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Source strength functions from long-term monitoring data and spatially distributed mass discharge measurements

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Abstract

Source strength functions (SSF), defined as contaminant mass discharge or flux-averaged concentration from dense nonaqueous phase liquid (DNAPL) source zones as a function of time, provide a quantitative model of DNAPL source-zone behavior. Such information is useful for calibration of screening-level models to assist with site management decisions. We investigate the use of historic data collected during long-term monitoring (LTM) activities at a site in Rhode Island to predict the SSF based on temporal mass discharge measurements at a fixed location, as well as SSF estimation using mass discharge measurements at a fixed time from three spatially distributed control planes. Mass discharge based on LTM data decreased from ~300 g/day in 1996 to ~70 g/day in 2012 at a control plane downgradient of the suspected DNAPL source zone, and indicates an overall decline of ~80% in 16 years. These measurements were compared to current mass discharge measurements across three spatially distributed control planes. Results indicate that mass discharge increased in the downgradient direction, and was ~6 g/day, ~37 g/day, and ~400 g/day at near, intermediate, and far distances from the suspected source zone, respectively. This behavior was expected given the decreasing trend observed in the LTM data at a fixed location. These two data sets were compared using travel time as a means to plot the data sets on a common axis. The similarity between the two data sets gives greater confidence to the use of this combined data set for site-specific SSF estimation relative to either the sole use of LTM or spatially distributed data sets.

Keywords

Mass flux; Mass discharge; Source strength function; Source zone characterization; Passive flux meters; Long-term monitoring data

1. Introduction

Research conducted over the last fifteen years has shown that dense nonaqueous phase liquid (DNAPL) source-zone response and dissolution behavior are strongly influenced by the DNAPL architecture (Sale and McWhorter, 2001; Christ et al., 2006; Falta et al., 2005a; Fure et al., 2006; Jawitz et al., 2005; Lemke et al., 2004; Parker and Park, 2004).

Consequently, the utility of site management decisions based on predictive models depends on the extent to which the DNAPL architecture can be appropriately and reliably quantified. The DNAPL architecture can generally be defined as the distribution of the DNAPL relative to the distribution of pore water velocities in the flow field, and a complete description of the DNAPL architecture would entail a complete description of the spatial DNAPL distribution and groundwater flow field.

Field-scale characterization needed to obtain the necessary level of detail to make meaningful, site-specific predictions of source-zone behavior from a process-based model with spatially distributed parameters is difficult and expensive. The level of source-zone characterization needed to ensure these types of models provide reliable, site-specific results is not collected in many cases, presumably due to resource limitations. Data requirements needed for meaningful site-specific predictions can be relaxed by adopting a stochastic modeling framework conditioned to field measurements (e.g., Trolldberg et al., 2012; Koch and Nowak, 2016). However, application of inverse stochastic modeling concepts requires a level of expertise and modeling resources that are not routinely used in practice. As such, more practical albeit less rigorous methods of DNAPL source-zone characterization are needed. At the very least, these methods could be viewed as important steps in the process of data collection and evaluation when building towards the more ambitious goals of site specific, distributed parameter, process based models, whether deterministic or stochastic in nature.

Over the last decade, a variety of simplified, screening-level models have been introduced to describe DNAPL source-zone behavior (Parker and Park, 2004; Zhu and Sykes, 2004; Falta et al., 2005a; Falta et al., 2005b; Newell and Adamson, 2005; Christ et al., 2006; Marble et al., 2008; Difilippo and Brusseau, 2011; Johnston et al., 2013). These models reduce the level of complexity of the real systems through the use of up-scaled, lumped parameters to represent the details of the DNAPL source-zone architecture, and are fundamentally related because they express mass flux as a power law function of DNAPL mass. Alternative approaches have also been proposed in which the source-zone architecture is described using stream tubes with statistical distributions of travel time and DNAPL saturation (Jawitz et al., 2005; Enfield et al., 2005). Select comparisons between models have been made by Basu et al. (2008), Parker and Falta (2008), Difilippo and Brusseau (2011), Johnston et al. (2013), and Kokkinaki et al. (2014). An important question to be addressed in the application of these models is what consistent and appropriate level of characterization is needed to make meaningful site-specific predictions of source behavior.

Recently, flux based site management concepts have been proposed for DNAPL site management purposes (e.g., Basu et al., 2006; Annable et al., 2014; Johnston et al., 2014). Key source-zone attributes to be characterized in this framework are the spatial advective

flux (J ; $\text{ML}^{-2} \text{T}^{-1}$) distribution, flux-averaged concentration (C_f ; ML^{-3}), and mass discharge ($\dot{m}$; MT^{-1}) across control planes. The term source-strength function (SSF) is used to refer to $\dot{m}$ or C_f from the DNAPL source zone as a function of time. The SSF is a valuable tool for site management purposes because of its use in predicting source zone behavior, assessing responses to various remedial approaches, and providing insights to site-wide mass balance. In addition, it can be used to characterize other contaminant sources, such as secondary diffusion domains. A related relationship is that between $\dot{m}$ and the DNAPL mass in the source zone, which has recently been called a defining characteristic of system behavior (Brusseau et al., 2013). These relationships are inherently a function of DNAPL architecture. Characterization of the SSF from field data therefore provides a means to characterize the DNAPL architecture. A benefit for using SSF data to calibrate screening-level models is that $\dot{m}$ measurements integrate information over a large spatial scale (i.e., control plane) relative to the scale of local processes, and therefore match the up-scaled approach of screening-level models. Another benefit to DNAPL source-zone characterization using $\dot{m}$ measurements relative to the characterization of DNAPL mass, for example, is that the latter is inherently a three-dimensional problem, while the former is inherently a two-dimensional problem, thus the scale of the domain to be investigated is reduced. Consequently, using SSF data based on $\dot{m}$ (or C_f) measurements is considered a beneficial approach for calibrating screening-level source-zone models as noted above.

Annable et al. (2014) identify five methods that might be used to estimate the SSF from field data, two of which are based on $\dot{m}$ measurements at control planes oriented perpendicular to the mean groundwater flow direction. One of these is based on multiple temporal measurements at a fixed location, and the other is based on measurements at multiple locations at a fixed point in time. Difilippo and Brusseau (2008) refer to the case of only two temporal measurements (before and after remediation) at one location as an end-point analysis, and reviewed results from this type of analysis for 21 remediation projects. Brooks et al. (2008) reported results from two sites where source control planes were installed for the specific purpose of comparing pre- and post-remedial $\dot{m}$ measurements as an assessment of DNAPL source remediation. As noted by Difilippo and Brusseau (2008), the limitation of only two points in this approach means a higher level of uncertainty when it comes to estimating the SSF.

Of the remaining methods identified by Annable et al. (2014) to estimate the SSF, two are based on concentration-time series data from monitoring wells at the site, and differ in whether a single SSF model is fit to all data simultaneously or whether individual SSF models are fit to each well. With respect to the use of concentration-time series data from monitoring wells, most DNAPL contaminated sites have extensive multi-year data sets that were collected to define the scope of the problem, evaluate remediation options, and meet long-term monitoring (LTM) requirements. Such data sets typically include contaminant concentration-time series information from at least a select set of wells, and some level of testing to estimate hydraulic conductivity at one or more locations. Well locations however may not be ideal for the estimation of SSFs. Nonetheless, these historic data sets are a valuable source of information, and may provide rough predictions of the SSF. Moreover, these predictions may be improved when combined with a limited number of flux measurements in select locations. As an example, Basu et al. (2009) used concentration-time

series data from three monitoring wells within the source zone to estimate source depletion behavior, although the SSF was not estimated from explicit estimates of $\dot{m}$.

The last method for estimating SSFs as identified by Annable et al. (2014) is based on flux-averaged concentration-time series data measured from one or more extraction wells. Examples of this method can be found in Difilippo and Brusseau (2008), Brusseau et al. (2013), Johnston et al. (2013), and Wang et al. (2014). What is particularly interesting to note about the three more recent cases based on extraction well data is that initial source mass was one of the fitting parameters in the calibration process, and the estimate of the DNAPL mass based on SSF calibration was comparable to independent estimates of DNAPL source mass. Estimates of DNAPL mass are important for the design and evaluation of source-zone remediation systems, however, they can be difficult to obtain and may have high uncertainty. Consequently, their estimation based on SSF calibration to field data offers an alternative, and possibly more convenient, means to obtain them.

To our knowledge what has not been explored to date is the characterization of the SSF using $\dot{m}$ measurements at multiple locations at a fixed point in time. This approach is the central focus of this manuscript, and we demonstrate SSF estimation using $\dot{m}$ measurements at a fixed time from three spatially distributed control planes at a site. A comparison is provided of these results to the SSF obtained using temporal $\dot{m}$ measurements at a fixed location. Moreover, a hybrid approach is used for the latter in which $\dot{m}$ estimates are derived predominately from a 16-year record of concentration-time series data associated with LTM activities. The advantages and disadvantages of each approach are evaluated, and it is shown that the two approaches complement one another. Their combined use results in a more robust SSF estimate for site management purposes by providing two lines of evidence of source-zone behavior. As an illustration, an exponential model is fit to the SSF data, and used in a site-wide mass balance assessment.

2. Site description and history

The Calf Pasture Point site is located in North Kingstown, Rhode Island, on a coastal peninsula surrounded to the west, south, and east by Allen Harbor, an entrance channel, and Narragansett Bay, respectively (a site location map is shown in Fig. SI-1 in Supplementary Information). A description of the site geology is provided by EA Engineering, Science, and Technology (1998) and Church and Brandon (1999), and consists of surficial sand, underlain by silt, till, and a lower sand. These unconsolidated units overlie a quartzite and phyllite bedrock that slopes to the southeast and south. The thickness of the unconsolidated units above the rock vary from ~9 to ~30 m, and the silt, till, and lower sand layers are discontinuous across the site. However, the silt and till layers were present in the immediate vicinities of the three control planes used in this study. EA Engineering, Science, and Technology (1998) reported hydraulic conductivities ranging from approximately 0.03 m/day in the silt to 120 m/day in the till.

An outcrop of rock occurs in the northwest portion of the site, and groundwater is considered to conceptually flow in a semi-radial pattern from this vicinity to the coastline. The site is tidally influenced, and daily variations in groundwater elevations due to tidal

action range from approximately 1 m for wells close to the shoreline to <0.003 m for select inland shallow wells, based on measurements completed during the study (data not shown). Moreover, salinity likewise varies from saline or brackish water at the coastline to freshwater inland (Church and Brandon, 1999). Density corrections to groundwater elevations measured in the vicinities of the contaminant flux transects used in this study were deemed unnecessary based on the salinity distribution as described by Church and Brandon (1999). See Figs. SI-2 and SI-3, and Table SI-1 in Supplementary Information for further information.

The site was formerly part of the Naval Construction Battalion Center, Davisville, which was operational from 1942 until its closure in 1994. It is estimated that between 1968 and 1974, ~28,000 l of a decontaminating agent, non-corrosive (DANC), were buried in the region bounded by wells 04D, 05D, and 14D (Fig. 1), and figures from various reports show an inferred release location immediately south of 14D (e.g., EA Engineering, Science, and Technology, 2002; Tetra Tech, 2013). Site characterization activity was initiated in the mid 1980s, and has continued since. The limits of the DNAPL source zone have not been defined through specific characterization activities to assess the presence and spatial extents of DNAPL. However, DNAPL is still suspected because recent aqueous trichloroethylene (TCE) concentrations in monitoring well 17D (with a ten-foot screen section) are ~40 mg/l or higher. A Record of Decision for the site was signed in 1999, which specified deed restrictions and long-term monitoring activities to manage the contaminant risk. Remedial action was taken in 2011 consisting of excavation between wells 15D and 14D (shown as the cross hatched pattern in Fig. 1) due to the observance of a geophysical anomaly in this area. The excavation extended to ~1.8 m below ground surface (bgs) over an area of ~186 m². Remnants of drums were found, but no evidence of DNAPL was observed. It is uncertain if this activity had any impact on the SSF at the site given the absence of DNAPL observations in the excavated area and the fact that the unconsolidated material extends to 11.3 m bgs or greater in this area based on the boring logs for wells 14D and 15D.

Smart (2005) describes DANC as a two-part mixture: a dry chlorine based powder and the solvent 1,1,2,2-tetrachloroethane (PCA), that were mixed together when used for decontamination purposes. It was reportedly stored in either 11-l or 17-l containers with two sections: the top section contained the powder and the bottom section contained the solvent. Using a density of 1.6 g/cm³ for PCA (Montgomery, 2000), the estimated mass assuming 28,000 l of PCA is 45,000 kg. As typically is the case, the estimated release mass has a high degree of uncertainty. Given the predominance of TCE in the plume relative to PCA, 1,2-dichloroethylene (DCE), or vinyl chloride, PCA is presumed to rapidly degrade to TCE through a hydrolysis reaction (e.g., Washington, 1995), but further degradation is not considered significant at the site. Therefore, the two main contaminants of concern for this study were PCA and TCE.

3. Methods

3.1. SSF based on temporally distributed measurements at a fixed location

The SSF, $\dot{m}(t)$, based on temporally distributed measurements at a fixed location used concentration-time series information collected as part of LTM activities, and data collected as part of site characterization activities. It was estimated using

$$\dot{m}(t) = \int_A J_{\perp}(\vec{r}, t) da \cong \sum_{i=1}^n A_i C_i(t) K_i I_i(t) \quad (1)$$

where t is time [T], A is the area [L^2] of the source-zone control plane (SZCP), $J_{\perp}$ is the component of contaminant flux [$ML^{-2} T^{-1}$] normal to the control plane at location $\vec{r}$ [L], n is the total number of wells in the SZCP, A_i is the SZCP area [L^2] associated with the i^{th} well, $C_i(t)$ is the concentration-time series [ML^{-3}] for the i^{th} well, K_i is the hydraulic conductivity [LT^{-1}] of the i^{th} well, and $I_i(t)$ is the hydraulic gradient [–] of the i^{th} well. A single subscript is used here and elsewhere in the manuscript to denote a spatially-averaged property associated with the monitoring well as a whole. Eq. (1) makes use of $J = Cq$ and $q = KI$, where q is the Darcy or groundwater flux [LT^{-1}], and reflects the transect method for estimating mass discharge (e.g., ITRC (Interstate Technology and Regulatory Council), 2010; Farhat et al., 2011). Comparisons between this method and other flux measurement methods can be found elsewhere (e.g., Brooks et al., 2008), and it was selected here to specifically make use of the LTM data. Finally, as expressed in Eq. (1), it was assumed that the only sources of temporal variability were C_i and I_i .

The location of the SZCP relative to the source was subject to uncertainty given uncertainty in the location of the DNAPL source zone. For this analysis, the SZCP location was based on: a) wells with LTM data, b) the proximity of the wells to the inferred DNAPL release location, and c) the location of the wells relative to the groundwater flow field. The wells included in the LTM program with closest proximity to the inferred release location were 04D, 05D, 17D, 22D, and 38D (Fig. 1). Of these wells, 04D, 05D, and 17D had the highest concentrations, with 17D being highest. Other wells in the vicinity of the inferred release location included 03D, 14D, 15D, and 31I, but these wells were not included in the LTM program. High concentrations were not noted in shallow wells near the inferred source zone, and the shallow zone was therefore excluded from the SSF analysis based on LTM data. Consequently, the SZCP was primarily based on wells 04D, 05D, and 17D; the historic high concentration wells downgradient of the inferred DNAPL release area.

An analysis of the groundwater flow field indicated non-uniform flow conditions, and a curvilinear SZCP was therefore used. The SZCP was defined to be parallel to groundwater contours based on the average groundwater elevation. Groundwater elevations from 23 measurement episodes completed between July 1995 and April 2010 were averaged at each well location within the D horizon (not all wells were measured within each episode), and that information was used with a Kriging algorithm in a commercial software contouring package (SURFER) to generate groundwater elevation contours (Fig. 1). Finally,

consideration was given in the placement of the SZCP to generally minimize the distance of the wells from the SZCP, resulting in the SZCP as shown in Fig. 1.

Once the SZCP was established, the well locations were projected either upstream or downstream along flowlines perpendicular to the average groundwater elevation contours. The resulting SZCP consisted of three interior wells (04D, 05D, and 17D), with end locations defined by 03D to the east and 10D to the west. The two end well locations were assumed to have zero concentrations for the purposes of estimating the SSF based on historic data due to the low concentrations measured in these wells relative to the interior wells (roughly 1% or less). The horizontal length of the SZCP assigned to each well was equal to one-half the distance to each neighboring well along the curvilinear SZCP. The total length of the SZCP was ~100 m, with an average well spacing of ~34 m. Information was not available on the vertical distribution of contaminant near the inferred source zone, therefore the vertical depth was assumed to equal the 3.05 m screened interval of the wells.

The relatively small variability in the groundwater elevations (coefficient of variations <25%) near the inferred source area suggested temporal variability in I_i may not be significant. Moreover, when considering the importance of temporal variability, short-term sporadic behavior is of less importance compared to long-term trends in the development of screening-level models for source behavior from LTM data. Comparisons of the linear trend line to the average water elevation in wells near the inferred source zone (03D, 04D, 05D, 15D, and 17D) did show a gradual increase in water elevation over time (see Fig. SI-4 in Supplementary Information). Therefore, as further assessment a plane was fit to the water elevation data from these five wells using multiple linear regression for 22 measurement episodes (the first was neglected due to missing measurements). The magnitude and direction of the plane vector serves as a measure of the hydraulic gradient magnitude and direction. Next, a linear control plane was defined to be perpendicular to the mean direction of the hydraulic gradient. Variations in the direction of the hydraulic gradient were accounted for by calculating the component of the hydraulic gradient normal to the control plane. Results are shown in Fig. 2. While short-term variability is evident, the long term trend in the data, as represented by the linear trend line, is only slightly different from the average hydraulic gradient of 0.0094. Consequently, temporal variations in $I_i(t)$ were neglected, and a temporally averaged estimate for each well (hereafter denoted as $\tilde{I}_i$) was used.

Evaluation of the average groundwater elevation contours (Fig. 1) yielded well-specific estimates of $\tilde{I}_i = 0.01$ for 04D, 05D, and 17D each. Values of $K_F = \{0.03, 1.4, 0.98\}$ m/day were used for wells 04D, 05D, and 17D, respectively, and were from slug test results reported by EA Engineering, Science, and Technology (1998). The resulting well-specific groundwater flux estimates were $\tilde{q}_i = \{0.03, 1.40, 0.98\}$ cm/day for wells 04D, 05D, and 17D, respectively (where the tilde is used to indicate an estimate based on $\tilde{I}_i$).

The concentration-time series for wells 04D, 05D, and 17D consisted of twelve measurements associated with LTM activities between 1996 and 2012 (see Fig. SI-5 in Supplementary Information). Calculations for m were based on the sum of DCE, TCE and PCA, where DCE and PCA were converted to an equivalent TCE mass concentration on a

molar basis because TCE is the predominant contaminant in the plume. Other chlorinated chemical species were not included in the historic data analysis because they were generally an order-of-magnitude smaller than PCA and TCE concentrations.

3.2. SSF based on spatially distributed measurements at a fixed time

To obtain a SSF using spatially distributed $\dot{m}$ measurements, contaminant flux measurements were completed in a number of existing and newly installed wells distributed across the site. In general, flux measurements can be completed using either point measurement methods or pumping methods, and each of these approaches have unique advantages and disadvantages. For this study point measurement methods were deemed the better option because there was no onsite infrastructure to manage or treat pumping effluent. As such, pumping effluent would have had to be collected in transportable tanks and shipped offsite for disposal, which would have made this option very expensive. Moreover, access to the site was only possible through a paved pedestrian walk; and heavy vehicular traffic, while possible, would have been disruptive to the local community utilizing the walk. Point measurement methods have traditionally been completed using either multilevel samplers or passive flux meters (PFMs). The former requires the construction and/or installation of specific equipment, while the latter has the advantage of being deployed in conventional wells, which meant existing wells at the site could be utilized for measurements of J . Moreover, PFMs provide measurements of both q and J . Consequently, PFMs were used to complete flux measurements in this study. The PFM theory is described by Hatfield et al. (2004), experimental methods for the deployment and recovery of PFMs are described by Annable et al. (2005), and a comparison of PFM measurements to conventional characterization measurements can be found in Verreydt et al. (2013). See Section SI-2 in Supplementary Information for PFM method details.

The depth-averaged flux at the i^{th} horizontal location J_i was calculated weighting the local contaminant flux measurement $J_{i,k}$ by the length of the k^{th} vertical interval $b_{i,k}$ [L] over which a segment of the PFM had been homogenized:

$$J_i = \frac{\sum_{k=1}^p J_{i,k} b_{i,k}}{\sum_{k=1}^p b_{i,k}} \quad (2)$$

where p is the number of vertical sampling intervals. In most cases, $b_{i,k} = 0.25$ m, in which case Eq. (2) reduces to an arithmetic average. An exception was the first PFM deployment, where the lower 1.5 m of the PFM deployment was divided into $b_{i,k} = 0.13$ m segments to investigate potential fine-scale variations in soil descriptions as reported in the well completion records for wells 4D and 5D. The J_i values were then numerically integrated over the width of the control plane to estimate $\dot{m}$ using

$$\dot{m}(t) = \sum_{i=1}^n A_i J_i \quad (3)$$

This was procedurally identical to the method used in the analysis discussed in Section 3.1. A curvilinear control was defined parallel to groundwater contours generated in SURFER

using averaged groundwater elevations based on pressure transducer data collected during the PFM deployment. Streamlines, also defined in SURFER using pressure transducer data, were used to project well positions onto the curvilinear control plane. The segment of the control plane assigned to each well is one half the distance to the neighboring wells along the control plane; with the exception of the end wells where the distance is equal to the distance along the control plane to the lone neighboring well. Alternative straight-line control planes were also explored, and similar results were obtained (See Section SI-3 in Supplementary Information).

Four PFM deployment events occurred over the course of the study as summarized in Table 1. Well locations for PFM events 1 and 2 are shown in Fig. 3, and well locations for PFM events 3 and 4 are shown in Fig. 4. Moreover, a detailed well map for the fourth PFM event is shown in Fig. SI-6, and monitoring wells assigned to each control plane are shown in Table SI-2 in Supplementary Information. The first PFM event was conducted to investigate groundwater and contaminant flux within and near the inferred source zone. Moreover, the intent was to use the PFM results to reduce the uncertainty of source strength estimate based on the LTM data analysis. The second PFM event was conducted to evaluate conditions within the plume. Results from this event are included in Supplementary Information, but are not discussed further. The third deployment was the first deployment considered to provide complete flux measurements across three control planes. The most upgradient control plane was called CP15, because it was based on existing well 15D; the middle control plane was called CP17, because it was based on existing well 17D; and the furthest downgradient control plane was called CP39, because it was based (in part) on existing well 39D. Control plane locations are shown in Fig. 4. Additional wells were installed after the third PFM episode to augment the well distribution in CP39. Consequently, a fourth and final PFM deployment was subsequently conducted. During this last event, the lower PFM installed in well 17–2D could not be retrieved. To account for its loss, $\dot{m}$ for this well was estimated by scaling the $\dot{m}$ results of the upper PFM using the ratio of $\dot{m}$ for the entire well from PFM event 3 to $\dot{m}$ from the upper half only from PFM event 3.

Pressure transducers were used to assess groundwater flow direction during the third and fourth PFM events. Hydraulic head measurements were collected every 15 min, and were subsequently used to calculate the average hydraulic head field during PFM deployments. Pressure transducers were deployed in 15 wells across the site during the third PFM event, but two of these failed while deployed, leaving a total of 13 hydraulic head measurement locations. Of these, one was installed in a shallow well, four were installed in intermediate wells (Fig. 4b), and the remaining in deep wells (Fig. 4c). For the shallow zone, one well was insufficient to define groundwater flow direction, therefore the shallow groundwater contours based on pressure transducer measurements during a previous period were assumed to apply. This previous period was March 21, 2012 to June 11, 2012, and it included 11 shallow wells across the site (Fig. 4a; three wells are located outside the area of interest shown). The purpose of measurements during this period was to assess tidal influences at the site. Pressure transducers were deployed in 36 monitoring wells across the site during the fourth PFM deployment, and were likewise used to monitor the direction of the hydraulic gradient. However, 2 of these failed, leaving 34 pressure transducers. Of these, 11 were

deployed in shallow wells (Fig. 4d; two wells are located outside the area of interest shown), 9 were deployed in intermediate wells (Fig. 4e), and the remaining in deep wells (Fig. 4f).

Flux measurements were completed in both existing monitoring wells, and newly installed monitoring wells. Well installation and construction details for existing wells varied somewhat, but typically consisted of 5.1-cm (2-in.) diameter PVC or stainless steel well screens, 3.05 m (10 ft) in length, and were installed with a surrounding sand filter pack. The new wells were constructed using Geoprobe 3.8-cm (1.5-in.) ID pre-packed PVC well screens and 3.8-cm (1.5-in.) ID PVC casing. Most of these wells were installed using direct push technology. In a few instances however, hollow stem augers were used due to difficulties getting to target depths.

4. Results and discussion

4.1. SSF based on temporally distributed measurements at a fixed location

Using LTM data, the estimated $\dot{m}$ at the SZCP ranged from ~300 g/day in 1996 to ~70 g/day in 2012 (Fig. 5a). These values are similar to $\dot{m}$ measurements for chlorinated contaminants at other sites (e.g., Brooks et al., 2008), and this range is among the most frequently reported values of $\dot{m}$ as reported by Newell et al. (2011). The data indicates a decreasing trend, with an overall decline of ~80% in $\dot{m}$ over 16 years. One notable exception to the decreasing trend occurs at October 2008, where $\dot{m}$ (219 g/day) was significantly different from results immediately before (61 g/day) and after (76 g/day) this date. This increase reflects increases in the aqueous concentrations measured in well 17D, as no significant increases in concentration were noted in wells 4D or 5D. The reason for the increase in concentration at 17D on this date is unknown, but similar results were obtained from the first PFM event.

Using the data from the first PFM event completed in September and October 2010, the $\dot{m}$ across the SZCP is estimated to be 188 g/day. This is comparable to the estimate of 219 g/day based on the LTM data from October 2008, but ~3 times higher than the estimate of 54 g/day based on data from the previous LTM sampling episode in April 2010. The higher $\dot{m}$ can again be attributed to results from 17D. The PFM flux-averaged TCE concentration (defined as the ratio J/q) for well 17D is 182 mg/l, and differs from the previous LTM concentration for that well by a factor of ~4. It is however similar to the TCE concentration measured in well 17D during the LTM sample from October 2008 (150 mg/l). The fact that the PFM results are similar to the October 2008 LTM results suggests the latter should not be dismissed as a potential sampling artifact, but rather suggest variability stemming from some currently unknown source. Sporadic behavior is not uncommon in monitoring data sets (e.g., McHugh et al., 2011), and while important to understand in the context of overall site management, the long-term data trend is more important in the evaluation of the 16-year data record to estimate the SSF.

Results from the first PFM event were also used to evaluate estimates of q used in the historic data analysis. Measurements of $q_{i,k}$ in all wells ranged from 0.3 to 3.7 cm/day, with a spatial average of 1.0 cm/day and a spatial standard deviation of 0.4 cm/day (Table 2). In general, the groundwater flux appeared fairly uniform with depth (profile plots for the first PFM event are included as Fig. SI-7 in Supplementary Information), and estimates of $\dot{m}$

from the LTM analysis that assumed constant q over the well screen interval appear to have been reliable in this regard. The depth-averaged estimates from PFM data were $q_i = \{0.96, 1.49, 0.90\}$ cm/day for wells 04D, 05D, and 17D, respectively. Well 04D had the largest discrepancy in q_i estimates based on slug test and PFM results (0.03 cm/day versus 0.96 cm/day, respectively), however, when comparing these estimates it is important to note that PFM theory assumes advective dominated flow, and flow rates as low as 0.03 cm/day may hinder PFM accuracy because advective flow may not dominate the transport process (e.g., Hatfield et al., 2004). Nonetheless, if the PFM estimate of q_i for well 04D is used in the $\dot{m}$ calculations (without presuming which of the two q_i estimates is more correct), the revised $\dot{m}$ estimate increases by only 11%. This is due to the fact that the $\dot{m}$ estimate is dominated by the $\dot{m}$ contribution from well 17D. Consequently, there would have been significant changes in the estimate of the SSF if there had been a similar discrepancy in the value of q_i used for well 17D. Having data from the first PFM event that corroborates the value of q_i used provided additional confidence to estimates of $\dot{m}$ based on the LTM data.

4.2. SSF based on spatially distributed measurements at a fixed time

Results from all four PFM sampling events are summarized in Table 2, which lists the minimum, median, average, and maximum values of q , equivalent TCE J , and equivalent TCE C_f . The equivalent TCE was based on the molar summation of PCA, TCE, and DCE. Table 3 summarizes the $\dot{m}$ estimates based on the third and fourth PFM deployments for the three depth horizons at each control plane, and Fig. 5b shows the $\dot{m}$ based on the third and fourth PFM deployments for the three control planes as a function of down-gradient horizontal distance. Profile plots for measurements completed in all wells during PFM events 1, 2, 3, and 4 are included as Figs. SI-7, SI-8, SI-9, and SI-10, respectively, in Supplementary Information.

Differences in summary statistics (Table 2) between events may reflect the impact of different sampling locations and changes in hydrologic conditions between PFM sampling events. For comparison, histograms of q for each of the four PFM deployments is shown in Fig. 6, and results from PFM event 4 appear notably different from the other three. The average and maximum q increased by factors of 2.5 and 1.9, respectively, between PFM events 3 and 4. The maximum q from PFM event 3 (6.0 cm/day) occurred in well 39I at an elevation of -7.18 m, while the maximum q from PFM event 4 (11.3 cm/day) occurred in well 19S at an elevation of -3.46 m.

Differences in the distribution of q between PFM events 3 and 4 are believed to be in large part the result from a significant rain event which occurred early in the fourth PFM deployment. Rainfall records from two nearby climate stations (National Oceanic and Atmospheric Administration, 2017) were reviewed. For the East Greenwich station located ~ 4 km to the north of the site, data was available from 2008 to 2014, and the rainfall amount received on March 30, 2014 was the second largest for this station. For the Providence station located ~ 11 km to the north of the site, data from 2004 to 2014 was reviewed and the rainfall amount received on March 30, 2014 was the third largest (see Fig. SI-11 in Supplementary Information). Further support for this is evident by comparing the groundwater elevation contours in Fig. 4f to those in Fig. 1, Fig. 4c, and SI-3. Taking well

17D as a reference for example, the contour during PFM event 4 is ~0.3 m higher than the contour based on the LTM, PFM event 3, and tidal study data sets. Consequently, hydrological conditions are believed to be the primary factor for the difference in PFM events 3 and 4. This was further tested by analyzing a subset of the PFM event 4 results restricted to those wells included in PFM event 3, and the results are not significantly different from those obtained with the entire PFM event 4 sample set (see Table 2 and Fig. 6d), indicating differences between results from PFM event 3 and 4 are not associated with the additional wells included in PFM event 4.

Measurements of $\dot{m}$ across control planes CP15, CP17, and CP39 differ by factors of 23%, -2%, and 18%, respectively, between PFM events 3 and 4; in contrast to average q , which differs by a factor of 85% between PFM events 3 and 4. Consequently, the average equivalent TCE C_F differs by -114% between PFM events 3 and 4, indicating concentration dilution. If as suspected differences in the q distribution between PFM events 3 and 4 result from the unusually high rainfall event that occurred early in the PFM event 4 deployment, then increases in q were offset by concentration dilution, resulting in similar $\dot{m}$ estimates between PFM events 3 and 4. Consequently, PFM event 4 is still valuable to the original goal to provide a $\dot{m}$ measurement at CP39 with greater certainty compared to that in PFM event 3 through the installation of additional CP39 wells.

Results from PFM events 3 and 4 indicate that $\dot{m}$ increases in the downgradient direction, ranging from approximately 5 to 7 g/day at CP15, 38 g/day at CP17, and 400 to 500 g/day at CP39. Fig. 5b illustrates increasing $\dot{m}$ for the three control planes as a function of down-gradient horizontal distance using results from PFM events 3 and 4. This behavior is expected given the decreasing trend in $\dot{m}$ versus time observed at the SZCP based on the LTM data analysis (Fig. 5a).

Since a SSF relates $\dot{m}$ and time, the spatial distribution under this approach as depicted in Fig. 5b must be related to time as depicted in Fig. 5a. This can be accomplished under simplified conditions (i.e., neglecting longitudinal dispersion and mass loss processes) by using the definition of travel time: $\tau = \eta R \ell / q$, where η is porosity [-], R is the retardation factor [-], and ℓ is distance in the flow direction [L]. For convenience, the spatial origin is taken to be CP17, and the temporal origin is selected as May 1996 (the first date for which historical monitoring data is available), and a relative elapsed travel time is defined as $\dot{t} = [(t - t_0) - \tau]$, where $t_0 = \text{May 1996}$. Consequently, $\dot{t} = 0$ at CP17 in May 1996. A $\dot{m}$ measurement completed at CP17 in May 1996 reflects $\dot{m}$ at CP15 at $\dot{t} = -\tau_1$, where τ_1 is the travel time from CP15 to CP17; likewise, it reflects $\dot{m}$ at CP39 at $\dot{t} = \tau_2$, where τ_2 is the travel time from CP17 to CP39.

Estimates of τ were based on $\eta = 25\%$, which was the value assumed in previous characterization work (Tetra Tech, 2013). The geometric mean value of q as measured in PFM events 3 and 4 was used as an estimate of the site-wide, spatially averaged groundwater flux (denoted by $\bar{q}$), resulting in $\bar{q} = \{1.4, 4.6\}$ cm/day for PFM events 3 and 4, respectively. An estimate of $R = 5$ came from assuming linear partitioning, therefore $R = 1 + \rho_b k_d / \eta$, where ρ_b is bulk density [ML^{-3}] and k_d is the distribution coefficient [$\text{L}^3 \text{M}^{-1}$]. A value of $\rho_b = 1.4 \text{ g/cm}^3$ was used as assumed in previous characterization work (Tetra Tech, 2013).

An estimate of k_d was based on the product $k_{oc}f_{oc}$, where k_{oc} is the organic carbon partitioning coefficient [$L^3 M^{-1}$] for TCE and f_{oc} is the organic carbon fraction [MM⁻¹]. A value of 94 L/kg was used for the former based on the geometric mean calculated in U.S. Environmental Protection Agency (1996) using 21 measurements reported in the literature, and a value of 0.0077 kg/kg was used for the latter based on the geometric mean of 64 total organic carbon measurements from the site as reported in EA Engineering, Science, and Technology (1998) and Tetra Tech (2013).

Fig. 7 presents the resulting SSF data set based on the spatially distributed $\dot{m}$ estimates from PFM events 3 and 4, as well as the SSF data set from the LTM analysis. Data from PFM events 3 and 4 are dissimilar, and the data from PFM event 3 appears to match the LTM data much more favorably than data from PFM event 4. Since $\dot{m}$ estimates based on the third and fourth PFM deployments were within ~20% of one another, differences between the two data sets as represented in Fig. 7 are predominately due to differences in τ , which in turn reflect differences in $\bar{q}$ between the two deployments. As discussed earlier, it is believed that measurements of q during PFM event 4 were unduly influenced by a rainfall event at the start of the deployment. This highlights the importance of evaluating groundwater and mass flux measurements in the broader context of historic site conditions, as interpreting any one event in isolation may lead to misleading conclusions.

4.3. Evaluation of the two approaches

The estimate of the SSF based on temporally distributed $\dot{m}$ measurements at a fixed location relied on data that had been collected as part of initial characterization and LTM activities. As such, it did not require the installation of any additional wells, nor the use of any specialized methods for the measurement of q or J . It was therefore by far the less expensive of the two approaches. Two large sources of uncertainty in this approach, if not the largest, are the well spacing within the control plane, and the estimates of $\tilde{q}_i$, especially given the dependence of the SSF on results from a single well (17D).

Well spacing impacts the uncertainty of $\dot{m}$ estimates, and therefore the SSF, and the large un-sampled space between the available wells suggested high uncertainty. For example, the average well spacing and screen interval depth result in a depth-averaged sampling density of ~0.01 points per square meter. Results from MacKay et al. (2012) suggest relative percent difference between measured and true mass discharges may range from -100% (the minimum possible) to >150% for this sampling density; while results from Chen et al. (2014) and Brooks et al. (2015) suggest the uncertainty (expressed as the standard deviation of error and coefficient of variation in $\dot{m}$, respectively) may be ~300% depending on the plume width and maximum J .

The other source of large uncertainty with this approach stems from the estimate of $\tilde{q}_i$ based on K_i and $\tilde{I}_i$. Uncertainty may exist in both measurements, and it may arise in the product of the two when the support volumes associated with the two measurements are not similar (e.g., Kübert and Finkel, 2006). As conducted in this study, an independent measurement (e.g., PFMs) was used to confirm the value of $\tilde{q}_i$, at least in the well with the greatest impact on the SSF, and therefore reduce the uncertainty associated with this estimate. The

agreement between the two measurements in our study, however, does not mean similar confirmation is unwarranted at other sites. Finally, this approach provides estimates of $\dot{m}$ at one control plane. If attempts had been made to use these $\dot{m}$ measurements to predict $\dot{m}$ at downgradient locations, there would have been uncertainty in the predictions because of various fate and transport properties between the locations.

The second approach relied on spatially distributed $\dot{m}$ at a fixed time to measure the SSF. In this study, these were completed using PFMs to measure J in a combination of existing and newly installed monitoring wells. The sampling density was 0.6 points per square meter for both control planes CP15 and CP17 during both PFM events 3 and 4. As a result, it is estimated that the uncertainty in $\dot{m}$ estimates based on PFM measurements is an order-of-magnitude less than uncertainty in $\dot{m}$ estimates based on LTM data in the first approach. The sampling densities used in control plane CP39 were not as high, and for PFM events 3 and 4 were 0.1 and 0.2 points per square meter, respectively. However, uncertainty in $\dot{m}$ estimates are still believed to be an order-of-magnitude less than those based on the LTM data. Supporting details for these statements are provided in Section SI-4 of Supplementary Information.

The second approach also relied on an estimate of $\bar{q}$ to calculate the τ between control planes. However, given that J measurements were completed using PFMs, a device which also provides estimates of q , data was available upon which to base an estimate. Nonetheless, a source of uncertainty in this approach is the need to estimate $\bar{q}$ in a heterogeneous environment. In theory, only one deployment in time would be needed to estimate a SSF using spatially distributed $\dot{m}$ measurements. However, results from the fourth PFM deployment illustrate the potential hazards of doing so if unaverage conditions prevail during the deployment. Moreover, it might be difficult to assess how well conditions during the deployment represent average conditions over the life of the contaminant plume. While estimates of $\dot{m}$ did not appear to be sensitive to changes in hydrologic conditions that occurred during PFM events 3 and 4, the estimate of $\bar{q}$ was different, resulting in a SSF different from those based on the LTM and PFM event 3 data sets.

Relative to the first approach, the second approach required significantly more expense to complete. This expense may have been reduced by using less wells at greater spacing, or by averaging PFM samples over larger intervals, which reflects the tradeoff between cost and certainty. However, the utility of the generated data extends beyond that associated with estimation of the SSF alone, and it is useful for other site management purposes. For example, while details of the spatial J distributions across a given control plane were not discussed in this work, it is useful to note that further efforts at addressing the risk associated with the remaining DNAPL mass could be guided by this distribution. For example, the $\dot{m}$ associated with CP17 is predominately centered on the lower part of well 17D. This indicates that the best place for any further DNAPL characterization activities is the area upgradient of this location, but downgradient of CP15, at a depth comparable to the hotspot in 17D. Moreover, spatial flux distributions could also be used to target remediation activities, whether in the source or plume.

The combined use of both approaches provided complimentary lines of evidence for a site-specific estimate of the SSF. Similarity between SSFs based on the LTM and PFM event 3 data sets helped address uncertainty in τ estimates based on an estimate of $\bar{q}$, and the dissimilarity in results between LTM and PFM event 4 highlighted the unusual hydrologic conditions during that deployment. Likewise, the similarity between the LTM and PFM event 3 data sets helped address uncertainty associated with the wells spacing and $\bar{q}_i$ estimates in the approach based on the LTM data. The similarity in the data sets also supports the use of the SSF estimate as a site-wide estimate, given the spatial distribution of the three control planes in the second approach.

The $\dot{m}$ data can be used for SSF model calibration, which then can be used to support site management decisions. Perhaps the most common and simplest model to adopt is an exponential function:

$$\dot{m} = \dot{m}_0 \exp\left[-\frac{\dot{m}_0}{M_0} t\right] \quad (4)$$

Where $\dot{m}_0$ and M_0 are the initial mass discharge [MT^{-1}] and mass [M], respectively. Another reason for selecting an exponential model for illustration is that results from Chen and Jawitz (2009) indicate that as the DNAPL source zone ages, the SSF converges to an exponentially decreasing model. The exponential model was fit to the data by treating $\dot{m}_0$ and M_0 as fitting parameters to minimize the difference between the modeled and measured data. As noted above, measurements upon which to base the model fits were first collected in May 1996, and that date was therefore used as the initial year. Model fits are summarized in Table 4 for the LTM, PFM event 3, and PFM event 4 data sets, as well the combined LTM/PFM event 3 data set. Moreover, the model fit for the LTM data is shown in Fig. 5a, and the combined LTM/PFM event 3 model is shown in Fig. 7. Model parameters are within a factor of two for the LTM data and PFM event 3 data. However, parameters differ by as much as two orders of magnitude for the fit associated with PFM event 4. Given the similarity in $\dot{m}$ estimates between PFM events 3 and 4, this difference must stem primarily from the high value of $\bar{q}$ for PFM event 4.

4.4. Modeling to demonstrate the complementary nature of the two approaches

The similarity between the LTM and PFM event 3 data as illustrated in Fig. 7 gives confidence to the use of this combined data set for site-specific SSF calibration relative to either the LTM or PFM event 3 data sets being solely used. To illustrate how both approaches provide data to support a common SSF, modeling simulations were completed using REMChlor (Falta, 2008) based on the input parameters summarized in Table 5. REMChlor assumes a Power Law Model (PLM) to describe the DNAPL architecture and dissolution behavior, and an exponent of 1 was used to represent an exponential function as used in the previous section. The values for $\dot{m}_0$ and M_0 were based on the exponential model fit to the combined LTM-PFM event 3 data set as shown in Fig. 7. The basis for the remaining values used are summarized in Table 5, and are generally based on conditions at this site. However, use of this model with the parameters shown in Table 5 is not meant to be a strict calibration exercise, but rather an exercise to illustrate the similarity in $\dot{m}$ obtained

by temporal measurements at a fixed location versus spatially distributed measurements at a fixed time. Two cases were investigated: Case 1 with minimal longitudinal dispersion, and Case 2 with moderate longitudinal dispersion. REMChlor uses a streamtube-based approach for simulating longitudinal dispersion, which results in a scale-dependent dispersivity value (i.e., dispersivity is a linear function of travel distance, or the ratio of dispersivity to travel distance is constant). For Case 1, the ratio of dispersivity to travel distance was assumed to be $5\text{E-}11$, and for Case 2 the ratio was assumed to be 0.02 . These values result in $\text{SigmaV} = \{0.00001, 0.2\}$, respectively, as shown in Table 5, where SigmaV represents the groundwater velocity coefficient of variation (Falta, 2008).

Modeling results are shown in Fig. 8. The r^2 value based on fitting an exponential model to both data sets is 0.999 in Case 1, and the slope (in linear-natural log space) is $0.00043 \text{ days}^{-1}$, which is equal to the source decay term (i.e., $\dot{m}_0/M_0$) used as input to the PLM. Case 1 illustrates that, in the absence of longitudinal dispersion and decay processes, the original source function is recovered using either approach. Moreover, estimation of the SSF is insensitive to transverse dispersion since $\dot{m}$ is based on the integration of measurements across the control plane. Case 2 illustrates that for the modeling simulation investigated longitudinal dispersion has a minor impact on the estimation of the SSF. The r^2 value based on fitting an exponential model to the simulated data in this case is 0.996 , and the slope (in linear-natural log space) is still $0.00043 \text{ days}^{-1}$, again equal to the input source decay term. A comparison of the spatially distributed $\dot{m}$ data at a fixed time to the temporally distributed $\dot{m}$ at a fixed location in Case 2 indicates the former appears to have a slightly more negative slope than the latter. This same pattern is evident in Fig. 7 when comparing the LTM data to that from PFM event 3.

4.5. Mass balance applications

Using the SSF based on the combined LTM/PFM event 3 data sets with the assumed exponential SSF, it is estimated that $\dot{m}_0 \cong 400 \text{ g/day}$ and $M_0 \cong 1000 \text{ kg}$. These numbers reflect $\dot{m}$ at CP17 in May 1996, and the mass remaining upgradient of CP17 at that time. An estimate of the remaining DNAPL as of 2017 based on the SSF is $\sim 60 \text{ kg}$. Lacking data to suggest more specific uncertainty bounds on the estimate of remaining DNAPL, plus or minus an order-of-magnitude is assumed (i.e., 6 to 600 kg). One way by which to gage the significance of this number is to compare it to the contaminant mass in the plume. This comparison has been used to define the relative age of a DNAPL source by Chen and Jawitz (2009). A relatively young site has the majority of contaminant mass in the source zone, and a relatively aged site has the majority of the contaminant mass in the plume.

Tetra Tech (2010) estimated an average, equivalent TCE dissolved phase mass of $\sim 2000 \text{ kg}$ for the period between 2005 and 2009. This estimate accounts for abiotic and biotic degradation using a molar sum of PCA, TCE, and DCE. Further degradation is not considered significant to plume mass estimates because DCE concentrations have been roughly an order-of-magnitude smaller than TCE concentrations. Mass loss due to volatilization was neglected, an assumption supported by the fact that a large fraction of the contaminant mass is located well below the water table. Sorbed mass is accounted for using $R = 5$ as estimated previously. Values of retardation factors specific to PCA and DCE are not

used, which is not considered to be a significant issue since the dominant chemical species in the plume is TCE. The plume mass accounting for sorbed mass is therefore ~10,000 kg. Mass estimates were presumably restricted to the borders of the site, and did not account for any mass that may have migrated beyond the site borders. Another source of uncertainty is the potential loss of mass to the underlying rock formation. Consequently, plume mass estimates may have a negative bias. This is likewise suggested by comparing the estimate of 10,000 kg to the estimate of the total mass released (45,000 kg) based on historic data, assuming little to no DNAPL remains. However, given the potential uncertainty in both estimates, a factor of 4.5 difference may not be significant. Finally, comparisons between the source and plume mass when considering the relative age of the DNAPL source are made within an assumed framework of a single source that creates the entire contaminant plume for the site. There is uncertainty that this is the case for the Calf Pasture Point site given the extent of contamination to the west of the control planes. However, the majority of the contaminant plume is captured by the control plane locations, and as such the evaluation of relative age is useful for a screening-level analysis.

Using the SSF, an estimate of the DNAPL mass upgradient of CP17 at the midpoint of the time frame for the plume mass estimate (2007) is ~200 kg. The difference between DNAPL mass in 2007 (~200 kg) and 2017 (~60 kg) is ~140 kg. Adding this mass to the estimate of plume mass from 2007 (10,000 kg) gives a 2017 plume mass estimate of ~10,140 kg, which given the uncertainty of the former, essentially results in the same plume mass estimate. Moreover, given the relative insignificance of ~60 kg compared to ~10,140 kg, the site is considered to be an aged site, with the majority of the DNAPL mass in the plume. This statement is valid even with the assumed order-of-magnitude uncertainty range on DNAPL mass. Given the relative amount of DNAPL mass compared to the plume mass, it is estimated that the source has limited potential to enlarge the contaminant plume, and that since the plume contains the majority of the contaminant mass, addressing the remaining DNAPL mass may represent a secondary priority compared to eliminating or minimizing the risk associated with the contaminant plume. Other factors however may impact evaluations of relative risk, and comparisons of DNAPL mass to plume mass is but one facet of such an evaluation.

5. Summary and conclusions

Source strength functions provide a quantitative model of DNAPL source zone behavior, and as such are useful for contaminated site management. Two approaches were used to estimate SSFs for the Calf Pasture Point site: one based on temporally distributed $\dot{m}$ measurements at a fixed control plane, and the other based on spatially distributed $\dot{m}$ measurements across three control planes at the same time. The combined use of both approaches provided complimentary lines of evidence for a site-specific estimate of the SSF.

The former was based exclusively on data that had been collected as part of site characterization and as part of the LTM activities, and demonstrates the utility of this type of data in flux-based site management. Results of this analysis indicated $\dot{m}$ across a control plane downgradient of the assumed source location had been as high as ~300 g/day in 1996, and has decreased to ~70 g/day in 2012. A limited set of groundwater and contaminant flux

measurements using passive flux meters were used to provide additional support for these measurements, and showed that, in this particular application, detailed vertical information did not significantly impact $\dot{m}$ estimates. In large part, this outcome stemmed from the fact that $\dot{m}$ estimates were largely impacted by results from a single well (17D), and estimates of concentration and groundwater flux compared favorably between PFM results and the LTM analysis at this well. However, this outcome is dependent on location-specific conditions of heterogeneity, and similar results at other locations are not necessarily expected.

A SSF was also estimated for the site using $\dot{m}$ measurements across three spatially distributed control planes at a fixed point in time, and is the first such demonstration to our knowledge. These measurements were completed using PFM deployments. The control planes were located at increasing distances downgradient from the assumed source zone. Moving downgradient from the source is comparable to moving backwards in time. Moreover, for the decreasing trend in $\dot{m}$ as measured based on the LTM data, moving downgradient from the source should yield increasing $\dot{m}$ measurements, assuming mass loss processes, such as biotic and abiotic degradation are negligible. For this site, measurements at control planes CP15, CP17, and CP39 (listed in order of increasing downgradient direction) were ~6 g/day, ~37 g/day, and ~400 g/day, respectively. These measurements were compared to those from the LTM data using estimates of travel time.

For one of two complete PFM measurement events, $\dot{m}$ from the spatially distributed control planes compared favorably with the estimates from the LTM data, which provides a data set with more confidence upon which to calibrate a SSF model because each approach offered complimentary strengths. For the second complete PFM measurement event, $\dot{m}$ from the spatially distributed control planes also compared favorably with the estimates from the LTM data, relative to the magnitude of $\dot{m}$ (e.g., the $\dot{m}$ estimates from PFM events 3 and 4 were within 20% of one another); however, the timing of the $\dot{m}$ estimates using travel time did not compare well. This discrepancy was attributed with an unusually large rainfall event that occurred at the start of the PFM event, and highlights the need to evaluate conditions during deployment relative to conditions that usually prevail at a given site. Using SSF estimates from both approaches provided the means of comparison by which to identify the abnormal hydrologic conditions associated with the second complete measurement event.

A number of SSF models are available and can be used for assisting with contaminated site management decisions. As an illustration, an exponential model was assumed, and the measured data was used for model calibration. The SSF model was used to estimate DNAPL mass, and this was compared to the dissolved contaminant mass in the plume. The latter was roughly two to three orders of magnitude greater than the former. This comparison indicates an aged site, and suggests that the dissolution of any remaining DNAPL should not have a huge impact on contaminant mass in the plume.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

Groundwater elevation contour map based on average groundwater elevation measurements from the long-term monitoring data. Blue lines represent contour elevations in feet above mean sea level. The bold red line represents the curvilinear source-zone control plane based on historic data, and the blue arrows indicate the groundwater flow direction across it. The cross hatch represents the excavation area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2.
Hydraulic gradient normal to an assumed straight-line control plane at 17D based on the LTM data. The line with the long dashes represents the average hydraulic gradient, and the line with the short dashes represents a linear trend line.

Fig. 3.
Location of PFM deployments during PFM events 1 (open diamonds) and 2 (closed circles).

Fig. 4.

Location of PFM deployments (open diamonds) during PFM events 3 and 4, separated into shallow, intermediate, and deep horizons. Average groundwater elevation contours (thin blue lines) are based on groundwater elevation measurements in select wells (closed circles). Also shown are straight (bold dashed line) and curvilinear control planes (bold solid line) for CP39. Control planes are not shown for CP15 and CP17 to facilitate the illustration of well locations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5.

a) Equivalent TCE mass discharge at CP17 based on LTM data (closed circles) and an exponential SSF model (line), and b) equivalent TCE mass discharge at CP15, CP17, and CP39 for PFM event 3 (open diamonds), PFM event 4 (open triangles), and an exponential trend fit (line) to the average values at each control plane.

Fig. 6.

Histograms of groundwater flux for PFM events a) 1, b) 2, c) 3, and d) 4. The red bars in panel (d) represent the histogram using only those wells included in PFM event 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7.

Comparison of mass discharge estimates based on LTM data with spatially distributed mass discharge estimates based on PFM data. Travel time estimates for PFM events 3 and 4 were based on the geometric mean of the groundwater flux measured during each event.

Fig. 8. Modeling results from REMChlor comparing SSFs based on temporally distributed data at a fixed location (circles) versus spatially distributed data at a fixed time (triangles) for two cases: a) Case 1 minimal longitudinal dispersion, and b) Case 2 moderate longitudinal dispersion. The x-axis references 1996 with a travel time of zero as its starting point (i.e., $t_0 = 1996$ and $\tau = 0$).

Table 1.

Summary of PFM Deployments. Well locations are shown in Fig. 3, Fig. 4.

PFM deployment event	Deployment date(s)	Retrieval date(s)	Deployment duration	Number of wells
1	September 22, 2010	October 7, 2010	2 weeks	5 existing wells
2	March 23 and 24, 2011	April 6 and 7, 2011	2 weeks	12 existing wells
3	September 23 and 27, 2011	October 17 and 18, 2011	3 weeks	29 new and existing wells
4	March 25 to 27, 2014	April 14 and 16, 2014	3 weeks	44 new and existing wells

Table 2.

Summary of groundwater flux, equivalent TCE mass flux, and equivalent TCE flux-averaged concentration measured in the four PFM sampling events. The minimum TCE mass flux and flux-averaged concentration in each sampling event is not listed in the table, and they reflect method detection limits, estimated to be approximately 0.4 mg/m²/day and 0.04 mg/l, respectively.

PFM Event	Number of samples	Groundwater flux (cm/day)				TCE Mass flux (mg/m ² /day)			TCE flux-average concentration (mg/l)		
		Min	Med	Ave	Max	Med	Ave	Max	Med	Ave	Max
1	70	0.3	1.0	1.0	3.7	126	442	2186	11	47	248
2	123	0.7	1.5	1.7	5.3	147	305	2438	8	19	107
3	297	0.1	1.6	2.1	6.0	65	228	1833	5	25	247
4	435	0.4	5.1	5.2	11.3	81	274	5718	2	7	130
4 [*]	290	0.5	4.8	5.1	11.1	37	244	2876	1	7	130

* PFM event 4 refers to a subset of the PFM event 4 results that correspond to wells sampled in PFM event 3.

Table 3.

Summary of spatially distributed mass discharge measurements (g/day) using PFMs. PFM events 3 and 4 are labeled PFM3 and PFM4, respectively.

Control Plane	Mass Discharge (g/day)		
	PFM3	PFM4	PFM4*
15I	0.1	0.0	–
15D	5.3	6.8	–
15 Sum	5.4	6.8	–
17I	2.0	0.8	–
17D	36	37	–
17 Sum	38	38	–
39S	71	75	49
39I	86	143	19
39D	265	285	252
39 Sum	422	503	320

* PFM4 are mass discharge estimates using PFM4 results from the same set of wells used in PFM3.

Table 4.

Summary of exponential SSF fits.

Data	$\dot{m}_0$ (g/day)	$\dot{m}_0 / M_0$ (1/day)	r^2
LTM Data	260	3E-4	0.55
PFM3	360	4E-4	1.00
PFM4	210,000	1E-3	1.00
LTM&PFM3	370	4E-4	0.85

Table 5.

Summary of REMChlor model input. Case 2 parameter values are the same as Case 1 unless otherwise noted. Simulations assumed no contaminant degradation and no DNAPL remedial activities.

Parameter	Units	Case 1	Case 2	Basis
Instantaneous DNAPL release date	–	1968		(1)
Initial mass discharge	g/day	9800		(2)
Initial DNAPL mass	kg	23,000		(2)
PLM Gamma	–	1		(3)
DNAPL source zone width	m	30		(4)
DNAPL source zone height	m	10		(4)
Groundwater flux	cm/day	2		(5)
Porosity	–	0.25		(1)
Retardation	–	5		(1)
Transverse dispersivity	m	0.1		(3)
Vertical dispersivity	m	0.1		(3)
Number of stream tubes	–	200		(3)
SigmaV	–	0.00001	0.20	(3)
Vmax	cm/day	1.00004	1.8	(3)
Vmin	cm/day	0.99996	0.22	(3)

Basis: (1) Site characterization information, (2) Model fit to the combined LTM-PFM event 3 data set, (3) Assumed value, (4) SZCP area from LTM data analysis, (5) Spatially averaged values from PFM Event 3.