a refrigerator at a temperature of 39°F until VOC analysis by gas chromatography-mass spectrometry (GC-MS). Concentrations of VOCs were measured by GC-MS adopting a method based on EPA Method 524.3 (Prakash et al., 2009). The measured concentrations were then used in calculating diffusivity of VOCs in gasket materials according to Equation 1.

C.3.3. Measurement of tensile strength of gasket samples

After retrieving and transferring gasket samples to the lab, samples were placed in an electric oven set at a temperature of $104 \pm 3^\circ\text{F}$ for 24 hours to remove remaining water and VOCs diffused in the sample which would affect the tensile strength measurements. Specimens were considered “dry” when less than 0.1% change in the weight of specimen within an hour was measured. The tensile strength measurement results were then normalized to the tensile strength of original (unaged) samples to reflect the rate of degradation of tensile strength during the exposure period.

C.3.4. Estimation of tensile strength degradation of gasket materials

To assess the developed model for estimating tensile strength degradation of gasket materials exposed to pure water contaminated with benzene and PCE (Hosseini et al., 2019; Hosseini et al., 2020), data from tensile strength measurements on gasket samples deployed at the contaminated sites were employed. The percentage of difference between the measured values and the predicted ones were then reported.

Model for estimating tensile strength degradation of gasket materials exposed to pure water contaminated with VOCs is shown in Equation C1. Depending on the type of contaminant (benzene or PCE), gasket material, and concentration of VOCs various coefficients can be adopted to estimate tensile strength of gasket materials after a specific exposure time (Hosseini et al, 2019; Hosseini et al., 2020).

$$T_N = ae^{-b\beta t} \quad (C1)$$

where T_N is the tensile strength of gasket samples normalized to the tensile strength of original or unaged sample, t is the exposure duration to the contaminant of interest (in day), β is a factor to account for the concentration of VOCs in water and can be calculated using either Equation C2 or Figure C9, and coefficients a and b depend on the type of VOC and gasket material presented in Table C2.

$$\beta = \text{Ln} \left(\frac{\frac{S}{100}}{1 - \frac{S}{100}} \right) \quad (C2)$$

where S is the saturation level or percentage of solubility limit of contaminant of interest in the aqueous exposure media (e.g., water in monitoring well). The solubility limits for benzene and PCE are 1790 mg/L and 206 mg/L, respectively.

Note that values of β for linear and nonlinear models were calculated based on the concentration of benzene and PCE in the monitoring wells (Table D2 – Appendix D) and presented in Table D4 (Appendix D).

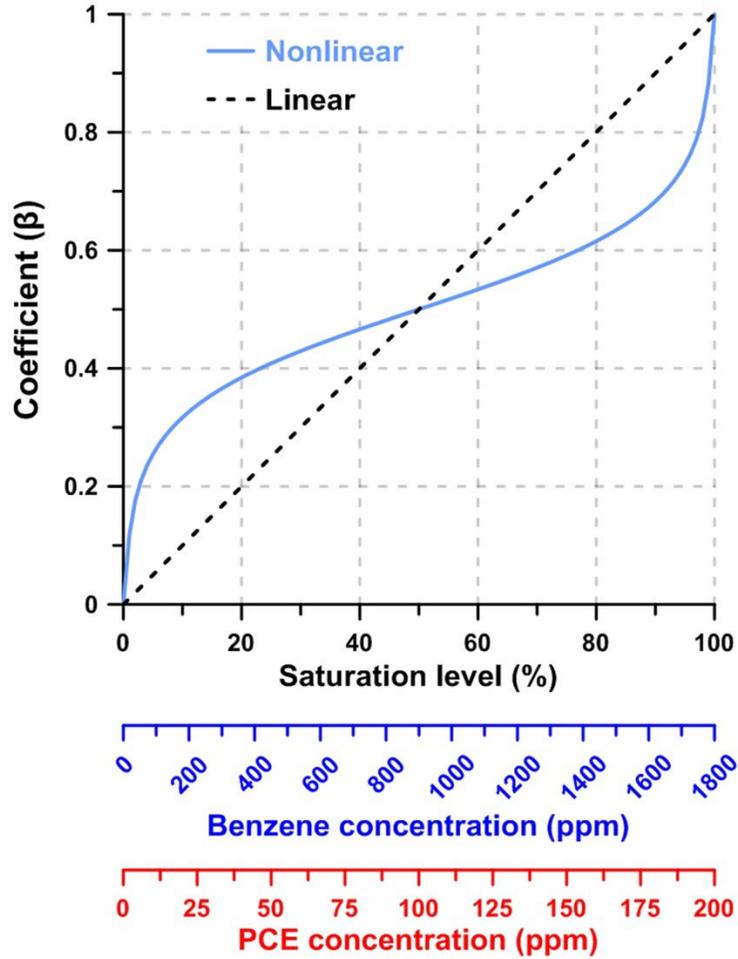


Figure C9. Calculation of saturation dependence constant factor (β). Note that saturation or solubility limits for benzene and PCE in water are 1,790 mg/L and 206 mg/L, respectively. (Hosseini et al., 2019)

Table C2. Coefficients of tensile strength degradation model for gasket materials exposed to water contaminated with benzene or PCE. (Hosseini et al., 2019; Hosseini et al., 2020)

Material type	Contaminant type in water	Model coefficients	
		a	b
Neoprene	PCE	0.91	0.0018
	benzene	0.86	0.0025
Nitrile	PCE	0.87	0.0010
	benzene	0.73	0.0016
Viton	PCE	0.90	0.0010
	benzene	0.89	0.0019

Appendix D: Experimental part 2

D.1. General information

In this section, the data of VOC concentration measurements from monitoring well groundwater samples as well as capsules for the selected sites are provided. These data are used in the calculation of diffusivity of VOCs in gasket materials (section 4.1.1).

D.2. Concentration of VOCs in the monitoring wells

Dates and exposure period for the capsules at the selected sites are provided in Table D1. Table D2 presents results of concentration quantification of benzene and PCE at the selected sites during deployment and/or retrieval of capsules and gasket samples for tensile strength measurements.

Table D1. Dates for deployment/retrieval events at the selected sites.

Site location	Major contaminant	Event	Date	Exposure duration (month)
Newton	Benzene	First deployment	03/03/2020	NA
		Second deployment / First retrieval	12/01/2020	9
		Second retrieval	01/29/2021	2
Nashville	Benzene	First deployment	03/04/2020	NA
		Second deployment / First retrieval	07/08/2020	4
		Second retrieval	02/12/2021	7
Durham	PCE	First deployment	03/04/2020	NA
		Second deployment / First retrieval	09/03/2020	6
		Second retrieval	06/02/2021	9

Table D2. Concentration of VOC of interest in monitoring wells at the selected sites during deployment/retrieval events (mg/L).

Site location	Contamination type	Major contaminant	Well ID	Deployed/retrieved items	First deployment	Second deployment/first retrieval	2nd retrieval
Newton	Gasoline	Benzene	MW-3	Capsules / Gasket samples	1.38	1.60	1.23
Nashville	Gasoline	Benzene	PW-3	Capsules / Gasket samples	17.60	6.05	16.93
			MW-3	Capsules / Gasket samples	0.51	8.99	18.21
Durham	Chlorinated solvent	PCE	RW-2	Capsules / Gasket samples	7.12	9.90	15.40

D.3. Concentration of VOCs in the capsules

Concentrations of VOCs of interest in the capsules for different gasket materials deployed at the selected sites are presented in Table D3.

Table D3. Concentration of diffused VOCs in the capsules for various gasket materials.

Gasket material	Site location	Contaminant	Exposure duration (month)	Concentration (mg/L)	COV* (%)
Neoprene	Newton	Benzene	2	1.12	1.3
			9	1.73	2.2
	Nashville	Benzene	4	7.07	2.1
			7	15.86	3.9
	Durham	PCE	6	17.92	0.3
			9	9.55	0.6
Buna-N	Newton	Benzene	2	0.68	3.6
			9	1.69	0.7
	Nashville	Benzene	4	4.95	1.4
			7	17.15	3.4
	Durham	PCE	6	13.79	0.6
			9	10.55	4.9
Viton	Newton	Benzene	2	Not detected (< 5 µg/L)	Not determined
			9	0.21	4.9
	Nashville	Benzene	4	0.06	5.7
			7	Not detected (< 5 µg/L)	Not determined
	Durham	PCE	6	Not detected (< 5 µg/L)	Not determined
			9	Not detected (< 5 µg/L)	Not determined
None – Blank sample	Newton	Benzene	2	Not detected (< 5 µg/L)	Not determined
			9	Not detected (< 5 µg/L)	Not determined
	Nashville	Benzene	4	Not detected (< 5 µg/L)	Not determined
			7	Not detected (< 5 µg/L)	Not determined
	Durham	PCE	6	Not detected (< 5 µg/L)	Not determined
			9	Not detected (< 5 µg/L)	Not determined

* COV: Coefficient of Variation

D.4. Calculation of saturation dependence constant factor (β)

By employing concentrations of VOCs from the monitoring well groundwater samples (Table D2) and Figure C9, a saturation dependence constant factor (β) was computed, and the results are presented in Table D4.

Table D4. Saturation dependence constant factor (β) used for estimating tensile strength of gasket samples deployed at the selected sites.

Site location	Contaminant	Exposure duration (month)	Saturation level (%)	β	
				Linear model	Nonlinear model
Newton	Benzene	2	0.07	0.0007	0.0029
		9	0.09	0.0009	0.0033
Nashville	Benzene	4	0.34	0.0034	0.0266
		7	0.94	0.1187	0.0102
Durham	PCE	6	4.81	0.0481	0.2512
		9	7.48	0.0748	0.2904

Appendix E: Modeling part

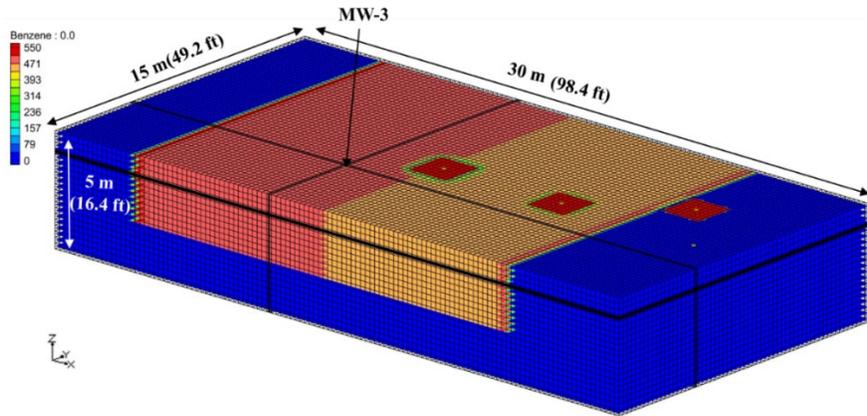
E.1. Model development

E.1.1. Nashville gasoline contaminated site

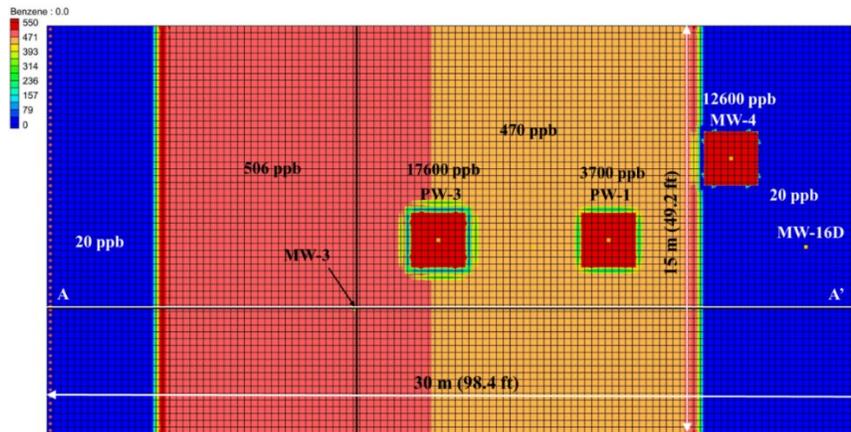
A 3-dimensional model domain has been developed using finite difference method incorporated in GMS transient mass-transport domain. Figure E1(a) shows simulated model domain with dimensions 30 m × 15 m × 5 m (98.4 ft × 49.2 ft × 16.4 ft) based on the extent of benzene plume. The dimensions were chosen to cover field concentrations more than 50 ppb as delineated on the site map in Figure B1. The total number of grids is 310,000 with grid size of 0.25 m far from the location of capsule becoming as fine as 0.002 m towards the monitoring well where capsule has been deployed. The hydraulic gradient in the domain is 1% toward the southwest (right to the left in the model) simulated with constant head boundaries. To avoid complexity, the impact of groundwater level fluctuation on flow regime and hydraulic gradient was not considered in the model, however, the fluctuation in monitoring well's concentration has been applied using transient functions. Figure E1(b) presents a plan view of the model developed herein while the distribution of the initial soil and groundwater contamination was assigned based on the field measurements of samples from monitoring wells and borings (Wood Inc. 2019, Pace analytical services report 2020, 2021). An area of 1.75 m around monitoring and purge wells was selected to define high concentrations at PW-3 (18,200 ppb), PW-1 (3,700 ppb) and MW-4 (12,600 ppb). Section A-A' shown in plan view is displayed in Figure E1(c). The capsules have been deployed in MW-3. The location of MW3 is also shown along with benzene distribution throughout the domain depth. A capsule with 2.54 cm diameter and 7.8 cm height was simulated at 75 cm below the groundwater level in MW-3 with 5.0 cm diameter (Figure E1(c)). The gasket material test sample on the top of the capsule is 3.2 mm in thickness and an initial concentration of zero is assumed inside the capsule. The water table elevation and benzene concentration are not constant with seasonal changes and fluctuate during capsules deployment period which is shown in the graph of Figure E2(a). A graph (Figure E2(b)) is presented for PW-3 which is the closest monitoring well to the location of capsules and has been used to deploy some pipe material samples to assess samples' tensile strength. Accordingly, transient sources have been defined in MW-3 and PW-3 to account for these fluctuations with time.

Table E1 presents the model flow and transport parameters used in modeling required to simulate advection, dispersion/diffusion, chemical reaction/adsorption, and degradation. The diffusion coefficient (D) and equivalent hydraulic conductivity (k_e) of samples are unknown and will be calibrated using the simulation (presented in results section). The material properties of the study site are shown in Table E2. Adsorption of the organic chemical onto the solid-phase is defined by linear equilibrium-controlled sorption isotherm and the soil-water partition coefficient (K_d). The partitioning of chemicals onto the soil particles is a function of the organic carbon fraction (f_{oc}) present in the soil (Table E2) that is defined based on site assessment and soil sampling reports illustrated in field sites description. The first-order reaction rate of dissolved phase (K_1) and sorbed phase (K_2) are employed to account for the decay or degradation of the contaminant due to natural biochemical attenuation. The diffusion coefficient, adsorption/degradation parameters of benzene, as long as the rationale for dispersivity have been described in the previous studies developed by these authors (Faelli et al. 2020, 2021, Hosseini et al. 2020, Alhomair et al. 2021). Different adsorption and degradation parameters have been considered for Durham site which is PCE contaminated

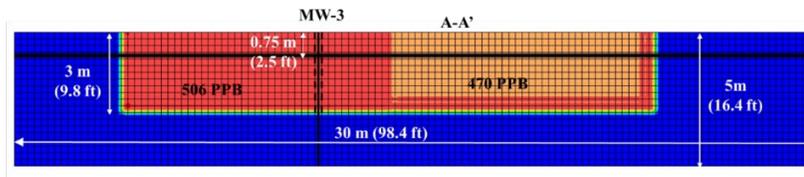
than the other sites with benzene from gasoline contamination (Aronson and Howard 1997). The diffusion coefficient value of benzene and PCE in water (D) was assigned as $9.5 \times 10^{-5} \text{ m}^2/\text{d}$ ($1.1 \times 10^{-9} \text{ m}^2/\text{s}$) and $8.8 \times 10^{-5} \text{ m}^2/\text{d}$ ($1.0 \times 10^{-9} \text{ m}^2/\text{s}$), respectively (GSI Environmental 2014). The longitudinal dispersivity parameter (α_x) was estimated based on Neuman (1990) ($\alpha_x = 0.0175 \times L^{1.46}$, L is domain size in the x -direction). The transverse (α_y) and vertical dispersivity (α_z) have been assumed 30% and 5% of α_x as recommended per ASTM (1994).



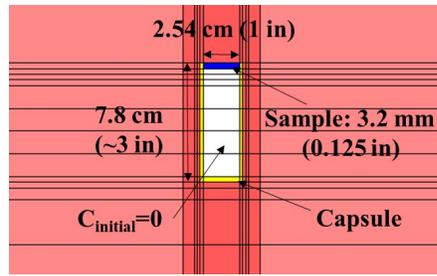
(a)



(b)

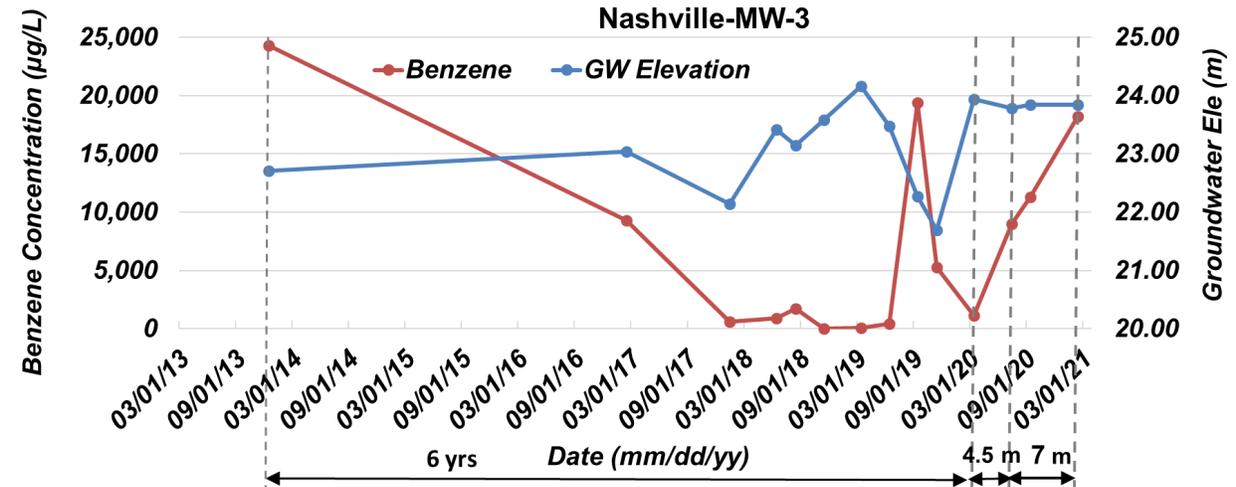


(c)

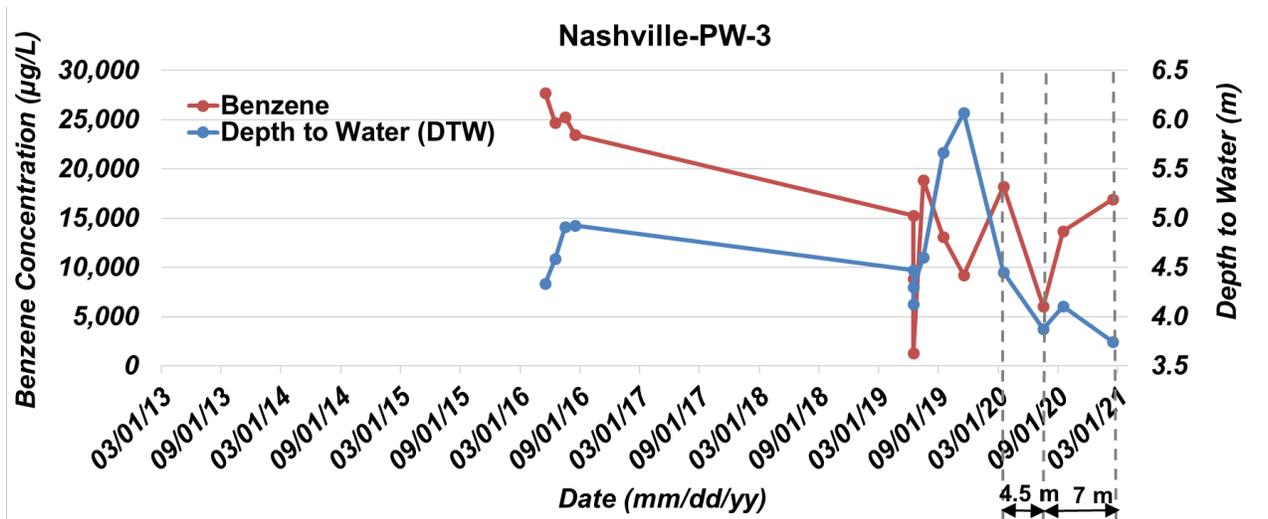


(d)

Figure E1. Model development of Nashville site, (a) 3D domain, (b) Plan view, (c) Cross section view of the simulated model and (d) the capsule being simulated in MW3.



(a)



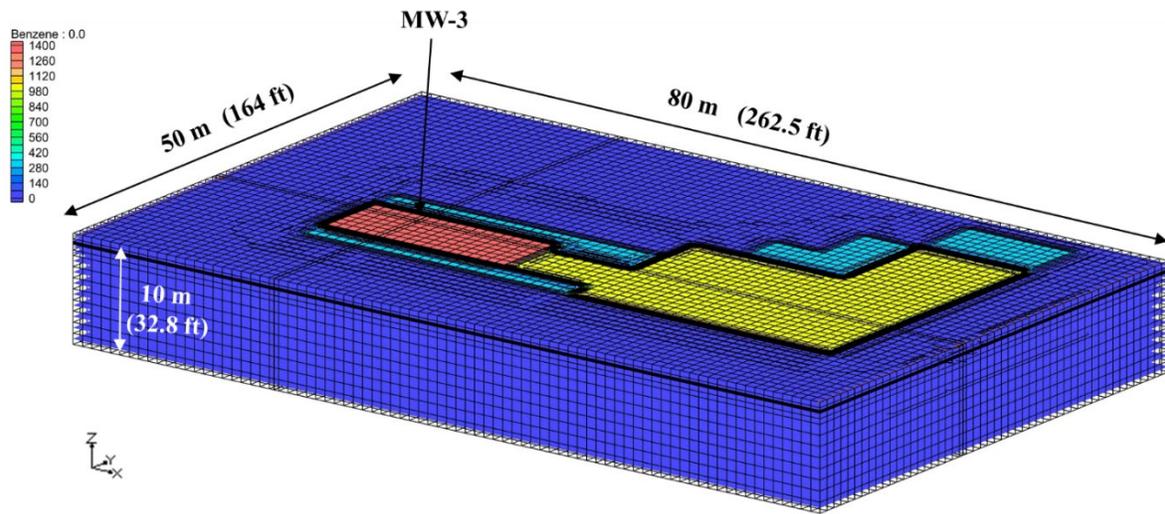
(b)

Figure E2. (a) Monitoring well (MW-3) concentration where the capsules have been deployed in Nashville site, (b) The concentration of monitoring well PW-3 located near MW-3 indicating groundwater level and benzene fluctuation (after Wood Inc., 2021).

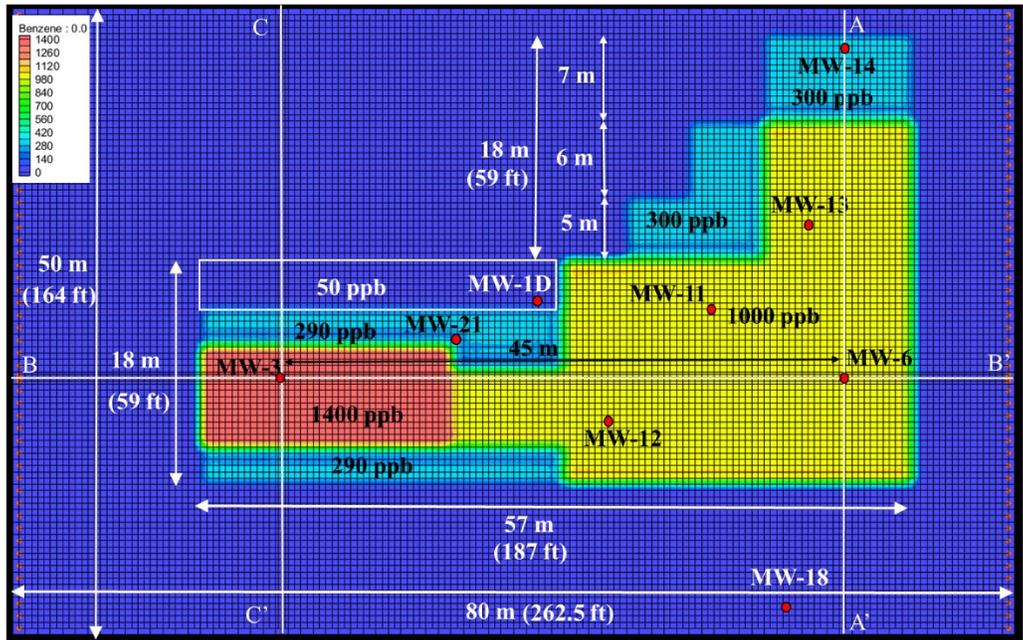
E.1.2. Newton gasoline contaminated site

To assess the performance of capsule at another gasoline contaminated site, a 3-D domain was developed for the Newton site shown in Figure E3(a) with the similar approach as used for the Nashville site. The model dimensions are 80 m × 50 m × 10 m selected based on the plume extent shown in Figure B2. Figures 7(b) and 7(c) show a plan view and cross-section views A-A', B-B', and C-C' of the model developed herein. The contamination distribution was assigned according to Hart & Hickman (2018), Pace

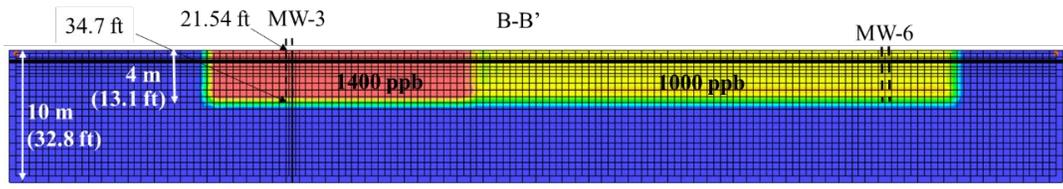
analytical services report (2020), and measurements during this study. The extent of plume in depth is considered to be 4 m that is more than Nashville site (3 m). The total number of grids is 1,123,000 with grid size of 0.5 m far from the location of capsule becoming as fine as 0.002 m towards the monitoring well where capsule has been deployed. The hydraulic gradient in the domain is 1% toward the west (right to the left in the model). A capsule is located 75 cm below the groundwater level in MW-3 (diameter of 5.0 cm). The location of MW-6 is shown in Figures E3(b) and (c) where USTs have been formerly installed. Due to the presence of free product in MW-6 and possible interference with the measurements in this study, this monitoring well was not selected for capsule deployment. The model flow and transport parameters of Newton site are defined following the same approach as described for Nashville and presented in Table E1 while the specific soil parameters of Newton site are presented in Table E2. A transient benzene concentration was defined in MW-3 according to the graph shown in Figure E4. The graph represents benzene fluctuation during capsules deployment time period in this study.



(a)



(b)



(c)

Figure E3. Model development of Newton site, (a) 3D domain, (b) Plan view, (c) Cross section view of the simulated model.

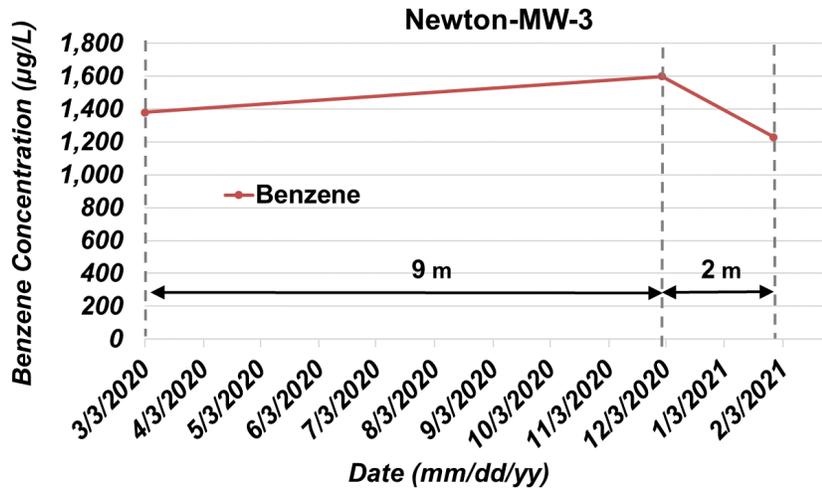


Figure E4. Monitoring well (MW-3) concentration where the capsules have been deployed in Newton site, indicating benzene fluctuation during deployment.

E.1.3. Durham chlorinated solvent contaminated site

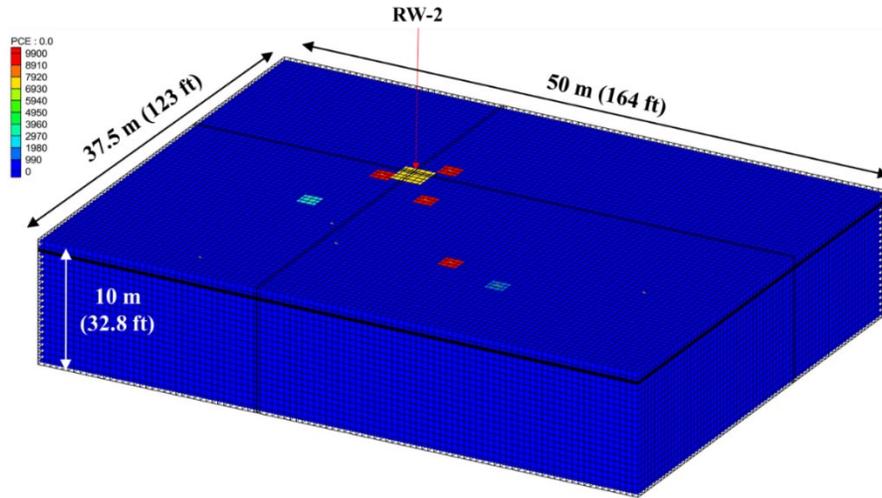
The 3D model domain, plan view, cross-section view, and the capsule configuration in the developed model of Durham site are shown in Figures E5(a), E5(b), and E5(c). The dimensions of model domain are 50 m × 37.5 m × 10 m as shown in Figure B3. The PCE concentrations in monitoring wells are defined according to the plan view of Figure B3 (URS 2015), Pace analytical services report (2020), and measurements during this study. The capsule is deployed in RW-2 with 10 cm well diameter. A hydraulic gradient of 1% in the down-gradient direction of plume extent was simulated using constant head boundaries at right and left sides of the model domain. The total number of grids is 320,000 with grid size of 0.5 m far from the location of capsule becoming finer towards the monitoring well and capsule location. Transient PCE source has been simulated in RW-2 according to the measured graph of Figure E6. The model parameters and site material properties are indicated in Tables E1 and E2, respectively.

Table E1. Model flow and transport parameters.

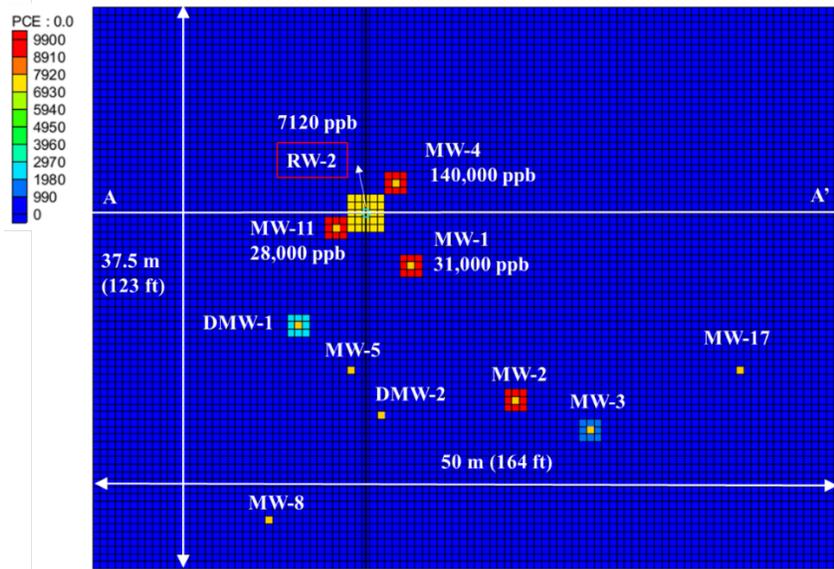
Parameter/Material	Symbol	Native soil	Sample	Capsule	Capsule inside	Well
Horizontal Hydraulic conductivity(m/s)	$kh_x=kh_y$	Site material	Calibrated	1×10^{-20}	1×10^{-2}	1×10^{-4}
Hydraulic conductivity ratio	kh_x/k_v	2	1	1	1	1
Porosity	n_e	Site material	1×10^{-2}	1×10^{-10}	0.99	0.99
Diffusion (m^2/s)	D	1.0- 1.1×10^{-9}	Calibrated	1×10^{-20}	1.0- 1.1×10^{-9}	1.0- 1.1×10^{-9}
Longitudinal Dispersion (m)	α_x	2	1×10^{-3}	1×10^{-3}	1×10^{-3}	2
Horizontal/Longitudinal disp.	α_y/α_x	0.3	0.3	0.3	0.3	0.3
Vertical/Longitudinal disp.	α_z/α_x	0.05	0.05	0.05	0.05	0.05
Density (kg/m^3)	ρ_b	Site material	1300	2700	1000	1000

Table E2. Site material flow and transport parameters.

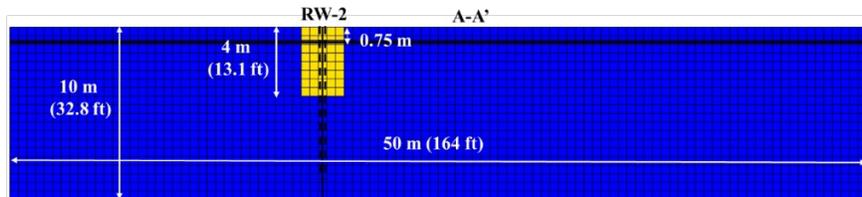
Parameter/Site	Symbol	Newton	Nashville	Durham
Soil type		Silty Clay- Sandy silt	Sandy Silt	Silty Clay
Horizontal Hydraulic conductivity(m/s)	$kh_x=kh_y$	2×10^{-7}	1×10^{-6}	4×10^{-8}
Porosity	n_e	0.25	0.22	0.27
Density (kg/m^3)	ρ_b	1600	1700	1710
Organic carbon fraction (%)	f_{oc}	0.1	0.1	2.4
Partition coefficient (m^3/mg)	K_d	8.5×10^{-11}	8.5×10^{-11}	1.1×10^{-10}
The first-order reaction rate of the dissolved (mobile) phase (d^{-1})	K_1	1×10^{-5}	1×10^{-5}	1.9×10^{-4}
The first-order reaction rate of the sorbed (immobile phase) (d^{-1})	K_2	1×10^{-5}	1×10^{-5}	1.9×10^{-4}



(a)



(b)



(c)

Figure E5. Model development of Newton site, (a) 3D domain, (b) Plan view, (c) Cross section view of the simulated model and the capsule being simulated in MW3.

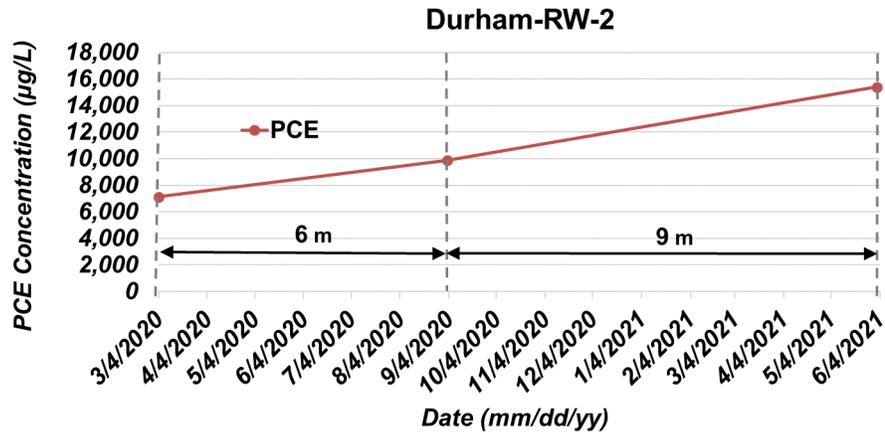


Figure E6. The graph of monitoring well (RW-2) where the capsules have been deployed in Newton site, indicating benzene fluctuation during deployment.