Transient Simulation of 1,4-Dioxane Fate and Transport During Enhanced Soil Vapor Extraction Treatment

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Abstract. 1,4-Dioxane is an emerging contaminant that is fully miscible in water and resistant to biodegradation. The presence of 1,4-Dioxane in vadose zone creates prolonged environmental issues and risk human health. To date, treatment technologies for 1,4-Dioxane vadose zone remediation are still being developed. In this work, a numeric simulation tool was developed to investigate the fate and transport of 1,4-Dioxane in the treatment zone of enhanced soil vapor extraction (XSVE) which utilizes heated air injection to improve contaminant removal efficacy. The results suggested identify source zone is critical for XSVE treatment, inaccurate heat injection point would prolong treatment duration.

1 Introduction

1,4-Dioxane is widely used as a stabilizer for chlorinated solvents such as 1,1,1-trichloroethane and trichloroethylene, and as a solvent for resins, vegetable oils, mineral oils and waxes¹ ². It is reported that 1,4-Dioxane exists in surface water and groundwater in the United States, Japan, Germany, the Netherlands, the United Kingdom and Canada³. It is considered to be a potential organic pollutant causing human disease⁵. Studies have shown³ ⁵ that the presence of 1,4-Dioxane will affect the secretion of sex hormones to a certain extent, damage the liver and cause renal failure. The international agency for research on cancer classified 1,4-Dioxane as class 2B carcinogen, which may have carcinogenic effect on humans, and it is reported that it has genotoxic liver cancer in rats⁷. Due to the existence of two oxygen atoms in the chemical structure of dioxane, it has strong hydrophilicity, good solubility and stability in water⁸ ⁹. Therefore, 1,4-Dioxane can transfer rapidly in the environment. It can evaporate from dry soil and spread rapidly to even low permeability soils, such as silt and clay⁹. At the same time, dioxane will quickly enter groundwater through soil and dissolve almost completely¹⁰. The physical and chemical properties of dioxane create challenges for removing this compound.

At present, most 1,4-Dioxane remediation technologies aimed at groundwater, including advanced oxidation, activated carbon adsorption and bioremediation¹⁰ ¹⁴. For soils containing chlorinated solvent VOCs and 1,4-Dioxane, SVE system can easily remove chlorinated solvent VOCs, but usually leaves a large amount of 1,4-Dioxane in aerated pore water, which becomes a long-term source of groundwater pollution. Enhanced soil vapor extraction (XSVE)¹⁵ ¹⁷ is recently reported technology that utilizes heated air injection and high rate extraction to achieve 1,4-Dioxane removal from vadose zone.

Although great successes were made in XSVE field experiments, the fate and transport of 1,4-Dioxane within the treatment zone are not well understood. There are very few studies on this topic. Previous studies have limitations. A previous modeling work only simulate 1,4-Dioxane in bulk¹⁸. HypeVent XSVE assumed to be isolated from exchange of 1,4-Dioxane¹⁵ ¹⁶. But the impact of processes like heat loss of soil, non-equilibrium distribution of temperature and humidity on XSVE performance is still unknown. This study aims to gain better understanding of the effect of such processes on the fate and transport of 1,4-Dioxane in soil.

2 Model development and validation

A numerical code was developed to simulate 1-dimensional energy and mass transport during XSVE process¹⁹. Building on the excel modeling tool Hypervent¹⁹, this model offers additional information (e.g. real-time 1,4-Dioxane and temperature profile) and also provide more accurate transient heat and 1,4-Dioxane transport simulation in vadose zone. A series of equations and boundary conditions are solved using a finite-difference numerical method. Gauss-Seidel iterative method was applied to obtain explicit solutions. The governing equations used in this work are summarized in Table 1.

3 Simulation scenarios

The simulation conceptual model was comprised of three soil columns with a bottom area of 180 square centimeters. The schematic of the simulation conceptual

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Table 1. Enhanced SVE Equations

Overall energy balance:

\[
\frac{d}{dt}(m_{\text{soil}}C_{\text{soil}}(T_{\text{soil}}-T_{\text{ref}})+m_{\text{air}}C_{\text{air}}(T_{\text{air}}-T_{\text{ref}})+m_{\text{w}}\Delta H_{\text{w,vap}}+m_{\text{e}}C_{\text{e}}(T_{\text{soil}}-T_{\text{w}})) =
\left(\frac{m_{\text{air}}C_{\text{air}}(T_{\text{air}}-T_{\text{ref}})+m_{\text{soil}}C_{\text{soil}}(T_{\text{soil}}-T_{\text{ref}})+\Delta H_{\text{w,vap}}}{m_{\text{soil}}} \right) + \frac{R_{\text{loss}}}{t}
\]

\[R_{\text{loss}} = \int_{0}^{t} r \times (T_{\text{soil}}-T_{\text{ref}}) \, dt\]

Temperature dependent partitioning coefficients:\n
\[H_{140}(T_{\text{soil}} + 273.15) = \frac{\exp\left(37.3025 - 24.3009 \frac{298.15}{(T_{\text{soil}} + 273.15)} + 4.80841 \ln\left(\frac{T_{\text{soil}} + 273.15}{298.15}\right) - 9.7034 \left(\frac{T_{\text{soil}} + 273.15}{298.15}\right)\right)}{(101.325)(0.0821)(T_{\text{soil}} + 273.15)(55.55)}\]

\[P_{\text{w,in}}(T_{\text{soil}} + 273.15) = \frac{10^{1730}}{760}\]

Mass balances on 1,4 dioxane, water, and air:

\[
\frac{dm_{140}}{dt} = -\frac{m_{140,\text{out}}}{m_{140,\text{in}}}
\]

\[
m_{140,\text{out}} = Q_{\text{air,STP}} \left(1 - \frac{T_{\text{soil}} + 273.15}{273.15}\right) \frac{m_{140}}{m_{\text{w,in}}}
\]

\[
\frac{dm_{\text{w,in}}}{dt} = \left[m_{\text{w,in}} - m_{\text{v,in}}\right]
\]

\[
m_{\text{w,in}} = Q_{\text{air,STP}} \left(1 - \frac{T_{\text{ambient}} + 273.15}{273.15}\right) \frac{M_{\text{w,H}_2\text{O}}}{R(T_{\text{ambient}} + 273.15)}
\]

\[
m_{\text{v,in}} = Q_{\text{air,STP}} \left(1 - \frac{T_{\text{ambient}} + 273.15}{273.15}\right) \frac{M_{\text{w,H}_2\text{O}}}{R(T_{\text{ambient}} + 273.15)}
\]

\[
m_{\text{e,in}} = m_{\text{e,air}} = Q_{\text{air,STP}} \frac{PM_{\text{vap}}}{R(273.15)}
\]

Table 2. Nomenclature for HypeVent XSVE equations presented

- \(C_{\text{p,air}}\) = heat capacity of air [kJ/kg-C]
- \(C_{\text{p,soil}}\) = heat capacity of soil [kJ/kg-C]
- \(C_{\text{p,water}}\) = heat capacity of liquid water [kJ/kg-C]
- \(C_{\text{p,water}}\) = heat capacity of water vapor [kJ/kg-C]
- \(\Delta H_{\text{w,vap}}\) = specific enthalpy of water vaporization [kJ/kg]
- \(H_{140}\) = 1,4 dioxane Henry’s Law Constant [L-water/L-vapor]


model is shown in Figure 1. Heated ambient air injection well and vapor extraction well were placed at each end of soil columns. 3 treatment zone conditions were investigated: a) 30 cm contaminant source near injection well followed by 30 cm clean soil; b) uniform source zone between two wells; and c) 30 cm clean soil near injection well followed by 30 cm contaminant source. Source zone 1,4-Dioxane concentration was 50 mg·1,4-Dioxane/g-soil. Ambient air was heated to 120°C and then was then injected into treatment zone at 2L/min.

4 Results

1,4-Dioxane mass removal rates vs time and % removal vs from different XSVE simulations are shown in Figure 2 and 3. Air injection locations played an important role on XSVE treatment duration. For the initial 700 min, XSVE hardly removed any 1,4-Dioxane in Condition A simulation. Then 1,4-Dioxane removal rates started to increase and reached the maximum value of 0.79 mg/min at about 1450 minutes. The total treatment period of Condition A was around 2100 minutes. On the other hand, treatment durations for XSVE to complete Condition B and Condition C remediation were 1100 and 1600 minutes, respectively. And the maximum removal rates were 740 mg/min for Condition B and 0.38 mg/min for Condition C.

These results suggested that source zone identification is critical for a successful XSVE design. For example, none 1,4-Dioxane was removed during the first 700 min treatment in Condition A. During this period, heated air drove 1,4-Dioxane vaporize in the source zone and migrate towards extraction point, however, once it reached clean, cool soil, vaporized 1,4-Dioxane would re-partition with soil water and re-participate. It was not until all treatment zone was heated that 1,4-Dioxane started to be removed. Whereas the most effective treatment was found when injection and extraction wells perfectly bracketed source zone. The
treatment time for Condition B was only ⅓ of Condition A.

![Graph 1](image1)

**Fig. 2.** 1,4-Dioxane removal rates from different XSVE simulations

![Graph 2](image2)

**Fig. 3.** % 1,4-dioxane Removal run for different XSVE simulations

5 Conclusions

In this paper, a screening-level model was established based on mass and energy balance calculation, and it was used to evaluate remediation of 1,4-Dioxane in the vadose zone using enhanced SVE with heated air injection. The results suggested source zone identification is an important factor affecting XSVE treatment efficacy. Accurate source zone delineation would reduce XSVE treatment duration and energy cost significantly.

References

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