June, 2001

FACT SHEET

Correcting the Henry's Law Constant for Soil Temperature

The U.S. EPA 1996 *Soil Screening Guidance* specifies a procedure for calculating inhalation soil screening levels (SSLs) for volatile contaminants in soils. Both the volatilization factor (VF) and the soil saturation concentration (C_{sat}) require the use of the dimensionless Henry's law constant for each volatile contaminant. The Henry's law constants in units of atm-m^3/mol and the dimensionless Henry's law constants provided in the *Soil Screening Guidance* are values at a temperature of 25 ^oC. Average subsurface soil temperatures, however, are typically less than this value. In such cases, use of the Henry's law constant at 25 ^oC may overpredict the volatility of the contaminant in water such that the resulting inhalation SSL and soil saturation concentration may be artificially low.

The dimensionless Henry's law constant may be corrected for the average soil temperature using the Clausius-Clapeyron relationship [1]:

$$H'_{TS} = \frac{\exp\left[-\frac{\Delta H_{v,TS}}{R_C}\left(\frac{1}{T_S}-\frac{1}{T_R}\right)\right] H_R}{RT_S} \qquad (1)$$

where:

H'_{TS}	=	Henry's law constant at the average soil temperature, dimensionless
$\Delta H_{v,TS}$	=	Enthalpy of vaporization at the average soil temperature, cal/mol
T_S	=	Average soil temperature, ^oK
T_R	=	Henry's law constant reference temperature, ^oK
H_R	=	Henry's law constant at the reference temperature, atm-m^3/mol
R_C	=	Gas constant (= 1.9872 cal/mol-^oK)
R	=	Gas constant (= 8.205 x 10^{-5} atm-m^3/mol-^oK).

The enthalpy of vaporization of the compound at the average soil temperature ($\Delta H_{v,TS}$) can be approximated from the enthalpy of vaporization at the normal boiling point by [2]:

$$\Delta H_{v,TS} = \Delta H_{v,b}\left[\frac{(1-T_S/T_C)}{(1-T_B/T_C)}\right]^n \qquad (2)$$

where:

$\Delta H_{v,TS}$	=	Enthalpy of vaporization at the average soil temperature, cal/mol
$\Delta H_{v,b}$	=	Enthalpy of vaporization at the normal boiling point, cal/mol
T_S	=	Average soil temperature, ^oK
T_C	=	Critical temperature, ^oK
T_B	=	Normal boiling point, ^oK
n	=	Exponent, unitless.

If data are not readily available for the average soil temperature, mean annual shallow soil temperature at depths of 100 cm or less can be estimated by [3]:

$$T_S = 4.646 + 0.986 T_A \qquad (3)$$

where T_S is the mean annual soil temperature (^{o}F) and T_A is the mean monthly air temperature (^{o}F) for one or more years. The mean monthly air temperature is typically calculated from daily minimum and maximum temperatures obtained from a representative National Weather Service station. The standard error of estimate (S_{yx}) using Equation 3 is approximately 4.15 ^{o}F. Seasonal estimates of average shallow soil temperature can be made using the following equations [3]:

$$\text{Summer } T_S = 16.115 + 0.856 T_A \text{ ; } S_{yx} = 3.62^o F \qquad (4)$$

$$\text{Fall } T_S = 1.578 + 1.023 T_A \text{ ; } S_{yx} = 3.01^o F \qquad (5)$$

$$\text{Winter } T_S = 15.322 + 0.656 T_A \text{ ; } S_{yx} = 3.41^o F \qquad (6)$$

$$\text{Spring } T_S = 0.179 + 1.052 T_A \text{ ; } S_{yx} = 3.45^o F \text{ .} \qquad (7)$$

The months of June, July, and August comprise the summer; September, October, and November, the fall; December, January, and February, the winter; and March, April, and May, the spring.

For depths greater than 100 cm, the mean annual soil temperature remains relatively stable throughout the year and can be estimated from the average shallow ground water temperatures shown in Figure 1.

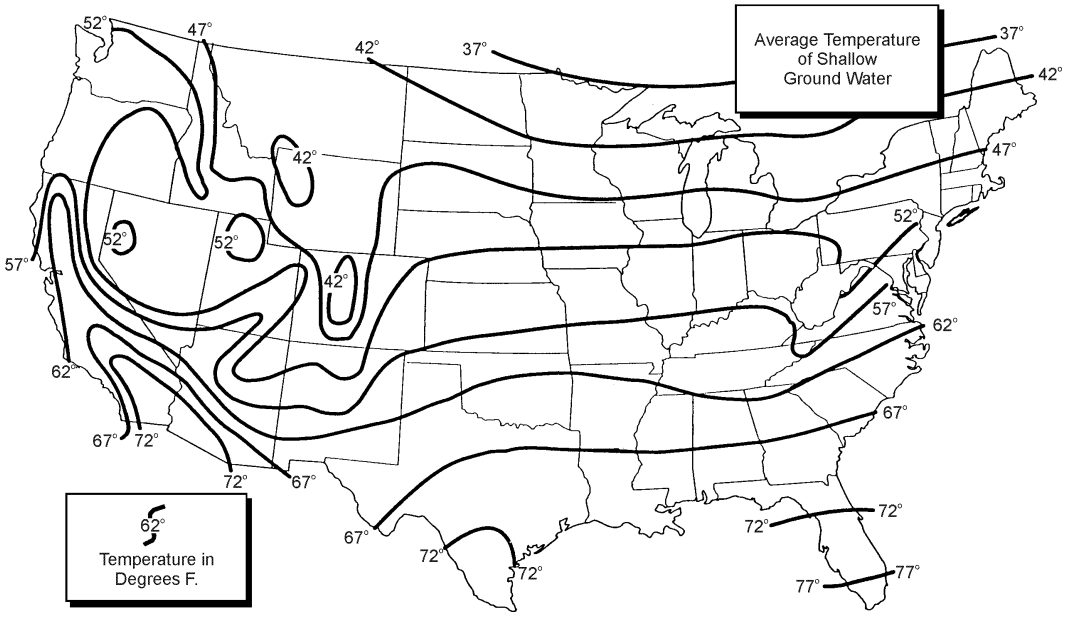

Figure 1. Average Shallow Ground Water Temperatures in the United States [4]

Table 1 gives the value of the exponent n in Equation 2 as a function of the ratio T_B/T_C.

Table 1. Values of Exponent n as a Function of T_B/T_C

Ratio T_B/T_C	Exponent n
< 0.57	0.30
0.57 – 0.71	0.74 (T_B/T_C) – 0.116
> 0.71	0.41

Chemical properties of many compounds such as the Henry's law constant (H_R), the normal boiling point (T_B), the critical temperature (T_C), and the enthalpy of vaporization at the normal boiling point ($\Delta H_{v,b}$) may be found in one or more of the following references:

- **CRC Handbook of Chemistry and Physics**, **79th Ed**. 1998. CRC Press, Boca Raton, FA
- **Lange's Handbook of Chemistry, 15th Ed**. 1999. McGraw-Hill, New York, NY
- **Perry's Chemical Engineers' Handbook**, **7th Ed**. 1997. McGraw-Hill, New York, NY
- **Superfund Chemical Data Matrix**. U. S. EPA, Office of Emergency and Remedial Response, Washington, DC, EPA/540/R-96/028 *(http://www.epa.gov/oerrpage/superfund/resources/scdm/index.htm)*
- **Water9 PC-Based Expert Systems**. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC *(http://www.epa.gov/ttn/chief/software/water/index.html)*
- W.G. Mallard and P.J. Linstrom, Eds., **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**. November 1998. National Institute of Standards and Technology, Gaithersburg, MD, 20899 *(http://webbook.nist.gov/chemistry/)*
- R. Sander. 1999. **Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Version 3** *(http://www.mpch-mainz.mpg.de/~sander/res/henry.html)*

The reader is reminded to use the correct chemical properties from the literature and to make any necessary units conversions. If the required properties cannot be found in the literature, general estimates of these values can be made with limited data. The critical temperature, for example, can be approximated from the normal boiling point by [2]:

$$T_C \approx 3T_B / 2. \qquad (8)$$

The enthalpy of vaporization at the normal boiling point may also be approximated to within two significant figures by [2]:

$$\Delta H_{v,b} = \frac{2.303 B R_C T_B^{\,2} \left(Z_g - Z_l\right)}{\left(t_b + C\right)^2} \qquad (9)$$

where:

$\Delta H_{v,b}$	=	Enthalpy of vaporization at the normal boiling point, cal/mol
B	=	Antoine coefficient, ^{o}C
R_C	=	Gas constant (= 1.9872 cal/mol-^{o}K)
T_B	=	Normal boiling point, ^{o}K
$(Z_g\text{-}Z_l)$	=	Compressibility factor difference, unitless (= 0.95 at T_B)
t_b	=	Normal boiling point, ^{o}C
C	=	Antoine coefficient, ^{o}C.

The Antoine coefficients *A* (not shown in Equation 9), *B*, and *C* are constants used to describe the vapor pressure curve of a volatile chemical as a function of temperature. As with the other chemical properties, Antoine coefficients may be found for many compounds in one or more of the references cited previously. If the Antoine coefficients are given in degrees Kelvin, the *C* coefficient should be converted to degrees Celsius by subtracting 273.15; the *B* coefficient, however, represents the slope of the curve and should not be converted. Care should also be taken to ensure that the value of the *B* coefficient listed in any reference does not already include a factor of 2.303 for converting base-10 to base-e logarithms. A simple method for determining whether this has been done is to check the value of *B* for methane. If the value is approximately 405.42 (^{o}C or ^{o}K), the value may be used directly in Equation 9. If the value of *B* for methane is approximately 930^{o}, the value has already been multiplied by 2.303.

If data are not available in the literature, the value of the Antoine *C* coefficient may be approximated from the normal boiling point using Table 2.

Table 2. Antoine Coefficient C for Organic Compounds

Boiling Point (^{o}C)	*C* (^{o}C)	Boiling Point (^{o}C)	*C* (^{o}C)
< -150	264 – 0.034 t_b	140	212
-150 to -10	240 – 0.19 t_b	160	206
-10	238	180	200
0	237	200	195
20	235	220	189
40	232	240	183
60	228	260	177
80	225	280	171
100	221	≥ 300	165
120	217		

For Polyhydric Alcohols (diols, triols, etc.): C = 230 ^{o}C.

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The value of the Antoine *B* coefficient can also be estimated with a value of the *C* coefficient, the normal boiling point, and one pair of vapor pressure/temperature data [2]:

$$B = \frac{(t_b + C)(t_{Pv} + C)}{t_b - t_{Pv}} \log\left(\frac{760}{P_v}\right) \qquad (10)$$

where:

B	=	Antoine coefficient, ^{o}C
t_b	=	Normal boiling point, ^{o}C
C	=	Antoine coefficient, ^{o}C
t_{Pv}	=	Known temperature at vapor pressure P_v, ^{o}C
760	=	Vapor pressure at the normal boiling point, mmHg
P_v	=	Known vapor pressure at temperature t_{Pv}, mmHg.

Typically, literature values for vapor pressure (P_v) are at a temperature (t_{Pv}) of 20 ^{o}C or 25 ^{o}C. Combining this vapor pressure/temperature pair with that of the normal boiling point yields a linear approximation of the vapor pressure/temperature relationship. Although this relationship is not linear, the approximation given by Equation 10 requires only two pairs of data. Overall, use of Equation 10 will yield a maximum error of less than 50%.

Example Calculations

Estimate the dimensionless Henry's law constant for 1,3-Dichloropropene at a soil temperature of 10 ^{o}C, given:

- Henry's law constant at 25 ^{o}C = 1.77*E*-02 atm-m^3/mol
- Dimensionless Henry's law constant at 25 ^{o}C = 7.26*E*-01
- Normal boiling point = 381.15 ^{o}K or 108.00 ^{o}C
- Vapor pressure at 25 ^{o}C = 31.24 mmHg
- Critical temperature = 587.38 ^{o}K.

1. From Table 2, the Antoine *C* coefficient is approximately 219 ^{o}C.

2. From Equation 10, the Antoine *B* coefficient is:

$$B = \frac{(108+219)(25+219)}{108-25}\log\left(\frac{760}{31.24}\right)$$

$$B = 1{,}332\ ^{o}\text{C}.$$

3. From Equation 9, the enthalpy of vaporization at the normal boiling point within two significant figures is:

$$\Delta H_{v,b} = \frac{2.303\times 1{,}332\times 1.9872\times 381.15^2\times 0.95}{(108+219)^2}$$

$$\Delta H_{v,b} = 7{,}900\ \text{cal/mol}.$$

4. From Equation 2, and Table 1, the enthalpy of vaporization at the soil temperature is:

$$\Delta H_{v,TS} = 7{,}900 \times \left[\frac{(1 - 283.15/587.38)}{(1 - 381.15/587.38)} \right]^{0.364}$$

$$\Delta H_{v,TS} = 9{,}100 \text{ cal/mol.}$$

5. From Equation 1, the dimensionless Henry's law constant at the soil temperature is:

$$H'_{TS} = \frac{\exp\left[-\frac{9{,}100}{1.9872} \left(\frac{1}{283.15} - \frac{1}{298.15} \right) \right] \times 1.77E-02}{8.205E-05 \times 283.15}$$

$$H'_{TS} = 3.38E-01.$$

The enthalpy of vaporization at the normal boiling point ($\Delta H_{v,b}$) was calculated using Equations 9 and 10 and Table 2 for a each of 57 organic compounds. These values were then compared with the actual values of $\Delta H_{v,b}$ taken from the literature. Results indicated a maximum error of 29%, a minimum error of 0.5%, and a mean error of 5%. Finally, the value of the dimensionless Henry's law constant for each of the same 57 compounds was calculated at a soil temperature of 10 ^{o}C. Equations 1 and 2 and Table 1 were used in these calculations; values of $\Delta H_{v,b}$ were taken from the literature. The values of the Henry's law constants at 10 ^{o}C were then compared to their reference values at 25 ^{o}C. Results indicated a maximum change in the value of the Henry's law constant of 90% and a minimum change of 30%. The largest changes occurred for the compounds with the highest boiling points and lowest vapor pressures.

The attachment to this fact sheet contains the chemical properties required to calculate the dimensionless Henry's law constant at the average soil temperature for the 93 volatile chemicals listed in the U.S. EPA 1996 *Soil Screening Guidance*.

REFERENCES:

1. *Perry's Chemical Engineers' Handbook, 7th Ed.* 1997. McGraw-Hill, New York, NY.

2. Lyman, J.L., W.F. Reehl, and D.H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods*, American Chemical Society, Washington, DC.

3. Toy, T.J., A.J. Kuhaida, Jr., and B.E. Munson. 1978. The prediction of mean monthly soil temperature from mean monthly air temperature, *Soil Science*, 126:181-189.

4. U.S. Environmental Protection Agency (EPA). 1995. *Review of Mathematical Modeling for Evaluating Soil Vapor Extraction Systems*. Office of Research and Development, Washington, D.C. EPA/540/R-95-513.

ATTACHMENT
Chemical Properties of Volatile SSL Chemicals

CAS No.	Chemical	Henry's Law Constant, H_R at 25 °C atm-m^3/mol	Normal Boiling Point, T_B °K	Normal Boiling Point, t_b °C	Critical Temperature, T_C °K	Vapor Pressure at 25 °C, P_v mmHg	Enthalpy of Vaporization at T_B, $\Delta H_{v,b}$ cal/mol	$\Delta H_{v,b}$ Ref.
50293	DDT	8.10E-06	533.15	260.00	720.75	3.93E-07	22,000	4
50328	Benzo(a)pyrene	1.13E-06	715.90	442.75	969.27	4.89E-09	19,000	4
51285	2,4-Dinitrophenol	4.44E-07	605.28	332.13	827.85	5.48E-03	25,000	3
53703	Dibenz(a,h)anthracene	1.47E-08	743.24	470.09	990.41	2.05E-11	29,995	3
56235	Carbon tetrachloride	3.05E-02	349.90	76.75	556.60	1.12E+02	7,127	1
56553	Benz(a)anthracene	3.34E-06	708.15	435.00	1,004.79	1.54E-07	16,000	4
57749	Chlordane	4.85E-05	624.24	351.09	885.73	2.70E-05	14,000	4
58899	gamma-HCH (Lindane)	1.40E-05	596.55	323.40	839.36	3.72E-05	15,000	4
60571	Dieldrin	1.51E-05	613.32	340.17	842.25	9.96E-07	17,000	4
65850	Benzoic Acid	1.54E-06	720.00	446.85	751.00	6.51E-03	12,094	3
67641	Acetone	3.88E-05	329.20	56.05	508.10	2.27E+02	6,955	1
67663	Chloroform	3.66E-03	334.32	61.17	536.40	2.04E+02	6,988	1
67721	Hexachloroethane	3.88E-03	458.00	184.85	695.00	4.72E-01	9,510	2
71363	Butanol	8.80E-06	390.88	117.73	563.05	6.54E+00	10,346	1
71432	Benzene	5.56E-03	353.24	80.09	562.16	9.50E+01	7,342	1
71556	1,1,1-Trichloroethane	1.72E-02	347.24	74.09	545.00	1.24E+02	7,136	1
72208	Endrin	7.51E-06	718.15	445.00	986.20	5.84E-07	15,000	4
72435	Methoxychlor	1.58E-05	651.02	377.87	848.49	1.23E-06	16,000	4
72548	DDD	4.00E-06	639.90	366.75	863.77	8.66E-07	17,000	4
72559	DDE	2.10E-05	636.44	363.29	860.38	5.66E-06	15,000	4
74839	Methyl bromide	6.24E-03	276.71	3.56	467.00	1.64E+03	5,714	1
75014	Vinyl chloride (chloroethene)	2.71E-02	259.25	-13.90	432.00	2.80E+03	5,250	2
75092	Methylene chloride	2.19E-03	313.00	39.85	510.00	3.70E+02	6,706	1
75150	Carbon disulfide	3.02E-02	319.00	45.85	552.00	3.40E+02	6,391	1
75252	Bromoform	5.34E-04	422.35	149.20	696.00	5.94E+00	9,479	1
75274	Bromodichloromethane	1.60E-03	363.15	90.00	585.85	5.84E+01	7,800	4
75343	1,1-Dichloroethane	5.61E-03	330.55	57.40	523.00	2.28E+02	6,895	1
75354	1,1-Dichloroethylene	2.61E-02	304.75	31.60	576.05	5.99E+02	6,247	1
76448	Heptachlor	1.09E-03	603.69	330.54	846.31	3.26E-04	13,000	4
77474	Hexachlorocyclopentadiene	2.71E-02	512.15	239.00	746.00	7.32E-02	10,931	2
78591	Isophorone	6.63E-06	488.35	215.20	715.00	4.09E-01	10,271	2
78875	1,2-Dichloropropane	2.80E-03	369.52	96.37	572.00	5.06E+01	7,590	2
79005	1,1,2-Trichloroethane	9.12E-04	386.15	113.00	602.00	2.52E+01	8,322	1
79016	Trichloroethylene	1.03E-02	360.36	87.21	544.20	7.20E+01	7,505	1
79345	1,1,2,2-Tetrachloroethane	3.44E-04	419.60	146.45	661.15	5.17E+00	8,996	1
83329	Acenaphthene	1.55E-04	550.54	277.39	803.15	3.75E-03	12,155	2
84662	Diethylphthalate	4.51E-07	567.15	294.00	757.00	1.65E-03	13,733	2
84742	Di-n-butyl phthalate	9.39E-10	613.15	340.00	798.67	4.22E-05	14,751	1

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85687	Butyl benzyl phthalate	1.26E-06	660.60	387.45	839.68	1.20E-05	14,000	4
86306	N-Nitrosodiphenylamine	5.00E-06	632.28	359.13	890.45	1.00E-01	7,300	4
86737	Fluorene	6.37E-05	570.44	297.29	870.00	6.21E-04	12,666	2
86748	Carbazole	1.53E-08	627.87	354.72	899.00	2.66E-04	13,977	2
87683	Hexachloro-1,3-butadiene	8.15E-03	486.15	213.00	738.00	1.77E-01	10,206	2
87865	Pentachlorophenol	2.44E-08	582.15	309.00	813.20	5.40E-04	16,109	3
88062	2,4,6-Trichlorophenol	7.78E-06	519.15	246.00	749.03	1.18E-02	12,000	4
91203	Naphthalene	4.83E-04	491.14	217.99	748.40	8.89E-02	10,373	2
91941	3,3-Dichlorobenzidine	4.00E-09	560.26	287.11	754.03	2.20E-07	20,000	4
95476	o-Xylene	5.20E-03	417.60	144.45	630.30	6.60E+00	8,661	1
95487	2-Methylphenol (o-cresol)	1.20E-06	464.19	191.04	697.60	3.16E-01	10,800	1
95501	1,2-Dichlorobenzene	1.90E-03	453.57	180.42	705.00	1.36E+00	9,700	2
95578	2-Chlorophenol	3.90E-04	447.53	174.38	675.00	2.11E+00	9,572	2
95954	2,4,5-Trichlorophenol	4.34E-06	526.15	253.00	759.13	1.63E-02	11,000	4
98953	Nitrobenzene	2.40E-05	483.95	210.80	719.00	2.44E-01	10,566	2
100414	Ethylbenzene	7.88E-03	409.34	136.19	617.20	9.58E+00	8,501	1
100425	Styrene	2.76E-03	418.31	145.16	636.00	6.24E+00	8,737	2
105679	2,4-Dimethylphenol	2.00E-06	484.13	210.98	707.60	1.26E-01	11,329	2
106423	p-Xylene	7.66E-03	411.52	138.37	616.20	8.89E+00	8,525	1
106467	1,4-Dichlorobenzene	2.43E-03	447.21	174.06	684.75	1.06E+00	9,271	2
106478	p-Chloroaniline	3.32E-07	503.65	230.50	754.00	2.35E-02	11,689	2
107062	1,2-Dichloroethane	9.78E-04	356.65	83.50	561.00	8.13E+01	7,643	1
108054	Vinyl acetate	5.12E-04	345.65	72.50	519.13	1.09E+02	7,800	2
108383	m-Xylene	7.34E-03	412.27	139.12	617.05	8.51E+00	8,523	1
108883	Toluene	6.63E-03	383.78	110.63	591.79	2.82E+01	7,930	1
108907	Chlorobenzene	3.71E-03	404.87	131.72	632.40	1.21E+01	8,410	1
108952	Phenol	3.98E-07	455.02	181.87	694.20	4.36E-01	10,920	1
111444	Bis(2-chloroethyl)ether	1.80E-05	451.15	178.00	659.79	1.34E+00	10,803	3
115297	Endosulfan	1.12E-05	674.43	401.28	942.94	9.96E-06	14,000	4
117817	Bis(2-ethylhexyl)phthalate	1.02E-07	657.15	384.00	806.00	6.45E-06	15,999	2
117840	Di-n-octyl phthalate	6.68E-05	704.09	430.94	862.22	4.47E-06	14,000	4
118741	Hexachlorobenzene	1.32E-03	582.55	309.40	825.00	1.23E-05	14,447	2
120127	Anthracene	6.51E-05	615.18	342.03	873.00	2.55E-05	13,121	2
120821	1,2,4-Trichlorobenzene	1.42E-03	486.15	213.00	725.00	3.36E-01	10,471	2
120832	2,4-Dichlorophenol	3.17E-06	482.15	209.00	708.17	5.48E-03	15,000	4
121142	2,4-Dinitrotoluene	9.27E-08	590.00	316.85	814.00	1.74E-04	13,467	2
124481	Chlorodibromomethane	7.83E-04	416.14	142.99	678.20	3.12E+01	5,900	4
127184	Tetrachloroethylene	1.84E-02	394.40	121.25	620.20	1.84E+01	8,288	1

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129000	Pyrene	1.10E-05	667.95	394.80	936.00	4.25E-06	14,370	2
156592	cis-1,2-Dichloroethylene	4.07E-03	333.65	60.50	544.00	1.75E+02	7,192	2
156605	trans-1,2-Dichloroethylene	9.39E-03	320.85	47.70	516.50	3.52E+02	6,717	2
193395	Indeno(1,2,3-cd)pyrene	1.60E-06	809.15	536.00	1,078.24	1.43E-10	19,000	4
205992	Benzo(b)fluoranthene	1.11E-04	715.90	442.75	969.27	8.06E-08	17,000	4
206440	Fluoranthene	1.61E-05	655.95	382.80	905.00	8.13E-06	13,815	2
207089	Benzo(k)fluoranthene	8.29E-07	753.15	480.00	1,019.70	2.00E-09	18,000	4
218019	Chrysene	9.46E-05	714.15	441.00	979.00	7.83E-09	16,455	2
309002	Aldrin	1.70E-04	603.01	329.86	839.37	1.67E-05	15,000	4
319846	alpha-HCH (alpha-BHC)	1.06E-05	596.55	323.40	839.36	4.26E-05	15,000	4
319857	beta-HCH (beta-BHC)	7.44E-07	596.55	323.40	839.36	4.90E-07	19,000	4
542756	1,3-Dichloropropene	1.77E-02	381.15	108.00	587.38	3.12E+01	7,900	4
606202	2,6-Dinitrotoluene	7.46E-07	558.00	284.85	770.00	5.68E-04	12,938	2
621647	N-Nitrosodi-n-propylamine	2.25E-06	509.60	236.45	746.87	3.52E+00	6,100	4
1024573	Heptachlor epoxide	9.51E-06	613.96	340.81	848.76	4.34E-06	16,000	4
7439976	Mercury (elemental)	1.14E-02	629.88	356.73	1,750.00	2.00E-03	14,127	1
8001352	Toxaphene	6.00E-06	657.15	384.00	873.31	4.19E-06	15,000	4

1 - CRC Handbook of Chemistry and Physics, CRC Press (1994).

2 - Design Institute for Physical Property Data, The American Institute for Chemical Engineers, on-line data search, 1997.

3 - Lange's Handbook of Chemistry 15th Ed., McGraw-Hill (1999).

4 - $\Delta H_{v,b}$ calculated from boiling point and vapor pressure using Equations and Tables in this fact sheet.