Vertical Screening Distance Criteria to Evaluate Vapor Intrusion Risk from 1,2-Dichloroethane (1,2-DCA)

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Abstract
Vapor intrusion (VI) involves migration of volatile contaminants from subsurface through unsaturated soil into overlying buildings. In 2015, the US EPA recommended an approach for screening VI risks associated with gasoline releases from underground storage tank (UST) sites. Additional assessment of the VI risk from petroleum hydrocarbons was deemed unnecessary for buildings separated from vapor sources by more than recommended vertical screening distances. However, these vertical screening distances did not apply to potential VI risks associated with releases of gasoline containing 1,2-dichloroethane (1,2-DCA), because of a lack of empirical data on the attenuation of 1,2-DCA in soil gas. This study empirically evaluated 144 paired measurements of 1,2-DCA concentrations in soil gas and groundwater collected at 47 petroleum UST sites combined with BioVapor modeling. This included (1) assessing the frequency of 1,2-DCA detections in soil gas below 10⁻⁶ risk-based screening levels at different vertical separation distances and (2) comparing the US EPA recommended vertical screening distances with those predicted by BioVapor modeling. Vertical screening distances were predicted for different soil types using aerobic biodegradation rate constants estimated from the measured soil-gas data combined with conservative estimates of source concentrations. The modeling indicates that the vertical screening distance of 6 feet (1.8 m) recommended for dissolved-phase sources is applicable for 1,2-DCA below certain threshold concentrations in groundwater, while 15 feet (4.6 m) recommended for light nonaqueous phase liquid (LNAPL) sources is applicable for sites with clay and loam soils in the vadose zone, but not sand, if 1,2-DCA concentrations in groundwater exceed 150 µg/L. This dependence of the predicted vertical screening distances on soil type places added emphasis on proper soil characterization for VI screening at sites with 1,2-DCA sources. The soil-gas data suggests that a vertical screening distance of 15 feet (4.6 m) is necessary for both dissolved-phase and LNAPL sources.

Introduction
A combination of 1,2-dichloroethane (1,2-DCA, also called ethylene dichloride) and 1,2-dibromoethane, also called ethylene dibromide (EDB) was added to leaded gasoline to prevent lead oxide deposits from fouling the internal combustion engines of automobiles (Falta et al. 2005). Use of lead scavengers in automobile gasoline started in the mid-1920s and continued until it was phased out beginning in the late 1980s (Falta 2004; US EPA 2006). Lead automobile gasoline contained 1,2-DCA and EDB at concentrations in the range of several hundreds of mg/L (Falta et al. 2005).

Concentrations of 1,2-DCA and EDB in groundwater at former leaded gasoline release sites could reach as high as approximately 3,700 and 1,900 µg/L, respectively, based on equilibrium partitioning with leaded gasoline (Falta 2004). In 2010, U.S. states were prompted by the US EPA to monitor for lead scavengers in groundwater at sites where leaded fuels were either stored or marketed prior to 1986 and where there was a suspected threat to drinking water resources. A nationwide survey of state leaking underground storage tank (UST) programs in the United States identified lead scavengers as a contaminant of concern in groundwater at up to 20% of petroleum UST sites (ASTSWMO 2014).

In 2015, the US EPA Office of Underground Storage Tanks (OST) published a technical guide (US EPA 2015a) recommending the use of vertical screening distances for assessing petroleum vapor intrusion (PVI) risks at leaking UST sites. No further PVI assessment was required at UST sites if the vertical separation distance between a dissolved-phase or light nonaqueous phase liquid (LNAPL) vapor source and an overlying building was ≥6 feet (1.8 m) or 15 feet (4.6 m), respectively. These distances were based on the vertical screening distances derived for benzene, which required the greatest source-building vertical separation distance for concentrations in soil gas to fall below risk-based screening levels of concern for PVI. However, no data were available to estimate vertical screening distances for lead...
scavengers. Hence, the US EPA guidance recommended the collection of soil-gas data at UST sites with gasoline releases with lead scavengers and comparison of measured concentrations to vapor intrusion screening levels (VISLs) available at: https://www.epa.gov/vaporintrusion/vapor-intrusion-screening-level-calculator (US EPA 2014). The VISLs are based on the OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air (US EPA 2015b). The VISLs for 1,2-DCA and EDB in indoor air, soil gas, and groundwater are presented in Table 1.

To help improve the understanding of vapor intrusion risks from lead scavengers, Ma et al. (2016) used a 3-D numerical model to validate the applicability of the vertical screening distances recommended by US EPA OUST for 1,2-DCA and EDB. The modeling was used to predict the potential for vapor intrusion assuming a range of first order rate constants reported in the literature (for aerobic/anaerobic biodegradation and chemical degradation), different soil types (sand, silt, and clay), and measured groundwater concentrations reported in Falta et al. (2005). Model results indicated that a vertical source/building separation distance of 15 feet (4.6 m) was generally sufficient to screen sites for EDB, but not for 1,2-DCA if the concentrations in groundwater exceeded approximately 3 and 30 μg/L, along with sand and silt respectively, in the vadose zone. Their study noted the importance of developing an empirical dataset to evaluate the potential for vapor intrusion of 1,2-DCA and EDB.

The goal of this study was to fill this data gap by assessing the applicability of the US EPA recommended vertical screening distances for 1,2-DCA and EDB through an evaluation of paired soil gas and groundwater concentration data collected at 47 UST sites with likely releases of leaded gasoline (based on UST operational history). Unfortunately, a meaningful evaluation of vertical screening distances for EDB could not be undertaken because soil-gas concentrations were all nondetect at reporting limits (2 μg/m³) that exceeded the soil-gas VISL for EDB at the 10⁻⁶ risk level (0.16 μg/m³). The data for 1,2-DCA were evaluated by two complementary methods. The first method involved empirical evaluation of the percentage frequency of 1,2-DCA detections in soil gas below risk-based screening levels at different vertical separation distances above dissolved-phase and LNAPL sources. This was analogous to the method used to derive vertical screening distances for petroleum hydrocarbons (Lahvis et al. 2013; USEPA 2013). The second method involved (1) calibration of first-order aerobic biodegradation rate constants from soil-gas concentration data using the BioVapor model (DeVaul 2007; API 2010) associated with the known soil types, and measured concentrations of 1,2-DCA in groundwater and (2) prediction of vertical screening distances using these rate constants in combination with the 95th percentile value of the 1,2-DCA concentrations in groundwater in this study as the source concentrations.

Figure 1 compares the cumulative frequency distribution of 1,2-DCA detections in groundwater in this study (N = 114, lowest detection limit of 0.5 μg/L) with the maximum site concentration reported between 2016 and 2018 from 471 petroleum UST sites in the California Geotracker database. These two distributions of 1,2-DCA concentrations in groundwater are very similar (median concentrations of 12 vs. 9 μg/L and 95th percentile concentrations of 360 vs. 474 μg/L, respectively for this study and UST sites in California). This suggested that conclusions of this study will be applicable to a broader population of petroleum UST sites. Figure 1 also indicated that concentrations of 1,2-DCA in groundwater exceed the groundwater VISL at the 10⁻⁶ risk level (2.2 μg/L) at approximately 80% of petroleum UST sites with 1,2-DCA detections in groundwater. Understanding the applicability of the US EPA recommended vertical screening distances to assess the potential vapor intrusion risk from 1,2-DCA will be extremely beneficial in optimizing future site investigations at such sites.

### Study Approach

#### Empirical Evaluation of Applicability of US EPA Recommended Vertical Screening Distances for 1,2-DCA

Data from UST sites were compiled from three main sources: (1) California (GeoTracker database—http://geotracker.waterboards.ca.gov/), (2) site data from other states across the United States and provinces in Canada, and (3) sites in Minnesota (MN) as facilitated by Minnesota Pollution Control Agency. The following criteria were used to filter data for the empirical evaluation.

#### Table 1

| Compound          | Indoor Air (μg/m³) | Soil Gas (μg/m³) | Groundwater (μg/L) |
|-------------------|-------------------|------------------|--------------------|
| 1,2-Dichloroethane | 0.11              | 3.6              | 2.2                |
| 1,2-Dibromoethane | 0.0047            | 0.16             | 0.18               |

Figure 1. Comparison of cumulative frequency distribution of 1,2-DCA detections in groundwater in this study (solid circles) with the 2016–2018 groundwater data from sites in California according to the Geotracker database (dotted line). Vertical line at 2.2 μg/L represents the groundwater VISL at the 10⁻⁶ risk level for 1,2-DCA.
1. Data from locations suggesting presence of LNAPL sources in the vadose zone soils were eliminated. These were identified by reviewing the associated soil boring logs for presence of elevated soil PID readings (e.g., more than 100 ppm) as well as observations of staining and odor due to hydrocarbons (Lahvis et al. 2013; ITRC 2014). In addition, soil-gas sampling locations within 20 feet (6.1 m) of UST, dispenser island or piping were excluded.

2. Data were excluded if the soil-gas sampling location and the paired groundwater well were separated laterally by more than 30 feet (9.1 m). In addition, data were excluded if the groundwater and soil-gas sampling dates were more than 90 days apart.

3. Site groundwater elevation maps were reviewed to ensure that the resulting pairs of soil gas and groundwater data represented site conditions where 1,2-DCA in soil gas were sourced from either a dissolved-phase or LNAPL source at the water table.

4. Only data collected using appropriate soil-gas sampling techniques and analytical protocols were used (California EPA DTSC 2015; NJDEP 2018). The data met all the following criteria:
   a. samples collected from properly constructed permanent soil-gas probes installed using either a hollow stem auger or a direct push tool, typically with a bentonite slurry seal in the annulus between the tubing and borehole wall above the screened interval;
   b. samples collected using Nylon® or Teflon® tubing into laboratory certified Summa® canisters at recommended sampling flow rates (less than 200 mL/min);
   c. samples collected using appropriate leak detection protocols using either helium, 1,1-difluoroethane or isopropanol as a tracer compound;
   d. samples analyzed using either EPA method TO-15, or 8260B.

This data filtering resulted in 200 pairs of soil gas and groundwater data that were suitable for empirical evaluation. The distribution of sites across states, number of data pairs and the range of 1,2-DCA concentrations in soil gas and groundwater are summarized in Table 2. Only data with concentration of 1,2-DCA in groundwater (or reporting risk level) were used for empirical evaluation or BioVapor modeling. This reduced the total number of data pairs to 144. These represented 55 monitoring wells along with the adjacent soil vapor probes (some installed at multiple depths) that were sampled between 2004 and 2017. The predominant vadose zone soil types observed at these locations included—sand (28 locations), loam/silt (16 locations), sandy clay (2 locations), silty clay (8 locations), and clay (1 location).

**Criteria to Distinguish Dissolved Sources from LNAPL Sources at the Water Table**

Distinguishing the vapor source type (LNAPL vs. dissolved phase) is essential for choosing the appropriate vertical screening distance (Lahvis et al. 2013; EPA 2015a). A number of LNAPL indicator criteria have been proposed to make this distinction (Peargin and Kolhatkar 2011; CRC CARE 2013; Lahvis et al. 2013; ITRC 2014; USEPA 2015a; NJDEP 2018).

In this study, we used a concentration of 1000 μg/L benzene in groundwater as the threshold to distinguish between dissolved-phase contamination in groundwater and LNAPL as the source of contamination in the soil gas. This was empirically derived as the 5th percentile of the distribution of average benzene concentrations in groundwater observed in time series data from 269 wells (83 sites) that historically showed measurable LNAPL at some point in time (Peargin and Kolhatkar 2011; ITRC 2014). This meant that if the benzene concentration in groundwater exceeded 1000 μg/L, then there was a 95% probability of residual LNAPL being present, even in the absence of measurable LNAPL in the well.

**Applicability of US EPA Recommended Vertical Screening Distances Based on Soil Vapor Transport Modeling**

Vapor transport modeling was conducted using BioVapor (DeVaull 2007; API 2010) to further support the empirical data assessment of vertical screening distances. BioVapor is an analytical vapor intrusion model that simulates one-dimensional diffusive vapor transport to indoor air and includes oxygen-limited biodegradation in the vadose zone (DeVaull 2007; API 2010). The modeling was conducted to calibrate first order aerobic biodegradation constants (in the

Table 2

| State/Province                  | Number of Sites | Number of Concurrent Soil Gas and Groundwater Concentration Data | Range of Soil-Gas Concentrations of 1,2-DCA (μg/m³) | Range of 1,2-DCA Concentrations in Groundwater (μg/L) |
|--------------------------------|----------------|-----------------------------------------------------------------|-----------------------------------------------|------------------------------------------------------|
| California                      | 32             | 126                                                             | <0.53 to <4400                              | <0.5 to 3300                                      |
| Western Canada¹                 | 5              | 31                                                              | 1 to 120                                    | 1 to 360                                           |
| Washington DC and certain states in the US² | 8              | 38                                                              | <0.3 to 510                                 | 0.5 to 13                                          |
| Minnesota                      | 2              | 5                                                               | <0.81 to <1600                              | <1 to 8.6                                          |
| **TOTAL**                      | **47**         | **200**                                                         |                                               |                                                     |

¹Includes British Columbia, Alberta, and Manitoba.
²Includes North Carolina, Michigan, Alaska, South Carolina, and Pennsylvania.

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aqueous phase) for 1,2-DCA, and then to apply these rate constants to estimate vertical screening distances assuming conservative source concentration and transport parameters and an indoor air VISL at the $10^{-6}$ risk level for 1,2-DCA (0.11 μg/m³). The model approach is described in greater detail in the following sections.

### Estimation of First-Order Aerobic Biodegradation Rate Constants for 1,2-DCA

First-order aerobic biodegradation rate constants for 1,2-DCA were estimated by a best fit of the measured and simulated soil-gas concentration data. A conceptualization of the model domain and boundary conditions used for model calibration is shown in Figure 2 (panels A and B). The model input and parameter values used in transport modeling are summarized in Table 3. The key model assumptions used in the derivation of rate constants are listed below.

First-order aerobic biodegradation reaction kinetics was assumed only when concentrations of oxygen in soil gas ≥1% v/v (API 2009). At concentrations of oxygen less than 1% v/v, only diffusive transport was considered. A 20% v/v constant concentration oxygen boundary condition was assumed at the land surface to be representative of the conditions at soil-gas sampling locations. Four constituents (1,2-DCA, benzene, the aliphatic fraction of Total Petroleum Hydrocarbon [TPH], and the aromatic fraction of TPH) were modeled to account for total biological oxygen demand resulting from a release of weathered gasoline.

It was assumed that the source vapor concentrations for 1,2-DCA, benzene, and the aliphatic and aromatic fractions of TPH were constant at the top of the capillary zone. These were estimated using measured concentrations of 1,2-DCA and benzene in groundwater as follows. Source vapor concentrations for benzene and 1,2-DCA were estimated assuming equilibrium partitioning according to Henry’s Law (assuming a constant and uniform subsurface temperature of 15°C) and a 10-fold reduction in vapor concentrations across the capillary zone (McCarthy and Johnson 1993).

A constant and uniform effective diffusion coefficient was estimated for the vadose zone based on site-specific soil types reported in the data base and default soil properties (total porosity, bulk density, and moisture content) recommended by Environmental Quality Management (2004) for VI modeling applications, and air-phase tortuosity values based on Millington-Quirk relations (Millington, 1959). A soil respiration rate was estimated based on an assumed fraction organic carbon value of 0.002 (g organic carbon/g soil) for all soil types (US EPA 1996).

Default values for building dimensions, foundation properties, and exposure parameters recommended by Environmental Quality Management (2004) for VI modeling applications were used. Advection caused by density or pressure effects in the vadose zone (associated with processes such as barometric pumping, fluctuations in water level table and methanogenesis) were assumed to be negligible compared to diffusion. Additional oxygen demand associated with the oxidation of methane resulting from methanogenesis was not considered in the BioVapor modeling. This was based on the analysis of the US EPA and Australian PVI databases (https://www.epa.gov/ust/petroleum-vapor-intrusion-database) which indicated that methane concentrations over 1% v/v were rarely detected in soil gas at petroleum UST sites (in 33 out of 519 samples, or 6%).

When 1,2-DCA was not detected in the soil-gas sample, the associated detection limit was used for calibration. The 1,2-DCA soil-gas concentration data used for model calibration were initially filtered to eliminate groundwater/soil-gas contamination.

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**Figure 2.** Conceptualizations of the model geometries used in (A) BioVapor model calibration and (B) estimation of vertical screening distance. In the figures, $C_{GW}$ is the measured concentration of 1,2-DCA or benzene in groundwater (μg/L), $C_{source}$ is the estimated source vapor concentration at the top of the capillary zone (μg/m³), $H$ is the chemical specific dimensionless Henry’s Law constant, $C_{SG}$ is the measured soil-gas concentration (μg/m³), $C_{IA}$ is the indoor air VISL at the $10^{-6}$ risk level for 1,2-DCA (0.11 μg/m³), $L$ is the depth below land surface of the vapor source, and $z$ is the soil-gas probe depth below land surface. In (A), $L$ and $z$ are site specific measurements and the location of the aerobic/anaerobic interface in the vadose zone varies as a function of the model input parameters (Table 3).
### Table 3
BioVapor Model Input Used in the Derivation of first-Order Aerobic Biodegradation Rate Constants and Vertical Screening Distances for 1,2-DCA

| Parameter                                                                 | Value   | Units          |
|---------------------------------------------------------------------------|---------|----------------|
| **Exposure and risk factors**                                            |         |                |
| Target hazard quotient for individual chemicals                           | 1       | Dimensionless  |
| Target excess individual lifetime cancer risk                             | 0.000001| Dimensionless  |
| Carcinogen averaging time                                                | 70      | yrs            |
| Non-carcinogen averaging time                                             | 30      | yrs            |
| Body weight—adult                                                         | 70      | kg             |
| Exposure duration                                                         | 30      | yrs            |
| Indoor inhalation rate exposure adjustment                               | 350     | days/yr        |
| **Building parameters**                                                  |         |                |
| Indoor mixing height                                                      | 244     | cm             |
| Air exchange rate                                                         | 6       | l/day          |
| Foundation thickness                                                     | 15      | cm             |
| Foundation area                                                           | 1,060,000| cm²          |
| Foundation crack fraction                                                | 0.000377| cm²-cracks/cm²-total |
| Total porosity (soil-filled cracks)                                       | 1       | cm²-void/cm²-soil |
| Water filled porosity (soil-filled cracks)                               | 0       | cm³-water/cm³-soil |
| Airflow through basement foundation¹                                      | 83      | cm³-air/s      |
| Oxygen concentration at the land surface¹                                 | 20      | % v/v          |
| **Vadose zone parameters**                                               |         |                |
| Soil Type                                                                 | Soil Porosity² | Soil Water Content² | Soil Bulk Density² |
| Sand                                                                     | 0.375   | 0.054          | 1.66             |
| Loam                                                                    | 0.399   | 0.148          | 1.59             |
| Clay                                                                    | 0.415   | 0.215          | 1.43             |
| Soil organic carbon fraction                                             | 0.002   | g-organic carbon/g-soil |
| Annual median soil temperature                                           | 15      | °C             |
| Baseline soil oxygen respiration rate                                    | variable| Calculated from fraction organic carbon⁴ |
| Depth to source (from bottom of foundation)                              | variable| cm             |
| Minimum oxygen concentration for aerobic biodegradation                  | 1       | % v/v          |
| **95% maximum constituent source groundwater concentrations (µg/L)**    |         |                |
| Constituent                                                              |         |                |
| 1,2 DCA                                                                  | 310     | 760            |
| Benzene                                                                  | 930     | 19,000         |
| **95% maximum constituent source vapor concentrations (µg/m³)⁶**        |         |                |
| Constituent                                                              |         |                |
| 1,2 DCA                                                                  | 769     | 1880           |
| Benzene                                                                  | 14,100  | 289,000        |
| TPH Aliphatics⁷                                                          | 804,000 | 16,400,000     |
| TPH Aromatics⁷                                                           | 63,400  | 1,340,000      |

¹Used for calibration of first-order aerobic biodegradation rate constants for 1,2 DCA.
²Recommended value for vapor intrusion modeling in Environmental Quality Management (2004).
³Used in conjunction with slab or basement foundation surface boundary condition for estimation of vertical screening distances for 1,2 DCA.
⁴Based on relations defined in DeVaull (2007).
⁵Defined as benzene concentration in groundwater >1000µg/L.
⁶Based on assuming equilibrium partitioning according to Henry’s Law (0.0248 at 15°C) and attenuation factor of 0.1 across the capillary fringe.
⁷Based on assuming relations defined in API (2010).
data pairs for which first-order aerobic biodegradation rate constants could not be calibrated. This occurred when the measured soil-gas concentrations were greater than those predicted by the BioVapor model based on Fick’s Law of diffusion without biodegradation. This could be caused by several factors, including error or bias in the measurement of the concentrations of 1,2-DCA in groundwater which resulted in reported concentrations that were less than the true concentrations (e.g., due to the effect of borehole dilution), or the presence of vadose-zone sources of vapors that could not be identified based on the available site data. In addition, soil-gas concentration data collected directly above locations (soil-gas probes) where soil-gas concentrations were nondetect were not used for model calibration.

After data filtering, only 30 of the 144 groundwater/soil-gas data pairs were suitable for BioVapor model calibration. This was done by varying the first-order aerobic biodegradation rate constant until best fits of model-predicted and measured soil-gas concentration data were achieved. Rate constants were estimated for dissolved-phase and LNAPL sources of petroleum hydrocarbons, which were differentiated using the benzene groundwater concentration threshold criterion (1000 μg/L) described earlier (Peargin and Kolhatkar 2011; ITRC 2014). The rate constants (and associated vertical screening distances) estimated by transport modeling were assumed to be conservative, yet suitable for screening-distance derivation, given the model was calibrated to largely nondetect soil-gas concentrations at analytical reporting limits greater than actual concentrations (28 out of 30 instances). The predominant types of vadose zone soils reported at these 30 locations were: sand (16 locations), loam (3 locations), silt (5 locations), sandy clay (2 locations), and silty clay (4 locations).

**Prediction of Vertical Screening Distances Using the BioVapor Model**

Vertical screening distances were determined for 1,2-DCA by varying the vertical source-building separation distance until predicted concentrations in indoor air were less than the indoor air target concentration at 10⁻⁶ risk level (0.11 μg/m³) as shown in Figure 2b. Conservative estimates of the vertical screening distances were derived for sand, loam, and clay soils and dissolved-phase and LNAPL sources assuming (1) aerobic biodegradation rate constants determined by model calibration for dissolved-phase and LNAPL sources, (2) 95th percentile source vapor concentrations of 1,2-DCA, benzene, and TPH aliphatic and aromatic hydrocarbons for dissolved-phase and LNAPL sources, (3) a constant airflow of 83 cm/s through a slab-on-grade building foundation, and (4) the model assumptions and parameter values previously presented (Table 3).

The source vapor concentrations for 1,2-DCA and benzene were determined based on the 95th percentile groundwater concentrations in the current dataset, assuming equilibrium partitioning according to Henry’s Law and attenuation factor of 0.1 across the capillary fringe (McCarthy and Johnson 1993). The source vapor concentrations of aliphatic and aromatic hydrocarbons were estimated by applying these source vapor concentrations of benzene to the constituent concentration relationships for weathered gasoline (API 2010). The 95th percentile source vapor concentrations were used for petroleum hydrocarbons (benzene and TPH aliphatic and aromatic fractions) to maximize oxygen demand (i.e., limit the potential for aerobic biodegradation of 1,2-DCA in the vadose zone) and thereby yield longer, more conservative vertical screening distance estimates. The poor correlation between 1,2-DCA and benzene concentrations in groundwater (R² = 0.27, Figure S1) indicates that the combined use of 95th percentile concentrations of 1,2-DCA and benzene to define source vapor concentrations is a very conservative assumption.

**Results and Discussion**

**Empirical Evaluation of the Applicability of US EPA Recommended Vertical Screening Distances for 1,2-DCA**

The vertical screening distances for benzene and the other petroleum hydrocarbons were derived as the vertical separation distances above the dissolved-phase and LNAPL sources required to reduce the contaminant concentration in soil gas below the risk-based screening level with ≥95% probability (EPA 2013; Lahvis et al. 2013). The applicability of these recommended vertical screening distances for 1,2-DCA was evaluated by examining the percentage frequency of 1,2-DCA detections in soil gas below the soil-gas VISL at the 10⁻⁶ risk level (3.6 μg/m³) for different vertical separation distances for dissolved-phase and LNAPL sources, respectively. Figure 3 shows concentration of 1,2-DCA in soil gas plotted as a function of the vertical separation distance (distance above water table) from dissolved-phase (panel A) and LNAPL sources (panel B). Concentrations of 1,2-DCA in groundwater for these data sets ranged from 2.2 to 310 μg/L for dissolved-phase sources and 3 to 3,300 μg/L for LNAPL sources.

As seen in panel A, 1,2-DCA was detected in soil gas in four instances (5%) and was nondetect in 76 instances (95%) associated with a dissolved-phase source. Concentrations of 1,2-DCA in soil gas in two out of these four detections were greater than 3.6 μg/m³ (soil-gas VISL at the 10⁻⁶ risk level) and occurred at vertical separation distances greater than 6 feet (1.8 m). The highest vertical separation distance for one detection (19 μg/m³) was observed at 10.5 feet (3.2 m). The two detections exceeding 3.6 μg/m³ at vertical separation distances greater than 6 feet (1.8 m) occurred at locations with predominantly sandy soil type in the vadose zone.

In the case of soil gas above LNAPL sources (panel B), 1,2-DCA was detected in five instances (8%) and was nondetect in 59 instances (92%). There were no detections of 1,2-DCA in soil gas at vertical separation distance greater than 15 feet (4.6 m). The highest vertical separation distance where 1,2-DCA was detected was 11.4 feet (3.5 m) at the concentration of 42 μg/m³. The large percentage of nondetect data (more than 90%) in this dataset indicated significant attenuation of 1,2-DCA within 15 feet (4.6 m) in the vadose zone above both dissolved and LNAPL sources.

Table 4 summarizes the frequency distribution of 1,2-DCA detections in soil gas at concentrations less than 3.6 and 5 μg/m³ at different vertical separation distances above the source. A large number of the soil-gas data were nondetect at a detection limit of 5 μg/m³, which is just above 3.6 μg/m³ (soil-gas VISL at the 10⁻⁶ risk level) and were
If 95% of the measured concentrations were less than the VISL at a particular separation distance, that distance can be considered protective. This analysis indicated that 6 feet (1.8 m) vertical screening distance may not be applicable for 1,2-DCA vapors from a dissolved-phase source (only 90% frequency of detection at ≤3.6 μg/m³), while 11 feet (3.4 m) might be adequately protective based on the current dataset (100% frequency of detection at ≤3.6 μg/m³).

On the other hand, the 15 feet (4.6 m) vertical screening distance recommended by US EPA could be applied to 1,2-DCA vapors from LNAPL source (100% frequency of detection at ≤3.6 μg/m³).

Table 4
Occurrence of 1,2-DCA Detections in Soil-Gas at Concentrations ≤3.6 μg/m³ (Soil-Gas VISL for 1,2-DCA at the 10⁻⁶ Risk Level) and ≤5 μg/m³ Above Different Vertical Separation Distances from Dissolved-Phase and LNAPL Sources in This Dataset

| Source Type (Data Points with Detection Limit <36 μg/m³) | Vertical Separation Distance (feet) | Number of Detections >3.6 and >5 μg/m³ | Total Number of Data Points | Frequency of 1,2-DCA Detections in Soil-Gas ≤ Specified Concentration (%) |
|---------------------------------------------------------|-------------------------------------|----------------------------------------|-----------------------------|--------------------------------------------------------------------------|
| Dissolved source (70)                                   | ≥0                                  | 4                                      | 29                          | 86                         | 93 |
|                                                         | ≥6                                  | 2                                      | 21                          | 52                         | 90 | 96 |
|                                                         | ≥8                                  | 2                                      | 21                          | 49                         | 90 | 96 |
|                                                         | ≥10                                 | 1                                      | 16                          | 43                         | 94 | 98 |
|                                                         | ≥11                                 | 0                                      | 14                          | 41                         | 100 | 100 |
| LNAPL source (52)                                       | ≥0                                  | 4                                      | 30                          | 42                         | 87 | 90 |
|                                                         | ≥8                                  | 2                                      | 22                          | 33                         | 91 | 94 |
|                                                         | ≥10                                 | 1                                      | 18                          | 29                         | 94 | 97 |
|                                                         | ≥12                                 | 0                                      | 15                          | 23                         | 100 | 100 |
|                                                         | ≥15                                 | 0                                      | 13                          | 23                         | 100 | 100 |

1Includes nondetect data only when detection limit ≤3.6 and ≤5 μg/m³, respectively.

2% Frequency = (1 − (Number of detections)/Total number of data points)) x 100.

3The shaded portions highlight data for ≥6 ft. (for dissolved source) and ≥15 ft. (LNAPL source).
First-Order Aqueous Phase Biodegradation Rate Constants for 1,2-DCA

The distribution of first order aerobic biodegradation rate constants for 1,2-DCA determined by model calibration are plotted in Figure 4 as a function of the entire data set (ALL) and source type (dissolved-phase and LNAPL sources). The distributions do not consider two outlier values, one estimated for dissolved-phase source (9 1/h) and another for LNAPL source (4 1/h). These were very high rate constants that could not be explained and thus were excluded from the analysis. The median aerobic biodegradation rate constants for a dissolved-phase source (9.54 \times 10^{-4} 1/h, half-life = 30 days) and an LNAPL source (1.12 \times 10^{-3} 1/h, half-life = 27 days) are nearly equivalent. The median rate constants in this study were approximately twofold lower than the geometric mean of the rate constants documented by Ma et al. (2016) based on numerous laboratory studies (2.6 \times 10^{-3} 1/h, half-life = 11 days) and approximately two orders of magnitude lower than the rate constants reported for petroleum hydrocarbons, such as benzene (7.9 \times 10^{-1} 1/h, half-life = 0.04 days) (DeVaull 2007).

The lower rate constant for 1,2-DCA compared to literature values from Ma et al. (2016) likely reflects the conservatism in the model calibration approach used in this study. The rate constants also showed little variability as a function of 1,2-DCA concentration in groundwater (3–3300 μg/L) and source type (see Figure 5, panel A). Figure 5 (panel B) also shows the lack of dependence of the biodegradation rate constants as a function of benzene concentration in groundwater, which ranged from 0.5 to 1000 μg/L (for dissolved-phase sources) and 1000 to 20,000 μg/L (for LNAPL sources) in this dataset. Any meaningful enhancement in the biodegradation rate of 1,2-DCA due to co-metabolism of petroleum hydrocarbon substrates (Hazen 2010) is not evident from this analysis. The median calibrated biodegradation rate constants for dissolved-phase (9.54 \times 10^{-4} 1/h) and LNAPL (1.12 \times 10^{-3} 1/h) sources were used as input in the derivation of vertical screening distances for sand, loam, and clay vadose zone soils as described in the following section.

Predicted Vertical Screening Distances for 1,2-DCA Using BioVapor

The vertical screening distances for 1,2-DCA predicted by BioVapor modeling ranged from 5 to 28 feet (1.5 to 8.5 m) for dissolved-phase sources and 6 to 50 feet (1.8 to 15 m) for LNAPL sources (Table 5). The vertical screening distances estimated for 1,2-DCA were generally equal to or less than the 6 feet (1.8 m) and 15 feet (4.6 m) screening distances recommended by US EPA (2015a) for all sites except for sites with sand soils in the vadose zone. This was generally consistent with the empirical observation that the only two detections of 1,2-DCA in soil gas more than 3.6 μg/m3 at vertical distance more than 6 feet (1.8 m) from dissolved-phase sources (Figure 3a) occurred at locations with sandy soil. The BioVapor model results were conservative compared to the empirical analysis of the vertical separation distances in this soil-gas data. This is expected given that vadose zones at most sites are likely to contain some interbeds of non-sand soils (e.g., loam, silt, and clay).

The sensitivity of the vertical screening distance to soil type was not observed for hydrocarbons such as benzene that aerobically biodegrade with rate constants that are more than 2 orders of magnitude higher (Lahvis et al. 2013; US EPA 2013). The dependence of the vertical screening
distance on soil type highlights the importance of proper characterization and classification of vadose zone soils (e.g., geotechnical analyses of soil type, soil properties) when assessing vapor intrusion risks from 1,2-DCA.

Figure 6 shows source concentrations of 1,2-DCA in groundwater and vertical separation distances in sand, loam, and clay soils that result in indoor air concentrations of 0.11 μg/m³ (indoor air VISL at the 10⁻⁶ risk level for 1,2-DCA). The nomograph was developed based on conservative BioVapor modeling using the median values of first-order rate constants (9.54 × 10⁻⁴ h⁻¹ for dissolved-phase sources and 1.12 × 10⁻³ h⁻¹ for LNAPL sources), 95th percentile source vapor concentrations for benzene and TPH aliphatic and aromatic hydrocarbons in combination with default soil and building parameter values (Table 3). The horizontal dash-dot line represents the maximum expected concentration of 1,2-DCA in groundwater (3700 μg/L) in equilibrium with leaded automobile gasoline (Falta 2004). Measured concentrations of 1,2-DCA in groundwater greater than this value indicate a potential vapor source other than leaded automobile gasoline.

The nomograph shown in Figure 6 can be used for site screening purposes based on the concentration of 1,2-DCA in groundwater, type of vapor source (dissolved-phase vs. LNAPL), and the predominant soil type in the vadose zone. For example, a minimum vertical separation distance of 8 feet (2.4 m) is needed to screen out a site with a LNAPL source, concentration of 1,2-DCA in groundwater of 500 μg/L, and a loam soil in the vadose zone (see dashed lines). No additional investigation of vapor intrusion risk from 1,2-DCA would be necessary for any combination of 1,2-DCA concentration in groundwater and vertical separation distance (or depth to groundwater) that plots below the individual curve for a given soil and source type.

Figure 6 can also be used to indicate the range of conditions for which the US EPA recommended vertical screening distances are applicable. The 6 feet (1.8 m) screening distance for dissolved-phase sources appears applicable only for concentrations of 1,2-DCA in groundwater lower than 30, 250, and 1100 μg/L at sites with sand, loam, and clay soils in the vadose zone, respectively. The vertical screening distance of 15 feet (4.6 m) for petroleum UST sites with LNAPL sources appears applicable across the entire range of expected source concentrations of 1,2-DCA in groundwater (less than 3700 μg/L) at sites with loam or clay soils, but not sandy soils in the vadose zone. These threshold groundwater concentration limits defined in Figure 6 are consistent with those reported by Ma et al. (2016) in model simulations that assumed aerobic biodegradation of 1,2-DCA across the entire vadose zone at rates of 2.6 × 10⁻³ 1/h.

In summary, soil type and source concentration are important factors to consider in screening vapor intrusion risks for 1,2-DCA. More refined estimates of vertical screening distances can also be obtained using BioVapor with site-specific soil property data (moisture content, total porosity, bulk density, and fraction organic carbon) and source concentrations (groundwater or soil gas) as input.

Conclusions

To our knowledge, this is the first study using soil-gas data for 1,2-DCA from petroleum UST sites to demonstrate that the US EPA recommended vertical screening distance of 15 feet (4.6 m) is applicable to 1,2-DCA at the 10⁻⁶ risk level.
Empirical data analysis was applied to 144 pairs of soil gas and groundwater concentration data from 47 UST sites to support this conclusion. These data were representative of conditions when 1,2-DCA soil vapors were sourced from either LNAPL or dissolved-phase sources at the water table (similar approach to that described in Lahvis et al. 2013 and US EPA 2015a for establishing vertical screening distances for benzene and other petroleum hydrocarbons).

At the 47 UST sites, 1,2-DCA was rarely detected in the soil gas above dissolved-phase and LNAPL sources (5% and 8% of locations, respectively) suggesting significant attenuation due to aerobic biodegradation in the vadose zone. In order to assess the applicability of the US EPA recommended vertical screening distances to 1,2-DCA, the frequency of occurrence of 1,2-DCA in soil gas at concentrations ≤3.6 μg/m$^3$ (soil-gas VISL at the 10$^{-6}$ risk level) at different vertical separation distances from the source was evaluated (Table 4). This analysis indicated that 6 feet (1.8 m) as the vertical screening distance for dissolved-phase source was not applicable for 1,2-DCA (soil-gas concentrations ≤3.6 μg/m$^3$ in only 90% of samples at separation distances ≥6 feet (1.8 m)). However, 15 feet (4.6 m) as the vertical screening distance for LNAPL source was applicable for 1,2-DCA (soil-gas concentrations ≤3.6 μg/m$^3$ in 100% of samples at separation distances ≥15 feet [4.6 m]).

First order aerobic biodegradation rate constants for 1,2-DCA were estimated by the best fit between the measured soil-gas concentrations and the predicted soil-gas concentrations using the BioVapor model. The median aerobic rate constants for 1,2-DCA (approximately $1 \times 10^{-3}$ 1/h) were twofold lower than those reported by Ma et al. (2016) and approximately two orders of magnitude lower than those reported for benzene (DeVaull 2007). The actual aerobic biodegradation rate constants for 1,2-DCA are likely to be greater than these estimates given that the soil-gas concentrations used for model calibration were largely nondetect.

The BioVapor model was used to predict vertical screening distances for 1,2-DCA in soil gas from dissolved-phase and LNAPL sources at the water table using conservative estimates of source concentrations (Table 5). Given the lower aerobic biodegradation rate constants for 1,2-DCA, the vertical screening distances were also dependent on the soil type in the vadose zone and the source concentration of 1,2-DCA in groundwater (Figure 6), in contrast to the US EPA recommended vertical screening distances for petroleum hydrocarbons. The relationships shown in Figure 6 can be used to screen sites based on the concentration of 1,2-DCA in groundwater and the vertical separation distance (or depth to groundwater) for the relevant source type and the predominant soil type in the vadose zone. This approach can potentially reduce unnecessary soil-gas sampling at numerous sites with historic releases of leaded fuels.

The modeling also indicated that the US EPA recommended vertical screening distance of 6 feet (1.8 m) for dissolved-phase sources was applicable for sites only below certain threshold concentrations of 1,2-DCA in groundwater (30, 250, and 1100 μg/L at sites with sand, loam, and clay soils in the vadose zone, respectively). Similarly, the modeling indicated that the US EPA recommended vertical screening distance of 15 feet (4.6 m) for LNAPL sources was applicable for sites with clay and loam soils in the vadose zone, but not sites with sand soil, if the concentration of 1,2-DCA in groundwater was more than 150 μg/L. This likely reflected the conservatism in the BioVapor modeling, as the empirical data representing multiple soil types (with approximately 50% locations with sand) suggested significant attenuation of 1,2-DCA vapors above dissolved-phase and LNAPL sources. The soil-gas data also supported the applicability of the US EPA recommended vertical screening distance of 15 feet (4.6 m) for both dissolved and LNAPL sources.

Although EDB was not detected in the soil gas in this dataset, the reporting limits were greater than 1.6 μg/m$^3$ (soil-gas VISL for EDB at the 10$^{-5}$ risk level). As a result, this dataset could not be used to empirically evaluate the applicability of US EPA recommended vertical screening distances for EDB. The conventional analytical methods (EPA TO-15 or EPA 8260B) used for soil-gas analysis in this dataset were not sensitive and selective enough to detect EDB at low enough concentrations to be meaningful for risk assessment, likely due to matrix interference from other constituents (i.e., BTEX and other gasoline range hydrocarbons). To address this data gap, there is a need to develop a more sensitive and selective analytical method for soil-gas analysis or to configure existing sampling procedures and analytical protocols to be able to detect EDB at or below 0.16 μg/m$^3$ (soil-gas VISL at the 10$^{-6}$ risk level). To evaluate vertical screening distance criteria for EDB using the approach described here, additional field studies using such an analytical method are needed to gather concurrent soil gas and groundwater data at sites with EDB detections in groundwater over 0.18 μg/L (groundwater VISL at the 10$^{-6}$ risk level).

**Supporting Information**

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally not peer reviewed.

**Figure S1.** Concentration of 1,2-DCA in groundwater as a function of concentration of benzene in groundwater (detections of 1,2-DCA shown as solid circles and nondetect data shown as open circles).

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