Determination of contaminant transport parameters for a local aquifer by numerical modeling of two plumes: Trichloroethylene and Hexavalent Chromium

Mahade Ibn Salam

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PREFACE

This dissertation is formatted based on the journal format of the *Journal of Contaminant Hydrology.*
ABSTRACT

The primary aquifer supporting the municipal wellfield in Collierville, Tennessee, has been contaminated with trichloroethylene (TCE) and hexavalent chromium (Cr (VI)) since the 1970s and 1980s. Both plumes generated from industrial operations near the municipal wellfield are now under remediation though the cleanup goals have not been achieved yet. This study determines the contaminant transport parameter, longitudinal ($\alpha_L$) and transverse dispersivities ($\alpha_T$, $\alpha_V$) in the aquifer using a simulation optimization-based approach. The contaminant transport model was simulated using MT3DMS using the outputs of a well-calibrated MODFLOW-NWT flow model. Transport models were most sensitive to source concentration and initial boundary conditions. The total simulation runtime was reduced 8-fold using the Python multiprocessing library. The optimum calibrated values for longitudinal dispersivity ($\alpha_L$) in the aquifer range from 5.5 m at 80 to 86 m from source to 20.5 m at a distance 950 m from source, while the transverse dispersivities range from 0.28 to 6.98 m for horizontal ($\alpha_T$) and 0.03 to 0.10 m for vertical ($\alpha_V$). This study proposes a fast and simplified approach to estimate all three dispersivity coefficients using a numerical model and quantifies the scale dependency of longitudinal dispersivity.
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1. Introduction

Predicting the propagation of dissolved contaminants in an aquifer requires adequate characterization of transport parameters. Due to the unknown complexity of the subsurface system, these parameters are often assumed and rarely quantified at the required spatial resolution. Many transport models implement the advection-dispersion equation, which considers advection, mechanical dispersion, and diffusion along with other parameters such as reaction and retardation. This dispersion parameter is crucial in describing the spreading of solute due to heterogeneity and is difficult to quantify due to its scale-dependent nature.

In many investigations, dispersivity is estimated through adjustments until the modeling plume best approximates observed concentrations (Coats & Smith, 1964; Chapelle, 1986; Avon & Bredehoeft, 1989; Chiang et al., 1989; Jensen et al., 1993; Zou & Parr, 1994; Engesgaard et al., 1996; Hyndman & Gorelick, 1996; Mallants et al., 2000; Schulze-Makuch, 2005; Cupola et al., 2015a). An alternative approach to estimating dispersivity is through field and laboratory experiments conducted at different spatial scales (Bai et al., 2016; Citarella et al., 2015; Cupola et al., 2015b; Frippiat et al., 2008; Kret et al., 2015; Shamir & Harleman, 1967; S. P. Sternberg et al., 1996; S. P. K. Sternberg, 2004; Tan et al., 2016; Zhang et al., 2018). Field tracer tests are often time-consuming and very expensive. Some researchers attempted upscaling the laboratory-derived values to apply in field experiments (Klotz et al., 1980), as well as to examine the scale-dependent nature (Pickens & Grisak, 1981) and to compare with field values (Taylor et al., 1987). However, Dagan (1986) and Gelhar (1986) showed that field-scale macrodispersion is affected by parameters including the integral scale of the log-conductivity and variance and thus cannot be assessed from the laboratory-scale experiment, which provides only a local dispersion.
Gelhar et al. (1992) did a critical review of 59 different field sites and found that longitudinal dispersivity ranged from $10^{-2}$ to $10^4$ m for scales ranging from $10^{-1}$ to $10^5$ m. Improving on that, Schulze-Makuch (2005) compiled 307 values of longitudinal dispersivity from 109 authors consisting of lab experiments, aquifer tests, and numerical models representing various types of aquifer media and found that longitudinal dispersivity increases exponentially with the scale of measurement. Also highlighted in this study was the wide range of reported longitudinal dispersivity, 0.0003 to 30.5 m for an observation distance of 0.2 and 8,800 m, respectively, in unconsolidated sediments, and 0.0016 to 48.7 m at an observation distance of 0.035 and 3,066 m, respectively, in consolidated sediment (Schulze-Makuch, 2005).

Numerical models offer a robust way to simulate contaminants on a larger scale in all three dimensions and are used in many studies (Anderson & Cherry, 1979; Chapelle, 1986; Avon & Bredehoeft, 1989; Guo et al., 2019; Hamzaoui-Azaza et al., 2020; Banaei et al., 2021). For a numerical model to simulate contaminants, a well-calibrated groundwater flow model is required to represent the flow field adequately. Given a properly defined boundary condition and starting concentration, a transport model can then predict the movement of a contaminant using the flow model results. Contaminants typically enter the groundwater system through some form of recharge. In numerical models, it is common to specify a Dirichlet boundary (constant concentration) to the grid's selected nodes, creating a solute flux by both advective and dispersive processes (Konikow et al., 1997). However, field hydrogeology conditions rarely support the conceptualization of a Dirichlet-type boundary due to the transient nature of groundwater movement and the change in concentration gradient over time. Hence, defining the proper source boundary condition is vital for a better predictive model for avoiding non-uniqueness against different dispersivity values.
Determination of the hydrodynamic dispersion coefficient requires the source concentration and observed concentration data over time from an active contaminant plume or tracer experiments. In Shelby County, Tennessee, the primary drinking water aquifer is the semi-confined unconsolidated Memphis aquifer (Criner & Parks, 1976; Kingsbury, 1996). The aquifer is threatened by the presence of localized preferential pathways (i.e., breaches) in the overlying aquitard (the upper Claiborne confining unit – UCCU), warranting concern that contaminants could easily by-pass the aquitard's natural protection (Parks and Carmichael 1990; Bradley 1991; Parks et al. 1995; Carmichael 1997; Larsen et al. 2003; Clark and Hart 2009; Waldron et al. 2009; Ge et al. 2010; Carmichael et al. 2018; Jazaei et al. 2018; Torres-Uribe et al. 2021). Very little is known about the contaminant transport properties of the Memphis aquifer. This study aims to derive longitudinal, transverse, and vertical dispersivity from two plumes of trichloroethylene (TCE) and hexavalent chromium (Cr(VI)) in the vicinity of a public utility wellfield and determine the dispersivity's scale dependency.

2. Methods

2.1 Study Area

In southeastern Shelby County, Tennessee, the Town of Collierville was selected because of the impact on one of Collierville's five wellfields by two U.S. Environmental Protection Agency (EPA) Superfund sites which include TCE and Cr (VI) as contaminants of concern (Figure 1). As shown in Figure 1, Collierville's Wellfield #2 (WF2) is adjacent to the north-northwest and downgradient from the Carrier facility and 0.8 km to the west, downgradient from Smalley Piper. WF2 came online in 1967, producing 6,166 m³/d from two that are screened in the Memphis aquifer at depths of 87.5 m (COLL-201) and 98.7m (COLL-202). The Memphis aquifer is
unconfined beneath portions of Collierville (Graham 1986; Parks 1990), making it easier for anthropogenic contaminants to reach the Memphis aquifer.

2.1.1 Carrier Corporation

The Carrier site began operations in 1967, producing air conditioning units. In 1979, a vapor degreaser unit failed, leaking approximately 7,500 to 19,000 liters of TCE on the southeast side of the property. Carrier also had an unlined 6 m³ lagoon since 1972 for storing TCE-contaminated paint sludge, which was filled in 1980. After a heavy rainfall in 1985, Carrier discovered that an unknown quantity of TCE leaked from underground pipes associated with a
TCE aboveground storage tank, all of which was removed within a month of the spill, and 2,052 liters of TCE were recovered. Low levels of TCE were detected in the nearby wellfield (WF2) in 1986, and in 1990 the site was listed as a U.S. EPA Superfund site. WF2 continued to operate until December 2003, when hexavalent chromium from the nearby Smalley Piper site reached the pumping wells.

Forty-three monitoring wells were installed between 1986 to 2016 for monitoring and remediation purposes at the site. An expansion of the main building in 2004 closed many wells whose locations were not determined. Among the remaining wells, the location of 19 wells were determined that had either concentration or water level data or both at different times. The locations of all the wells are shown in (Figure1). Among those 19 wells, 13 were selected to use in this study. Six wells among those 13, namely MW-1, MW-1B, MW-10, MW-15, MW-19, and MW-21 were used to determine the source concentration of the three sources (1979 spill, 1985 spill, unlined lagoon). The remaining 7 wells (MW-5, MW-101, MW-301, MW-501, MW-601, MW-701, MW-60) were used to find dispersivity values and are shown in (Figure2).

### 2.1.2 Smalley Piper

The second Superfund site, Smalley Piper, manufactured magnesium battery casings from 1970 to 1981. This site had two tarpaulin-lined ponds for treating chromic acid-induced wastewater (Black & Veatch Special Projects Corp, 2017). Approximately 2 m³ of chromic acid were discharged once a week via an underground pipe into the treatment ponds, where liquid sulphur dioxide (SO₂) was injected twice per week to precipitate chromic sulfide as less toxic trivalent chromium. However, the reaction efficiency depends on the quantity of SO₂ and mixing, and incomplete reactions result in hexavalent chromium present in the wastewater (Black & Veatch Special Projects Corp, 2017).
The remaining wastewater (100 m³/day) containing hexavalent chromium were discharged into onsite drainage ditches that flowed into Nonconnah Creek, approximately 0.4 km south of the facility. The manufacturing operation ceased in 1981-82, and the treatment ponds were closed. Since 2007, the former industrial processing buildings on the western portion of the site have remained, while the eastern portion of the site has been redeveloped and is currently operating as a public mini-storage facility (Black & Veatch, 2014).
A groundwater remediation investigation conducted in 2004 determined that the highest concentrations of Cr(VI) were found 23 to 30.5 m below land surface (bls), ranging between 20,000 to more than 250,000 micrograms per liter (µg/L). Groundwater samples from depths greater than 30.5 m bls exhibited total chromium concentrations below the 100 µg/L maximum contaminant level (MCL) specified by the World Health Organization and U.S. EPA. Chromium contamination was not detected in groundwater collected from the eastern part of the property boundary, which is hydrologically upgradient of the site (Figure 1) (ATSDR, 2006).

A total of 21 monitoring wells were installed between 2002 and 2006. Among those 21 wells, nine wells (Figure 1) were selected for this study due to the quality of data. Among these wells MW-8 was used to define the contamination source, and the remaining wells were used to determine the dispersivity values (Figure 2).

2.2 Numerical Flow Model

The Collierville area was included in a calibrated groundwater model (i.e., CAESER II) that simulated groundwater conditions beneath Shelby County between 1960 and 2021 within the shallow Memphis and Fort Pillow aquifers (Hasan, unpublished). CAESER-II is an updated model based on Villalpando-Vizcaino et al. (2021) (i.e., CAESER-I), which simulates the multi-layer aquifer system in the Shelby County area with a cell size of 250 m using MODFLOW-NWT. In CAESER-II, the shallow aquifer was represented as one layer, the UCCU as one layer, the Memphis aquifer as four layers, the Flour Island confining unit as one layer, and the Fort Pillow aquifer as one layer. Hasan (unpublished) extended CAESER-I from 2005 back to 1960 to account for flow conditions during the time when most contaminant spills in the area occurred, recalibrating the model with updated Memphis aquifer properties based on (Sahagún-
Covarrubias et al., 2022), historical pumping data, and hydraulic conductivities measured on a borehole sample obtained from a UCCU breach (Hasan, unpublished).

For this investigation, a submodel was created from CAESER-II to perform contaminant transport modeling. The smaller submodel was expected to reduce the numerical computational time while generating a more accurate spatial variation of the concentration field. The submodel has 736 stress period spanning from 1960 to 2021, with 79 rows by 101 columns and a uniform spatial resolution of 50 m by 50 m and increasing the vertical representation from 8 to 24 layers. In the submodel, the shallow aquifer was represented by 2 layers, Memphis aquifer by 14 layers, Flour Island confining unit as 4 layers, and the Fort Pillow aquifer as 4 layers (Figure 3).
Figure 3: Plan view of the model extent and model grid with different hydrogeological units. (A) plan view, (B) cross-section of model, and (C) 3d grid.

Aquifer parameters such as hydraulic conductivity (K), horizontal and vertical anisotropy ratios, specific storage ($S_s$), and specific yield ($S_y$) values were interpolated using inverse distance weighting (IDW) from CAESER-II onto the finer grid of the submodel. Time variant specified head boundary condition was implemented for the shallow aquifer. For the Memphis aquifer, a time-variant head was implemented in the eastern and western boundary, while the north and
south boundary was kept no-flow based on historical water level maps (Schrader, 2007). The Flour Island and Fort Pillow boundaries were kept as no-flow following the parent models (Villalpando-Vizcaino et al., 2021; Hasan, unpublished). A zonal flow budget (Table 1) was calculated to compare the submodel with CAESER-II, observing a close match between the two.

Table 1: Flow budget comparison between CAESER-II and submodel.

<table>
<thead>
<tr>
<th>Flow Budget</th>
<th>CAESER-II</th>
<th>Submodel</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STORAGE</td>
<td>125670.4872</td>
<td>125652.8994</td>
</tr>
<tr>
<td>CONSTANT HEAD</td>
<td>16975.0831</td>
<td>194.4989</td>
</tr>
<tr>
<td>WELLS</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>RECHARGE</td>
<td>119.3596</td>
<td>117.8313</td>
</tr>
<tr>
<td>Total IN</td>
<td>142764.9300</td>
<td>148819.2463</td>
</tr>
<tr>
<td>OUT:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STORAGE</td>
<td>126884.2000</td>
<td>119940.1340</td>
</tr>
<tr>
<td>CONSTANT HEAD</td>
<td>15880.7242</td>
<td>31.5263</td>
</tr>
<tr>
<td>WELLS</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>RECHARGE</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Total OUT</td>
<td>142764.9243</td>
<td>148819.2463</td>
</tr>
<tr>
<td>SUMMARY:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IN - OUT</td>
<td>0.0057</td>
<td>-0.0001</td>
</tr>
<tr>
<td>Percent Discrepancy</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Submodel heads were simulated from 1960 to 2021 using MODFLOW-NWT (Niswonger et al., 2011). A cell-by-cell head comparison between the submodel and CAESER-II was performed and, submodel heads were within 0.17 m of CAESER-II therefore, no recalibration was necessary.

2.3 Contaminant Transport Model

The contaminant transport model was calibrated and verified against the observed concentrations in the monitoring wells. Adjusted input parameters were longitudinal and transverse (horizontal and vertical) dispersivities. The source boundary conditions, and initial concentration values
were defined based on historical contaminant data from the monitoring wells adjacent to the source. Source concentration plays a vital role in concentration distribution, and a time-variant specified concentration boundary (Dirichlet) was defined for both sites. These boundaries are termed “source function” and mimic the increase, saturation, and decrease in concentration in groundwater through a rising limb, a plateau, and a receding limb, respectively (Figure 4).

The length of each limb was determined from field data adjacent to the source. Monitoring well MW-15 was used to define the source function for the 1979 spill, MW-19, MW-21 were used for the unlined lagoon, and MW-1, MW-1B, and MW-10 for the 1985 spill at the Carrier site. Of note, Brantley, (2017) infers the existence of the UCCU (termed Jackson Clay in their report) in the vicinity of the Carrier plant. Parks (1990) shows the Carrier facility and all monitoring wells within the Memphis aquifer unconfined zone, absent of the UCCU; however, Larsen et al. (2017) indicates the opposite being most confined. With greater detail of the subsurface provided by (Brantley, 2017) sources at Carrier fall either on the fringe of the UCCU subcrop (by 1-2 cell sizes) or outside its influence. Hence, it is assumed that dissolved phase TCE enters the Memphis aquifer and are not impacted by the UCCU. For the Smalley piper site, data from MW-8 was used. A numerical model approximates a physical process and computes an average concentration for each cell, making it not feasible to match the highly scattered observed data exactly. Therefore, an overall concentration trend match was attained. This type of calibration has been successfully demonstrated by Antonacci et al. (2013) and Avon & Bredehoeft (1989).
Figure 4: Contaminant Source Functions for (A) 1970 Carrier Spill, (B) 1985 Carrier Spill, (C) Unlined lagoon, and (D) 1970 Smalley Piper Source
The inverse transport simulations were done using a Python package called FloPy (Leaf & Fienen, 2022) and MT3DMS (Zheng & Wang, 1999). The FloPy script executed the MT3DMS transport model for both TCE and Cr(VI) plumes for different combinations of dispersivity values (Schulze-Makuch 2005), as shown in Table 2, and computed the root mean squared error (RMSE) between model-simulated and observed concentrations at observation wells. The workflow of the script is shown in Figure 5.

To improve the computational efficiency of multiple MT3DMS model runs, the Python multiprocessing library was used, significantly reducing the total runtime from 30 hours to 3.5 hours with an 8-core Intel Core i7-9700 CPU.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lower Bound (m)</th>
<th>Upper Bound (m)</th>
<th>Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal Dispersivity</td>
<td>0.5</td>
<td>60</td>
<td>0.5</td>
</tr>
<tr>
<td>Ratio of Transverse Horizontal Dispersivity to Longitudinal Dispersivity (TRPT)</td>
<td>0.01</td>
<td>0.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Ratio of Transverse Vertical Dispersivity to Longitudinal Dispersivity (TRVT)</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 2: Dispersion values for MT3DMS simulation
### 3. Results

#### 3.1 Simulated vs Observed Concentrations:

The advection in MT3DMS was solved using third-order TVD (total-variation-diminishing) scheme which is mass conservative and minimizes numerical dispersion and artificial oscillation.

The porosity of Memphis aquifer was assumed as 0.3 per studies done by Larsen & Brock (2014) and Lumsden et al., (2009). No dry cells were observed in the MODFLOW-NWT solutions which eliminates the possibility of contaminant mass accumulation in cells.

Simulated and observed concentration plots for the Carrier and Smalley Piper sites are shown in Figures 5 and 6, respectively. The dispersivity values for each well for both sites are given in Tables 3 (Carrier) and 4 (Smalley Piper).
Figure 6: Carrier Simulation vs Observation data (MW-5, MW101, MW-301, MW-501, MW-601, MW-701, MW-60). Concentrations are in log scale and well locations shown in Figure 2.
Figure 6 shows the simulated vs observed concentration of TCE in seven monitoring wells.

Among those, MW-5 is one of the oldest wells onsite with data available from 1987 to 1988. The other six wells have monitoring data from 2010 to 2019. From the analysis, longitudinal dispersivity values at this site range from 5.5 to 55.5 m, transverse horizontal values range from 0.82 to 24.97 m and vertical dispersivity from 0.03 to 2.22 m (Table 3).

**Table 3: Dispersivity Values (Carrier Site).**

| Well ID | Distance from source (1979) m | Distance from source (1985) m | Distance from Lagoon (1979) m | Longitudinal Dispersivity (m) $\alpha_L$ | Transverse Horizontal Dispersivity (m) $\alpha_T$ | Transverse Vertical Dispersivity (m) $\alpha_V$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MW_5</td>
<td>232.94</td>
<td>182.75</td>
<td>10.5</td>
<td>4.72</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>MW_101</td>
<td>540.88</td>
<td>506.32</td>
<td>31.00</td>
<td>55.5</td>
<td>24.97</td>
<td>2.22</td>
</tr>
<tr>
<td>MW_301</td>
<td>379.69</td>
<td>432.76</td>
<td>55.5</td>
<td>24.97</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>MW_501</td>
<td>119.90</td>
<td>303.37</td>
<td>25.5</td>
<td>1.27</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>MW_701</td>
<td>346.34</td>
<td>267.72</td>
<td>50.5</td>
<td>5.05</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>MW_60</td>
<td>963.03</td>
<td>993.77</td>
<td>448.28</td>
<td>20.5</td>
<td>8.2</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Figure 7: Smalley Piper Simulation vs Observation data (MW-11, MW-15, MW-12, MW-18, MW-20, MW-21, MW-27D). Concentrations are in log scale and well locations shown in Figure 2.
Figure 7 shows the simulated vs observed hexavalent chromium concentration at the Smalley Piper site. All seven observation wells have data ranging from 2005 to 2019. From the analysis, longitudinal dispersivity values at this site range from 5.5 to 55.5 m, transverse horizontal values range from 0.28 to 24.98 m, and vertical dispersivity from 0.03 to 2.50 m, (Table 4).

Table 4: Dispersivity Values (Smalley Piper Site)

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Distance from Source (m)</th>
<th>Longitudinal Dispersivity (m) $\alpha_L$</th>
<th>Transverse Horizontal Dispersivity (m) $\alpha_T$</th>
<th>Transverse Vertical Dispersivity(m) $\alpha_V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-11</td>
<td>80.06</td>
<td>5.5</td>
<td>0.28</td>
<td>0.03</td>
</tr>
<tr>
<td>MW-15</td>
<td>86.90</td>
<td>5.5</td>
<td>2.48</td>
<td>0.08</td>
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<td>MW-12</td>
<td>156.15</td>
<td>55.5</td>
<td>24.98</td>
<td>1.39</td>
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<tr>
<td>MW-18</td>
<td>219.19</td>
<td>20.5</td>
<td>9.23</td>
<td>0.10</td>
</tr>
<tr>
<td>MW-20</td>
<td>695.10</td>
<td>15.5</td>
<td>3.88</td>
<td>0.08</td>
</tr>
<tr>
<td>MW-21</td>
<td>750.91</td>
<td>55.5</td>
<td>24.98</td>
<td>2.50</td>
</tr>
<tr>
<td>MW-27D</td>
<td>954.42</td>
<td>15.5</td>
<td>3.88</td>
<td>0.08</td>
</tr>
</tbody>
</table>
3.2 Comparison with Empirical Dispersivity Equations:

Optimum dispersivity values found in both sites were compared against three empirical equations shown in (Table 5).

Table 5: Empirically derived values of longitudinal dispersivity with their respective equation.

<table>
<thead>
<tr>
<th>Empirical Dispersivity</th>
<th>Calculation – 5m length</th>
<th>Longitudinal Dispersivity (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelhar (1993)</td>
<td>$\alpha_L = 0.1 \times L$</td>
<td>5</td>
</tr>
<tr>
<td>Xu &amp; Eckstein (1995)</td>
<td>$\alpha_L = 0.0176 \times L^{1.46}$</td>
<td>5.32</td>
</tr>
<tr>
<td>Schulze-Makuch (2005)</td>
<td>$\alpha_L = 0.085 \times L^{0.81}$</td>
<td>0.313</td>
</tr>
</tbody>
</table>

Figures 8 show the calculated and optimized values of longitudinal dispersivity for the Carrier and Smalley Piper sites.
Figure 8: Comparison of longitudinal dispersivity values (m) with empirical equations for the (A) Carrier site and (B) Smalley Piper site. Empirical values are in orange (Gelhar, 1993), grey (Xu and Eckstein, 1995), and yellow (Schulze-Makuch, 2005). Model optimized values are shown in light blue.
4. Discussion

The primary goal of this study was to assess the range of all three dispersivity values derived from field-scale contaminant data, using a three-dimensional heterogeneous numerical model, examining the scale dependence of longitudinal dispersivity. A novel approach was employed to concurrently run parameterized MT3DMS simulations, reducing the overall simulation runtime by a factor of eight. The model demonstrated a satisfactory performance in replicating the general concentration trend observed in most wells.

Carrier wells, namely MW-5, MW-101, MW-501, and MW-701 demonstrate a good agreement between observed and model simulation concentrations. However, MW-301, MW-601, and MW-60 show some mismatch in simulated and observed concentrations.

To address the mismatch seen in wells MW-301, MW-601, and MW-60 (Figure 5), an analysis of possible reasons follows. First, the groundwater gradient could be considered in error such that if it shifted to be more in alignment longitudinally with the observation wells, the peak would arrive later in time. However, a comparison between historical water level data (Environmental and Safety Designs, Inc., 1988) and submodel generated heads are shown in (table 6). Among the historical water level data MW-1, MW-1A, MW-1B are within 3.5 m of each other spatially and with similar depth, but exhibit an error of 3 m. MW-5 shows a water level of 94.28 m above mean sea level where prior to any pumping the water level in Collierville was estimated to be 90 m amsl (B. Waldron & Larsen, 2015). Furthermore, Schrader (2007) estimated the water level in the Collierville area to be 85.34 m which is a mere 4.66 m change in 101 years. Submodel data shows a water level difference of 2 to 5 m compared to the historical data in most wells except for MW-5. More recently, a groundwater assessment performed for the Town of Collierville by the Center for Applied Earth Science and Engineering Research
(CAESER) in 2018/19 show groundwater levels to be between 84 to 85 m which is consistent with the submodel generated head values. Ignoring the historical data obtained from the reports (Environmental and Safety Designs, Inc., 1988) due to questionable measurement disparities and relying more on these other measures (Schrader, 2007; B. Waldron & Larsen, 2015), there is no reason to assume a possible shift in submodel gradients.

Table 6: Comparison of historical water level data with submodel heads.

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Depth (m amsl)</th>
<th>Date</th>
<th>Historical Water level data (m amsl)</th>
<th>Submodel head (m amsl)</th>
<th>Difference (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-15</td>
<td>87.57</td>
<td>4/18/1988</td>
<td>88.16</td>
<td>84.76</td>
<td>3.40</td>
</tr>
<tr>
<td>MW-1</td>
<td>71.97</td>
<td>4/18/1988</td>
<td>89.7</td>
<td>84.88</td>
<td>4.82</td>
</tr>
<tr>
<td>MW-1A</td>
<td>89.29</td>
<td>4/18/1988</td>
<td>86.7</td>
<td>84.88</td>
<td>1.82</td>
</tr>
<tr>
<td>MW-1B</td>
<td>72.58</td>
<td>4/18/1988</td>
<td>89.69</td>
<td>84.82</td>
<td>4.87</td>
</tr>
<tr>
<td>MW-5</td>
<td>87.57</td>
<td>4/18/1988</td>
<td>94.28</td>
<td>84.62</td>
<td>9.66</td>
</tr>
<tr>
<td>MW-6</td>
<td>79.21</td>
<td>4/18/1988</td>
<td>86.4</td>
<td>84.62</td>
<td>1.78</td>
</tr>
<tr>
<td>MW-11</td>
<td>88.82</td>
<td>4/18/1988</td>
<td>89.1</td>
<td>84.78</td>
<td>4.32</td>
</tr>
<tr>
<td>MW-12</td>
<td>72.22</td>
<td>4/18/1988</td>
<td>86.5</td>
<td>84.78</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Among the 10 TCE monitoring wells at the Carrier site, MW-3, MW-4, MW-601 are hydrologically upgradient wells (Figure 1). Based on historical concentration measurements on site, MW-3 had a concentration one order of magnitude higher than MW-4 between the period 1987-1989; however, these two wells are spatially 2.34 m apart, are separated 9 m vertically, and
are screened within the same hydrogeologic unit. Subsequently, no reason can be offered as to their drastic differences in concentration; thereby, making them not suitable to use in the numerical model as they fall in the same gid cell that calculates a single average concentration. MW-601 had 45,700 ppb of TCE in 2017, declining to 13,300 ppb in 2019, and is 50 m upgradient from MW-10 which provided the source concentration for the 1985 spill, being upgradient well against the primary direction of flow MW-601 yielded a high dispersivity value yet not reaching the peak.

Despite indicating a good match with observed TCE concentrations, other wells required higher longitudinal dispersivity values compared to empirically derived values. For instance, MW-501 matched well at a longitudinal dispersivity of 25.5 m though it is only 119.9 m from the 1979 source which would imply a lower longitudinal dispersivity (based on scale dependency). This is attributed to high variability of concentrations at MW-15 which, due to its proximity to the source. Between the period of record (1987-1989), MW-15 had concentrations varying two orders of magnitude with a peak value of 400,000 ppb in June 1989, yet two months prior (April) had a measured concentration of 140,000 ppb and 5,900 ppb in January of that same year. This dramatic fluctuation in concentrations leads to misinterpretation of source history and manifested a high dispersivity to match concentrations in observation well MW-501. On the other hand, MW-5 had a longitudinal dispersivity value well within the empirical range. This well is located 182 m downgradient of the 1985 source and the combination of concentration data from MW-1, MW-1B (data from 1986-89) and MW-10 (data from 2010 to 2019) into resulted in a better source characterization than that of 1979. Among other wells, MW-701, MW-301 and MW-101 all required high longitudinal dispersivities (50.5 to 55.5, see Table 3); although, MW-301 simulated concentrations still fell short of observed values (Figure 5). One possible solution to an
improved match is the possibility of preferential flow pathways within the Memphis aquifer (Larsen et al., 2020) which would increase the advective component of transport, and would allow for a decrease in longitudinal dispersivity thus raising the peak of simulated concentration.

Smalley Piper monitoring well simulated concentrations (MW-11, MW-15, MW-12, MW-18, MW-20, and MW-27D) indicate relatively good trend match (i.e., falling within the scatter) with observed hexavalent chromium Cr(VI) concentrations with MW-21 being the only exception. Measured during the same time period, MW-21 has an average concentration of 7,028 ppb and is 33 m downgradient from MW-20 which has an average concentration of only 185.8 ppb, despite their depth difference of only 3 m. This order of magnitude difference between the concentrations of these two wells resulted in two different estimates of longitudinal dispersivity for that location with large disproportionality: MW-20 at 15.5 m and MW-21 at 55.5 m (Table 4). MW-12 is another well which shows an early arrival time due to the high dispersivity values needed to reduce the RMSE errors. Hexavalent chromium concentrations at MW-12 decrease in 2016 while simulated concentrations, though showing a decline, do not match observed concentrations. However, MW-11 situated 85 m upgradient to MW-12 and of similar depth has concentrations an order of magnitude higher than MW-12. Both wells show a trend of decreasing concentrations with time, but MW-12 shows one order of magnitude decrease in concentration between 2010 to 2016 whereas MW-11 shows a gradual decrease. Simulated concentrations at MW-11 prove a much better match to observed values (Figure 6); however, assigning MW-11’s longitudinal dispersivity to this area based on concentration matching alone is undecided by the authors. The remaining wells produced reliable estimates of longitudinal dispersivity ranging from 5.5 m at wells near source (MW-15, MW-11) to 15.5 m at wells further downgradient from the source (MW-18) and 20.5 at the furthest from the source (MW-27D); hence, illustrating an
increase in longitudinal dispersivity with scale of observation following a power law suggested by (Schulze-Makuch, 2005; Xu & Eckstein, 1995).

Transverse horizontal and vertical dispersivity values obtained from this study varies by one order of magnitude for both sites and does not exhibit a scale dependency, deviating from the common practice of heuristic relationship with longitudinal dispersivity (1/10th for transverse horizontal and 1/100th for transverse vertical). Recent studies by Zech et al. (2019) compiled and compared existing reliable estimates of transverse dispersivity to be site specific and show a variation of three order of magnitude with no apparent scale dependency.

The analysis revealed that the concentration time series at observation wells generated by the model were more sensitive to source characterization (location and initial concentration). The Smalley Piper site showed relatively better match in concentrations and subsequent determination of longitudinal dispersivity compared to the Carrier site due to several reasons. Firstly, Smalley Piper had a single source whereas Carrier had three, two of which (1979 spill and unlined lagoon) had questionable data quality (i.e., MW-15 for 1979 spill; MW-19 and MW-21 for the unlined lagoon). This led to poor source characterization lending to high estimation of longitudinal dispersivities. Secondly, concentrations of a single species at a well downgradient from two sources at notable spatial offsets (i.e., MW-301, MW-101) produce two largely differing longitudinal dispersivities, each assigned to a source, that do not conform to the idea of scale-dependent dispersivity. A factor not considered are reactions which would only reduce simulated concentrations which, all other factors remaining the same, would require lower dispersivities to keep peaks (Figures 5 and 6) from declining below observed concentrations. At present, there is no additional data to suggest reactions to TCE and Cr (VI) are occurring.
Upon comparing the computed longitudinal dispersivity values with empirical estimates, it was observed that computed values for Smalley Piper are consistent with the empirical values.

5. Conclusion

This study demonstrates the complexity of quantifying dispersivity in a heterogenous aquifer system with multiple sources and the importance of proper identification of source concentrations as well as contaminant data from monitoring wells.

The range of dispersivity values obtained from this analysis, provides several benefits over analytical or empirical values as numerical models can estimate all three dispersivity values using a minimal amount of observation data at different depths, provided having a well calibrated flow model and known source concentration. The Memphis aquifer although mostly confined, is threatened by anthropogenic contaminations coming through the unconfined area or preferential pathways (i.e., breaches) in the upper Claiborne confining unit (Parks 1990; Waldron et al. 2009; Jazaei et al. 2018; Torres-Uribe et al. 2021) several of which are in the vicinity of municipal wellfields. Dispersivity values obtained in this study are crucial to simulate any existing or future contamination though those breaches.

In this study, contaminant data from two U.S. EPA Superfund sites in Shelby County were used to test the scale-dependent nature of longitudinal dispersivity and evaluate a range of all three dispersivity values using a three-dimensional numerical model. Source boundary conditions were calibrated using historical observation data near contaminant sources and dispersivity values were optimized by minimizing the root mean squared error (RMSE) between observed and simulated concentration. Here are the main conclusions from this study:
• Values of longitudinal dispersivity from the Smalley Piper site agree with empirical values provided by previous works (excluding MW-12). The Carrier site, due to questionable historical data (e.g., high variability within a 6-month period, large differences in concentrations between paired wells within meters of each other), created challenges in generating dispersivity estimates.

• Model derived longitudinal dispersivities range from 5.5 to 20.5 m, transverse horizontal dispersivities range from 0.28 to 6.98 m, and transverse vertical dispersivities range from 0.03 to 0.1 m.

These results show the complexity of estimating field scale dispersivity parameters in the presence of multiple sources (Carrier site) and the importance of calibration of transport parameters using a numerical model.
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