USER GUIDE

1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE)

Screening-Level Feasibility Assessment and Design Tool in Support of 1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE)

ESTCP Project ER-201326

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14. ABSTRACT
XSVE, or extreme soil vapor extraction, is an enhanced form of soil vapor extraction (SVE) for the remediation of 1,4-dioxane in vadose soils (Hinchee et al., 2017a and b). HypeVent XSVE for 1,4-Dioxane (HypeVent XSVE) is a spreadsheet-based tool that runs in Microsoft Excel. It was developed in anticipation of remediation professionals need for a screening-level feasibility assessment and design tool for XSVE applications. HypeVent XSVE facilitates quick exploration of the best-case performance for 1,4-dioxane removal from soils using the XSVE technology. HypeVent XSVE was found to adequately describe field XSVE data (Burris et al., 2017).

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Acronyms

°C	degrees celcius
atm	atmosphere
ft	feet/foot
HypeVent XSVE	*HypeVent extreme soil vapor extraction for 1,4-Dioxane*
K	kelvin
kg	kilogram
kJ	kilojoules
L	liter
mg	milligram
MTBE	methyl tert-butyl ether
TCA	1,1,1-trichloroethane
TCE	trichloroethene
SCFM	standard cubic feet per minute
SVE	soil vapor extraction
XSVE	extreme soil vapor extraction

Introduction

XSVE, or extreme soil vapor extraction, is an enhanced form of soil vapor extraction (SVE) for the remediation of 1,4-dioxane in vadose soils (Hinchee et al., 2017a and b). *HypeVent XSVE for 1,4-Dioxane* (HypeVent XSVE) is a spreadsheet-based tool that runs in Microsoft Excel®. It was developed in anticipation of remediation professionals need for a screening-level feasibility assessment and design tool for XSVE applications. HypeVent XSVE facilitates quick exploration of the best-case performance for 1,4-dioxane removal from soils using the XSVE technology. HypeVent XSVE was found to adequately describe field XSVE data (Burris et al., 2017).

Description of XSVE for 1,4-Dioxane

1,4-Dioxane is cyclic diether (Figure 1) that is often found as an additive with the chlorinated solvent 1,1,1-trichloroethane (TCA). It is totally miscible with water because of its polar character. It tends to be resistant to microbial biodegradation and has formed large groundwater plumes. 1,4-Dioxane favors the water phase in water/vapor partitioning; its temperature-dependent Henry's Law constant is shown in Figure 2. For context, VOCs typically treated using SVE have Henry's Law constants orders of magnitude higher than 1,4-dioxane (i.e., trichloroethene's [TCE's] Henry's Law constant is ~0.4 at 20 degrees celcius (°C). In vadose zone source areas, 1,4-dioxane tends to reside in vadose water. Conventional SVE readily removes chlorinated solvents. Although SVE removes some 1,4-dioxane, substantial amounts can remain after the chlorinated solvents have been remediated. XSVE is SVE that is enhanced by focused extraction and heated air injection to facilitate the removal of 1,4-dioxane from the vadose zone. A field demonstration of XSVE for 1,4-dioxane is described in Hinchee et al., 2017a and 2017b.

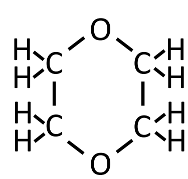

Figure 1. Structure of 1,4-Dioxane.

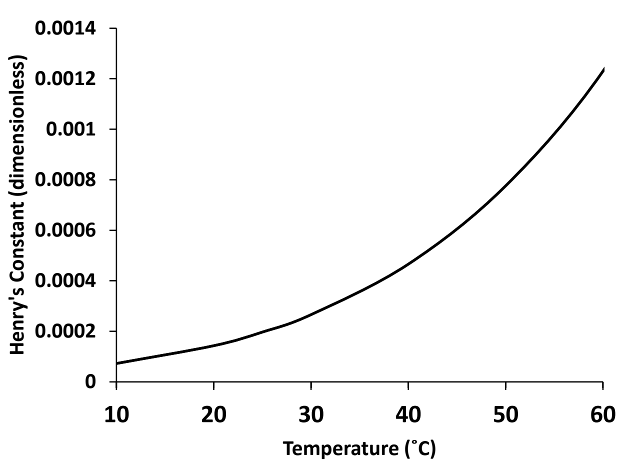

Figure 2. Dimensionless Henry's Law constant for 1,4-dioxane (ratio of vapor over aqueous concentrations; Ondo and Dohnal, 2007).

Focused extraction is where the SVE well screened interval is placed within the zone where 1,4-dioxane resides. If 1,4-dioxane soil concentrations are low between the source area and the SVE well, 1,4-dioxane will be sequestered in the vadose water between the source zone and the well and prolong efforts to remove it. Removal of 1,4-dioxane is facilitated by extracting vapor from directly within the source area. Heated air injection takes advantage of 1,4-dioxane's temperature-dependent Henry's Law constant. Soil temperature can be increased by injecting heated air with injection wells. The soil temperature reached is dependent upon an energy balance between the heat injected, heat of vaporization of water, heat capacities of water and soil, and heat extracted.

XSVE heated air injection can be accomplished using single cell of injection and extractions wells or an array of cells. Two possible XSVE configurations are shown in the Figure 3 example. The extraction center configuration has heated injection wells on the corners of the cell. Using the Figure 3 example, air flow in the extraction center configuration carries 1,4-dioxane directly in to the extraction well without 1,4-dioxane becoming sequestered in clean vadose water, however, more injected heat might be required. Conversely, the injection center configuration has more efficient use of injected heat, however cleanup may be prolonged due to 1,4-dioxane partitioning in areas of relatively clean vadose water prior to extraction. The extraction center configuration was used in the field demonstration for this ESTCP project.

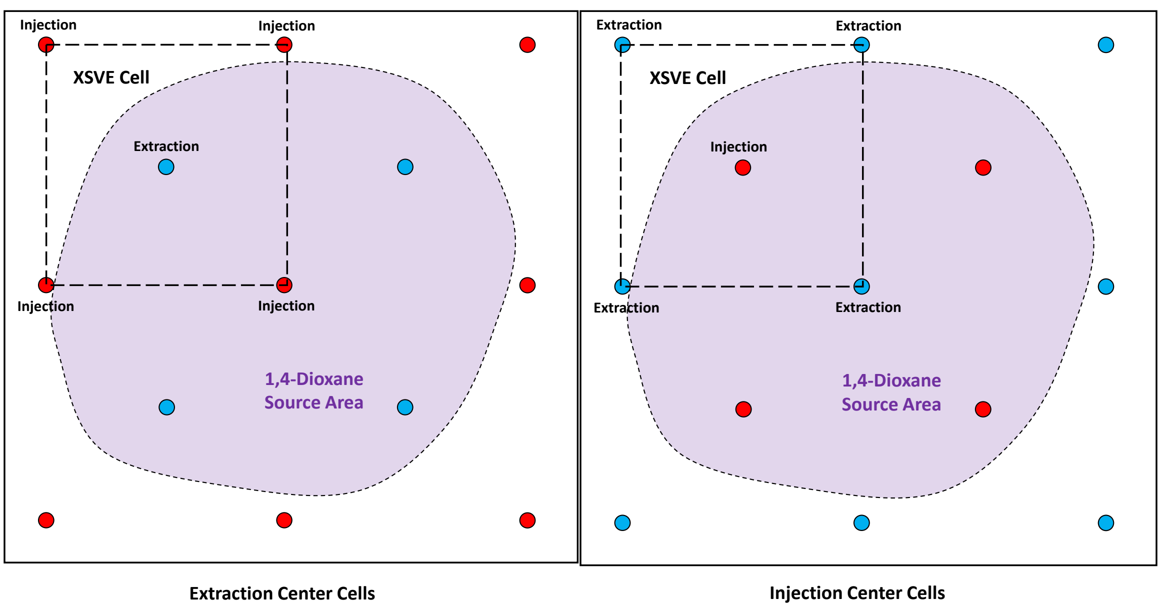

Figure 3. Example XSVE injection/extraction well cell configurations.

A simplified conceptualization of the XSVE treatment process in cross-section using the extraction center configuration is shown in Figure 4. The treatment zone, the soil between the screened intervals of the injection and extraction wells, contains the 1,4-dioxane contaminated soils.

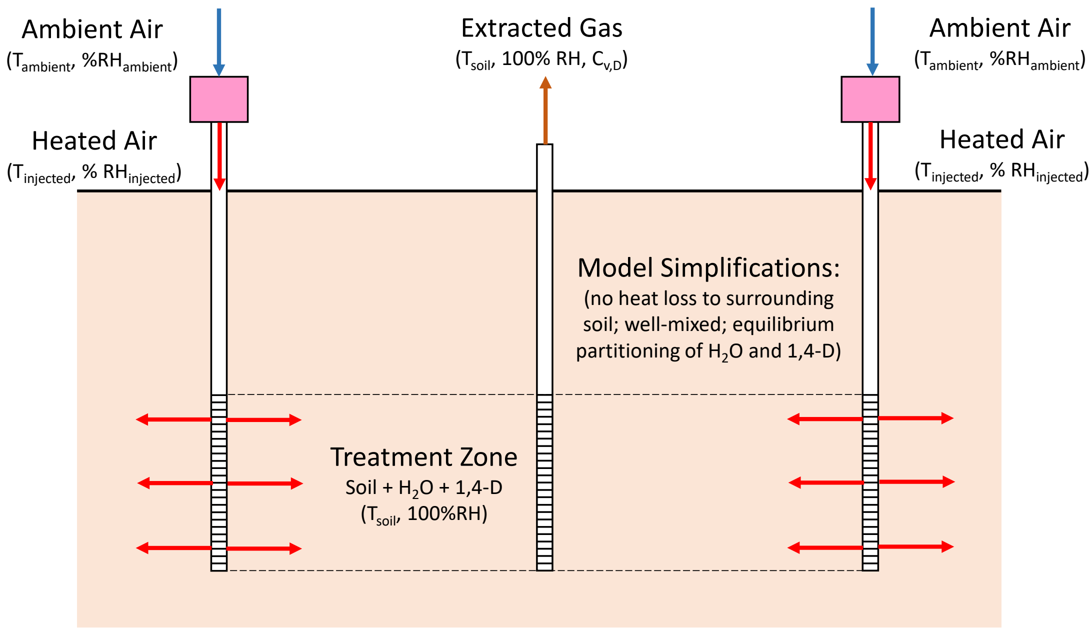

Figure 4. Simplified conceptualization of the XSVE treatment process in cross-section using extraction center configuration. HypeVent XSVE model assumptions are also shown.

Overview of HypeVent XSVE for 1,4-Dioxane

HypeVent XSVE is a spreadsheet-based tool that runs in Microsoft Excel®. HypeVent XSVE facilitates quick exploration of the best-case performance for 1,4-dioxane removal from soils using the XSVE technology. Considering the idealized nature of HypeVent XSVE, it was found to adequately describe the field demonstration (Hinchee et al., 2017a and Burris et al., 2017).

In brief, users enter the target treatment zone size, initial 1,4-dioxane and soil moisture concentrations, and ambient site conditions, and then they can assess the potential for XSVE to achieve their remediation goals (cleanup level, remediation time, etc.) under ideal conditions. The primary operating inputs that users manipulate are the vapor flow rate through the target treatment zone and temperature that ambient air is heated to prior to injection. Changes in relative humidity at injection temperatures can also be simulated. By changing the injected air temperature between ambient and elevated temperatures, the user can compare best-case performance of conventional SVE and XSVE treatments.

HypeVent XSVE predicts 1,4-dioxane and moisture removal rates and concentration changes in treatment zone soils with time for the idealized conditions (model assumptions discussed below). It also projects the corresponding changes in leachate and soil vapor concentrations as remediation progresses. Sample output is presented in Figure 5 for the case of 100 feet cubed per minute (ft^3/minute) air flow through a nominal 30-ft wide x 30-ft long x 20-ft thick treatment zone, 20 milligram per kilogram (mg/kg) initial 1,4-dioxane concentration, 10% initial soil moisture (by weight), and with ambient air (20˚C, 25% relative humidity) being heated to 100˚C prior to injection.

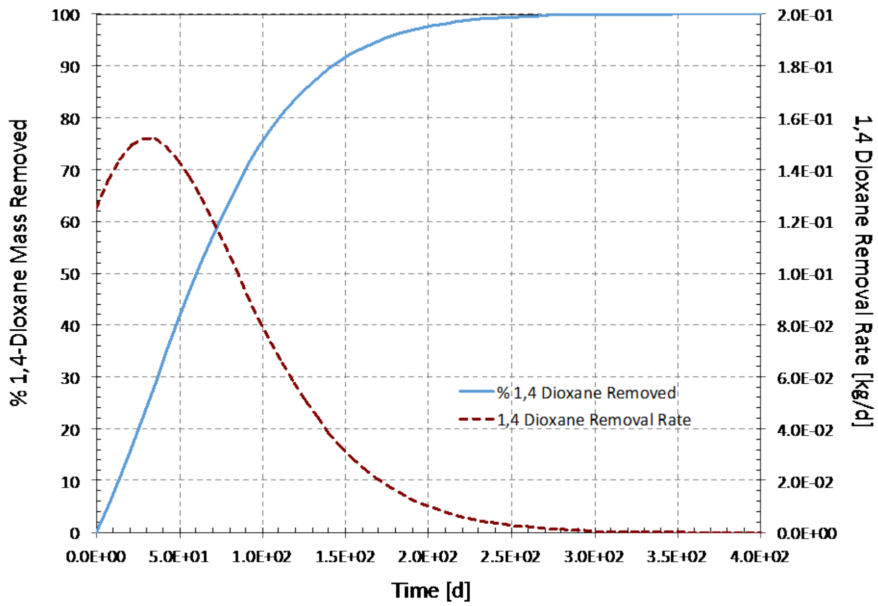

Figure 5. Sample HypeVent XSVE output ("Results – 1,4D Removal" chart tab).

HypeVent XSVE Screening-Level Calculations

HypeVent XSVE performs screening-level performance calculations, which provide an upper-bound best-case performance estimate. HypeVent XSVE is based on the simplified conceptualization of the XSVE process shown in Figure 4.

The equations embedded in HypeVent XSVE assume an idealized process involving the following:

- Uniform concentrations of 1,4-dioxane and water, and uniform temperature within the treatment zone.
- An isolated treatment zone with no exchange of 1,4-dioxane, water, air, or energy between soils inside and outside the treatment zone.
- 1,4-Dioxane is dissolved in the soil moisture without sorption to soil surfaces.
- Equilibrium partitioning between 1,4-dioxane dissolved in soil moisture and in soil vapor, and 100% relative humidity in the soil gas, as long as liquid water is present in the soil.
- Temperature-dependent 1,4-dioxane Henry's Law Constant and vapor pressure of water; constant (independent of temperature) soil, water, and air heat capacities and enthalpy of vaporization for water.

Actual XSVE applications will involve heat loss to soils outside the treatment zone, flow of some unheated ambient air pulled into the treatment zone, non-uniform temperature and moisture fronts that move outward from the heated air injection points, and non-equilibrium partitioning. Thus, the HypeVent XSVE predictions should be considered upper-bound best-case performance estimates when using them in decision-making.

HypeVent XSVE performs the following inter-connected energy and mass balances and partitioning calculations:

- An overall energy balance on the treatment zone, considering the energy delivered in the injected air and removed in the extracted gas flow. This equation yields the predicted changes in the treatment zone temperature with time.

- Temperature-dependent partitioning coefficients (1,4-dioxane Henry's Law Constant and water vapor pressure). These equations are central to predicting the vapor-phase concentrations and removal of 1,4-dioxane and water in the extracted vapors with time.

- Mass balances on 1,4-dioxane and water. The former is removed from the treatment zone by the extracted gas flow, while the latter is both delivered in the injected air (in proportion to the ambient air percent relative humidity) and removed by the extracted gas flow (at 100% relative humidity at soil temperature). These equations determine the 1,4-dioxane and moisture concentrations in soil with time.

The equations and associated definition of terms are presented in Tables 1 and 2. The time-dependent differential energy balance and mass balance equations are solved for discrete time steps using an explicit finite-difference algorithm.

Table 1. HypeVent XSVE equations.

Overall energy balance:

$$\frac{d}{dt}\{m_{soil} C_{p,soil}(T_{soil} - T_{ref}) + m_{w,T} C_{p,wL}(T_{soil} - T_{ref}) + m_{w,v} \Delta H_{w,vap} + m_{air} C_{p,air}(T_{soil} - T_{ref})\} =$$

$$\left\{\dot{m}_{air,in} C_{p,air}(T_{in} - T_{ref}) + \dot{m}_{w,in}[C_{p,wL}(T_{in} - T_{ref}) + \Delta H_{w,vap}]\right\} - \left\{\dot{m}_{air,out} C_{p,air}(T_{soil} - T_{ref}) + \dot{m}_{w,out}[C_{p,wL}(T_{soil} - T_{ref}) + \Delta H_{w,vap}]\right\}$$

Temperature dependent partitioning coefficients[1]:

$$H_{14D}(T_{soil}+273.15) = \frac{\exp\left(37.3025 - 24.3009\left(\frac{298.15}{T_{soil}+273.15}\right) + 4.8084\ln\left(\frac{T_{soil}+273.15}{298.15}\right) - 9.7034\left(\frac{T_{soil}+273.15}{298.15}\right)\right)}{(101.325)(0.0821)(T_{soil}+273.15)(55.55)}$$

$$P_{v,w}(T_{soil}+273.15) = \frac{10^{\left(8.07131 - \frac{1730}{(T_{soil}+233.426)}\right)}}{760}$$

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

$$\frac{dm_{14D}}{dt} = -\dot{m}_{14D,out}$$

$$\dot{m}_{14D,out} = Q_{air,STP}\left(\frac{T_{soil}+273.15}{273.15}\right) H_{14D}(T_{soil}+273.15)\left(\frac{m_{14D}}{m_{w,soil}}\right)$$

$$\frac{dm_{w,T}}{dt} = \left\{\dot{m}_{w,in} - \dot{m}_{w,out}\right\}$$

$$\dot{m}_{w,in} = Q_{air,STP}\left(\frac{T_{ambient}+273.15}{273.15}\right)\left(\frac{\%RH_{ambient}}{100}\right)\left(\frac{P_{v,w}(T_{ambient}+273.15)M_{w,H2O}}{R(T_{ambient}+273.15)}\right)$$

$$\dot{m}_{w,out} = Q_{air,STP}\left(\frac{T_{soil}+273.15}{273.15}\right)\left(\frac{P_{v,w}(T_{soil}+273.15)M_{w,H2O}}{R(T_{soil}+273.15)}\right)$$

$$\dot{m}_{air,in} = \dot{m}_{air,out} = Q_{air,STP}\left(\frac{PM_{w,air}}{R(273.15)}\right)$$

[1] Henry's Law Constant for 1,4-dioxane predicted by Ondo and Dohnal (2007) equation. Water vapor pressure equation from Yaws and Yang, 1989.

Table 2. Nomenclature for HypeVent XSVE equations presented in Table 1.

$C_{p,air}$	=	heat capacity of air (kilojoules [kJ]/kg-°C)
$C_{p,soil}$	=	heat capacity of soil (kJ/kg-°C)
$C_{p,wL}$	=	heat capacity of liquid water (kJ/kg-°C)
$C_{p,wv}$	=	heat capacity of water vapor (kJ/kg-°C)
$\Delta H_{w,vap}$	=	specific enthalpy of water vaporization (kJ/kg)
H_{14D}	=	1,4-dioxane Henry's Law Constant (L-water/L-vapor)
m_{14D}	=	mass of 1,4-dioxane in treatment zone (kg)
m_{air}	=	mass of air in treatment zone (kg)
m_{soil}	=	mass of soil in treatment zone (kg)
$m_{w,soil}$	=	mass of liquid water in treatment zone (kg)
$m_{w,T}$	=	total mass of (liquid + vapor) in treatment zone (kg)
$m_{w,v}$	=	mass of water vapor in treatment zone (kg)
$M_{w,air}$	=	molecular weight of air (kg/mole)
$M_{w,H2O}$	=	molecular weight of water (kg/mole)
$Q_{air,STP}$	=	air flow rate through the treatment zone as measured on a flowmeter calibrated to standard conditions (0°C and 1 atmosphere [atm]; L/minute)
P	=	atmospheric pressure (atm)
$P_{v,w}$	=	vapor pressure of water (atm)
R	=	gas constant (0.0821 L-atm/mole-kelvin [K])
t	=	time (minute[s])
$T_{ambient}$	=	average ambient air temperature (°C)
$T_{initial}$	=	initial temperature of soil in the treatment zone (°C)
T_{ref}	=	reference temperature for energy calculations (0°C)
T_{soil}	=	temperature of soil in the treatment zone (°C)
$\%RH_{ambient}$	=	percent relative humidity in ambient air (%)

HypeVent XSVE Use Instructions

HypeVent XSVE is a Microsoft Excel® file. It contains four worksheets identified by named tabs at the bottom of the HypeVent XSVE window ("HypeVent XSVE Inputs & Calcs"; "Results – 1,4D Removal"; "Results – Soil T and Water"; and "Flow Rate Estimates").

Project-specific information is input in worksheet "HypeVent XSVE Inputs & Calcs" shown below in Figure 6. Users enter numbers in the "Values" column for the ten rows with black text under the "Treatment Zone Characteristics" and "Operating Conditions" headings. Users can also choose to change some of the values under the "Physical-Chemical-Thermal Properties" section, although it is anticipated that most users will retain the values shown in Figure 6.

If ambient air is both heated and humidified prior to injection in order to increase the energy input, HypeVent XSVE can be used to simulate that situation. In the case of the injection air being 100% relative humidity at 80°C, make both $T_{ambient}$ and T_{in} equal 80°C and $\%RH_{ambient}$ equal 100%.

Cells formatted with blue text are calculation cells and should not be modified by the user. **It is recommended that users save an original copy of the HypeVent XSVE file for use in case they accidentally modify any of the blue cells.** (Note: It may be of interest to the user to examine a compound other than 1,4-dioxane such as acetone, methyl tert-butyl ether [MTBE] or other water-soluble contaminant with low sorption. This can be accomplished by entering the equation for that compound's Henry's Constant as a function of temperature in column Q for each time step.)

HypeVent XSVE for 1,4 Dioxane

PC Johnson 2014,2015,2016 (v1.3 July 2016)

Note: black =user inputs; blue= calculated values (do not change these cells)

Treatment Zone Characteristics	Values	Units	Notes
Soil Volume (V_{soil})	339600	L	1 ft^3 = 28.3 L
Initial 1,4-D Soil Concentration ($C_{soil,14D}$)	20	mg-1,4D/kg-soil	(from soil data)
Initial Soil Moisture (θ_m)	0.15	g-H_2O/g-soil	(max value is <n/ρ_{soil}, or saturated condition)
Total Soil Porosity (n)	0.4	L-pores/L-soil	(usually 0.3 < n < 0.5 L-pores/L-soil)
Soil Bulk Density (ρ_{soil})	1.7	kg-soil/L-soil	(usually 1.5 < ρ_{soil} < 1.8 kg-soil/L-soil)
Initial Temperature (T_{start})	20	C	(usually 15 < T_{start} < 25 C)
Vapor-filled Porosity (θ_v)	0.145	L-vapor/L-soil	(should be >0, or else θ_m is too large)
Soil Mass (M_{soil})	5.77E+05	kg-soil	(ρ_{soil} x V_{soil})
Operating Conditions			
Ambient Temperature ($T_{ambient}$)	17	C	(use average outdoor air temperature)
Ambient Relative Humidity (%$RH_{ambient}$)	58	%	(use average outdoor air relative humidity)
Treatment Zone Air Flowrate at STP ($Q_{air,STP}$)	2264	standard L/min	1 SCFM = 28.3 SLM (STP = 0 C, 1 atm)
Temperature that Injected Air Is Heated to (T_{in})	120	C	
Treatment Zone Air Flowrate if Measured at $T_{ambient}$	2.40E+03	actual L/min	1 ACFM = 28.3 ALM
Treatment Zone Air Flowrate if Measured at T_{in}	3.26E+03	actual L/min	1 ACFM = 28.3 ALM
Air Mass Flow Rate Through Treatment Zone	2.83E+00	kg/min	(volumetric flowrate converted to mass/time)
Physical-Chemical-Thermal Properties			
Heat Capacity of Soil ($C_{p,soil}$)	0.8	kJ/kg-solid °C	Bristow (1998) [value for quartz]
Heat Capacity of Water ($C_{p,water}$)	4.2	kJ/kg-water °C	http://www.engineeringtoolbox.com
Heat Capacity of Air ($C_{p,air}$)	1	kJ/kg-air °C	http://www.engineeringtoolbox.com
Heat Capacity of Water Vapor ($C_{p,wv}$)	1.84	kJ/kg-water-v °C	http://www.engineeringtoolbox.com
Enthalpy of Water Evaporation at 0 C ($\Delta H_{w,vap}$)	2257	kJ/kg-water	http://www.engineeringtoolbox.com
1,4-D Henry's Constant (H_i) at T_{start}	1.432E-04	L-H_2O/L-vapor	(based on Ondo and Dohnal (2007) equation)
Treatment Zone Mass Balance Quantities			
Initial Mass of 1,4-Dioxane in Soil	1.15E+01	kg-1,4-D	(ρ_{soil} x V_{soil} x $C_{soil,14D}$)/1000
Initial Mass of Liquid Water In Soil	8.66E+04	kg-H_2O	(ρ_{soil} x V_{soil} x θ_m)*1000
Vapor Pressure of Water at T_{start}	2.30E-02	atm	(based on Yaws and Yang (1989) equation)
Initial Concentration of Water Vapor in Soil Pores	1.72E-02	g-H_2O/L-vapor	(based on Ideal Gas Law)
Initial Mass of Water Vapor in Soil Pores	8.47E-01	kg-H_2O	($C_{w,v,soil}$ x V_{soil} x θ_v)
Total Initial Mass of Water in the Soil	8.66E+04	kg-H_2O	(liquid water + water vapor)
Vapor Pressure of Water at $T_{ambient}$	1.90E-02	atm	(based on Yaws and Yang (1989) equation)
Concentration of Water Vapor in Ambient Air	8.35E-03	g-H_2O/L-vapor	(based on Ideal Gas Law and ambient %RH)
Mass Rate of Water Addition from Injected Air	2.01E-02	kg/min	(ambient water concentration x actual flow rate)
Energy Addition Rate from Injected Heated Air	3.95E+02	kJ/min	(ambient water concentration x actual flow rate)

Figure 6. Input section of the HypeVent XSVE "HypeVent XSVE Inputs & Calcs".

Most entries are self-explanatory. The soil volume is the target treatment zone soil volume, which can be approximated by a simple rectangular box shape calculation (e.g., enter "=20*20*30*28.3" in the cell for a 20 ft long x 20 ft wide x 30 ft deep treatment zone volume in L units). Soil characteristics can be approximated if site-specific information is not available as suggested in the notes to the right of each quantity. Of those values, soil moisture is the most critical to HypeVent XSVE application (1,4-dioxane partitions significantly into soil moisture); and users are encouraged to collect site-specific information for that quantity or perform sensitivity analysis for a reasonable range of values.

Average ambient air conditions can be found through online weather data sources (e.g., https://weatherspark.com/averages/stations/United%20States/California).

The treatment zone vapor flow rate is entered as its equivalent value at "standard conditions" (0°C, 1 atm), which is common for vapor flow rate presentation in reports (e.g., standard cubic feet per minute [SCFM]).

The time-dependent mass balance equations occur in the columns to the right of the input cells in the "HypeVent XSVE Inputs & Calcs" worksheet. In the upper left corner of these columns is a black text user-specified input cell for "Time Step", as shown in Figure 7.

The time step value entry is critical to the screening-level calculations. It is suggested that this value be selected so that: a) temperature changes between initial time steps are <5°C (third column below); and b) changes in total 1,4-dioxane mass are <10% of the initial value (sixth column below). This usually requires some iteration. Time steps larger than this may cause instabilities in the calculations (e.g., negative 1,4-dioxane or soil moisture values may appear) and time steps that are too small may result in calculations for time periods that are not as long as the period of interest.

Time Step 10080 [min] (adjust the time step so that the temperature change between time steps is <5 C) and 1,4 dioxane mass change is <10%)

Treatment Time [min]	Treatment Time [d]	Soil Temp T_{soil} [°C]	Normalized Soil Abs. Temp (Tsoil/298.15)	Total Mass H_2O in Soil [kg-H_2O]	Total Mass 1,4-D in Soil [kg-1,4-D]	Vap Pres H_2O Soil at T_{soil} [atm]	Saturated H_2O Conc. in Soil Vapor at T_{soil} [g-H_2O/L-air]	Mass H_2O liquid in Soil [kg-H_2O]
0	0.00	2.000E+01	9.832E-01	8.66E+04	1.15E+01	0.0230	0.0172	8.66E+04
10080	7.00	2.296E+01	9.932E-01	8.638E+04	1.11E+01	0.0276	0.0204	8.64E+04
20160	14.00	2.559E+01	1.002E+00	8.608E+04	1.05E+01	0.0323	0.0237	8.61E+04
30240	21.00	2.789E+01	1.010E+00	8.569E+04	9.91E+00	0.0370	0.0269	8.57E+04

Figure 7. Time Step entry cell in "HypeVent XSVE Inputs & Calcs" worksheet.

Two pre-formatted charts are found at the "Results – 1,4D Removal" and "Results – Soil T and Water" tabs; these present the projected 1,4-dioxane removal and removal rate estimates as shown in Figure 5 and soil temperature and moisture changes with time as shown in Figure 8, respectively. Users can modify the axes scales and chart formatting in these figures to best show their results.

The worksheet tab “Flow Rate Estimates” contains calculations that allow users to estimate vapor extraction flow rates for user-defined well construction (radius, length), soil characteristics (permeability), and operating conditions (vacuum). These calculations are not coupled to HypeVent XSVE performance predictions in the first worksheet, so it does not have to be used to generate screening-level XSVE performance predictions. This worksheet is provided in case users are interested in estimating soil vapor flow rates for sites where they have yet to perform vapor extraction or injection pilot testing, or want to determine soil permeability from measured steady-state flow rate vs. vacuum pilot-test data.

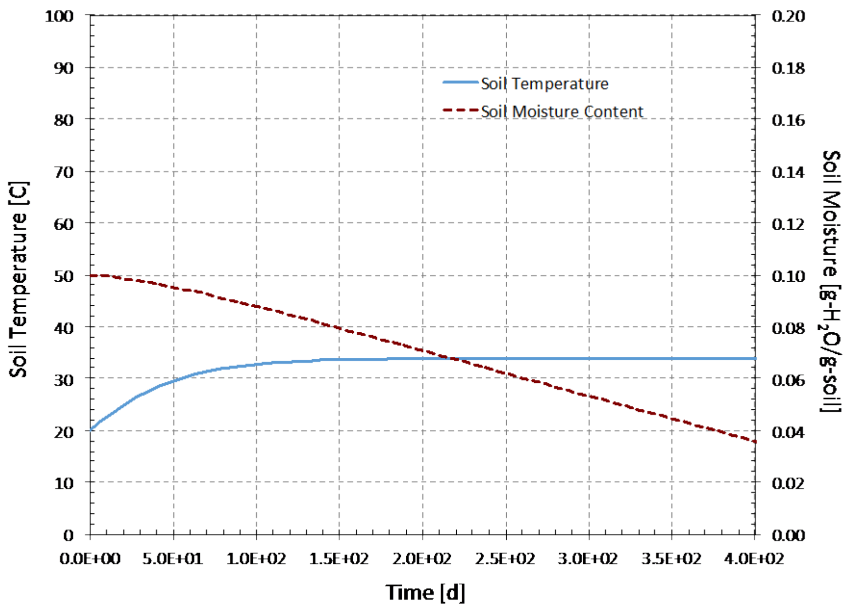

Figure 8. Sample HypeVent XSVE output (“Results – Soil T and Water” chart).

Field Demonstration Example

Details of the field demonstration of XSVE for 1,4-dioxane are provided in Hinchee et al., 2017a and 2017b. A detailed examination of HypeVent XSVE for the field demonstration example and sensitivity analyses are presented in Burris et al., 2017. A brief comparison of HypeVent XSVE results and the actual performance at the former McClellan AFB field demonstration in Figure 9. Considering idealized assumptions made in HypeVent XSVE, the results compare relatively well, indicating that HypeVent XSVE is a useful design and feasibility assessment tool for XSVE for 1,4-dioxane.

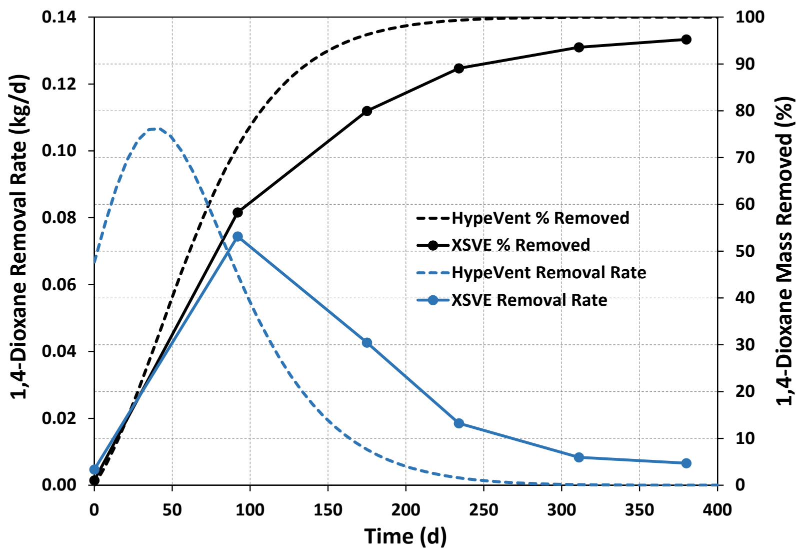

Figure 9. HypeVent XSVE output compared to field data at the Former McClellan AFB field demonstration site.

References

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