PALOS VERDES LANDFILL
REMEDIAL INVESTIGATION REPORT

APPENDIX E.7

GAS TRANSFER PHENOMENA AS EXPLAINED BY HENRY'S LAW

VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER DUE TO LANDFILL GAS TRANSFER

Landfill gas is comprised primarily of methane and carbon dioxide but also has traces of volatile organic compounds. Groundwater concentrations of volatile organic compounds resulting from contact with landfill gas are calculated from Henry's Law. Henry's Law is given by:

$$P_i = H_c * C_i$$

where P_i = Partial pressure of species i in landfill gas [atm]

C_i = Equilibrium concentration of species i in groundwater [mole/m^3]

H_c = Henry's Law constant [atm-m^3/mole]

Values of H_c are ideally obtained by measurement of concentrations of a compound in the gas and dilute aqueous phases at equilibrium. However, such measurements are often unavailable for volatile organics. In the absence of equilibrium data, Henry's Law constants can be estimated by (Dilling, 1979; Truong and Blackburn, 1984):

$$H_i = \frac{C_{air}}{C_{water}} = \frac{16.04 * P * M}{T * S}$$

$$H_c = H_i * R * T$$

$$H_c = 13.16 \times 10^{-4} \frac{P * S}{S}$$

where H_i = Dimensionless Henry's Law constant

H_c = Henry's Law Constant [atm-m^3/mole]

P = Vapor pressure of pure compound [mm Hg]

S = Solubility of solute in water [mg/l]

Measured and calculated Henry's Law constants are tabulated in Table 1. Table 2 presents the average concentrations of volatile organic compounds in landfill gas and the corresponding saturation values in water. There was typically two orders of magnitude in the range of detected values. Also presented are values found in wells containing water exposed to landfill gas. Comparison of measured and predicted values indicates that the concentrations of volatile organic compounds in the groundwater may be attributed to gas transfer processes alone. Higher measured concentration levels, which would be indicative of direct leaching of these materials into groundwater, were not found. The compounds are often either not detectible in groundwater or measured at concentrations 2 to 3 orders of magnitude lower than predicted. The relative absence of these compounds in the groundwater is probably attributable to various causes including slow rate and small amount of gas transfer into the water, attenuation effects in the soil, and subsequent volatilization of the compounds from the groundwater once out of the range of landfill gas migration. It should also be noted that there is a wide range in the concentrations of volatile organic compounds in landfill gas due to varying conditions of gas production and movement within a landfill. Because of these factors, the predicted levels in groundwater are probably representative of maximum concentrations although locally higher levels may occur.

TABLE 1

HENRY'S LAW CONSTANTS

COMPOUND	M [g/mole]	P [mm Hg]		S [mg/l]		Hc [atm-m3/mole]	NOTES
1. methylene chloride	84.9	424.5	(25)	16700	(25)	2.84x10-3	5
2. 1,1,1-trichloroethane	133.4	100	(20)	4400	(20)	1.50x10-2	1
3. 1,1-dichloroethylene	96.95	591	(25)	400	(20)	1.89x10-1	5
4. trichloroethylene	131.5	60	(20)	1100	(20)	9.26x10-3	5
5. tetrachloroethylene	165.8	19	(25)	150	(25)	2.76x10-2	5
6. chlororbenzene	112.56	8.8	(20)	500	(20)	2.61x10-3	5
7. vinyl chloride	62.5	2660		9500		2.30x10-3	2
8. 1,1-dichloroethane	98.96	180	(20)	5500	(20)	4.26x10-3	5
9. 1,1,2-trichloroethane	133.4	23		4420		9.14x10-4	5
10. 1,2-dichloroethane	98.96	82		8700		1.09x10-4	3
11. benzene	78.1	76	(20)	1780	(20)	4.39x10-3	5
12. toluene	92.1	22	(20)	515	(20)	5.18x10-3	5
13. ethylbenzene	106.2	9.5	(25)	206	(25)	6.45x10-3	5
14. trans-1,2-dichloroethylene	96.94	326		6300		6.60x10-3	5
15. chloroethane	64.52	1000	(20)	5740	(20)	1.48x10-2	5
16. 1,2-dichloropropane	113.0	42	(20)	2700	(20)	2.31x10-3	5
17. m-xylene	106.2	6		198*	(25)	4.23x10-3	5
18. o+p-xylene	106.2	6.5		198	(25)	4.59x10-3	5
19. freon 12	120.9	4250	(20)	280	(25)	2.25x10-1	4
20. freon11	137.4	687	(20)	1100	(25)	1.13x10-1	5
21. chloroform	119.4	202.5	(25)	9300	(25)	3.42x10-3	
22. carbon tetrachloride	153.8	113	(25)	1160	(25)	1.97x10-2	

* = assumed equal to p-xylene
NA = data not available

NOTES:

1. Henry's Law Contant from: Roberts, P.V. and P.G. Dandliker, "Mass Transfer of Volatile Organic Contaminants From Aqueous Solution to the Atmosphere During Surface Aeration", Env. Sci. and Technol., 17, 1983, pp 484-489.
2. Henry's Law Constant calculated from solubility reported by: DeLassus, P.T. and D.D. Schmidt, Solubilities of Vinyl Chloride and Vinylidene Chloride in Water", J. Chem. Eng. Data, 26, 1981, pp 274-276.
3. Henry's Law Contstant from: Bakin, V.M., "Liquid Vapor Equilibrium in the Water-1,2-Dichlorethane Systems Studied by the Method of Labeled Atoms", J. Phy. Chem. (Russian), 45 (7), 1971, p 1870.
4. Henry's Law Constant from: Roberts P.V., "Comment on 'Mass Transfer of Volatile Organic Contaminants from Auquous Solution to the Atmosphere During Surface Aeration'", Env. Sci., and Technol., 18, 1984, p. 894.
5. Henry's Law Constant calculated using solubility and parcial pressure data from: (A) Verschueren K., "Handbook of Environmental Data on Organic Chemicals", Van Nostrand Reinhold Co., NY, NY, 1983. and (B) Dilling, W.L., "Interphase Transfer Process.II. Evaporation Rates of Chloromethanes, Ethanes, Ethylenes, Propanes, and Proylenes from Dilute Aqueous Solutions. Comparisons with Theoretical Predictions", Env. Sci. and Technol., 11 (4), 1977, pp 405-409.

TABLE 2

PREDICTED AND MEASURED VOLATILE ORGANIC COMPOUNDS CONCENTRATIONS IN WATER EXPOSED TO LANDFILL GAS

COMPOUNDS	AVERAGE RAW* GAS CONC. (ppm)	EQUILIBRIUM* GROUNDWATER CONC. PREDICTED FROM HENRYS LAW (ppb)	MEASURED GROUNDWATER CONCENTRATION	
			% DETECTION	AVERAGE LEVELS** (ppb)
1. methylene chloride	52.5	1570	6	5.70
2. 1,1,1-trichloroethane	0.649	5.78	6	0.60
3. 1,1-dichloroethylene	0.661	0.339	0	0
4. trichloethylene	8.95	127	30	56.2
5. tetrachloroethylene	19.4	116	43	24.4
6. vinyl chloride	18.4	50	22	32.2
7. benzene	12.4	221	18	3.82
8. toluene	93.4	1660	10	14.4

NOTES:

* Typically the range in concentrations varies by two order of magnitude.

** Averages for detected values only; true averages are less.