Henry's law constants of volatile organic compounds in activated sludge and wastewater at 298 K

Jun-Hong Lin and Ming-Shean Chou

Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, R.O.C.

ABSTRACT. Henry's law constant is an important equilibrium factor in volatile organic compounds (VOCs) mass transfer process. The air-water dimensionless Henry's law constants (K_H) and the dimensionless apparent Henry's law constants (K'_H) in air-activated sludge mixed liquor and air-wastewater system for volatile organic compounds (VOCs) were measured at 298K. Hydrophilic VOCs (isopropanol and acetone) and hydrophobic VOCs (toluene and p-xylene) were used as target compounds. Deionized (DI) water, a pasteurized wastewater with a maximum dissolved total organic carbon (TOC) content of 700 mg/L and DI water diluted pasteurized activated sludge (mixed liquor) with a maximum suspended solid concentration of 40,000 mg/L were used as liquids.

K'_H of the hydrophilic compounds in the mixed liquor with the maximum suspended solid concentration were 13 to 21% higher than those in DI water. Those for toluene and p-xylene decreased up to 69 and 86%, respectively, in the mixed liquor. K'_H of all the test compounds in the wastewater was only 1 to 11% smaller than those in DI water. A model was proposed for correlating K'_H with wastewater TOC and activated sludge concentration using an organic carbon-water partition coefficient (K_{OC}) and activated sludge-water partition coefficient (K_P) as model parameters.

1 INTRODUCTION

Emissions of volatile organic compounds (VOCs) from wastewaters and exhaust gases are often overlooked as sources of exposure to hazardous substances. The biological treatment of gaseous pollutants has been popularized in the recent two decades for the emission control of biodegradable pollutants. In general, a suspended-growth system includes a sorption unit which utilizes an activated sludge liquid as a scrubbing liquor followed by an aerated activated sludge reactor for further oxidation of the scrubbed contaminants (Overcamp *et al.*, 1993; Burgess *et al.*, 2001). High concentration recirculated activated sludge has been applied to remove gas stream VOCs by a Venturi tube bioreactor (Zigmontienė and Baltrėnas, 2004).

For effective removal of the gaseous contaminants, equilibrium of organic compounds between air, wastewater and activated sludge has become an important topic. The

appearance of dissolved organic compounds (e.g., humic and fulvic acids) in water will affect the water solubility. The magnitude of the equilibrium constant can be described by a linear partition coefficient model (Haas and Kaplan, 1985). The organic carbon-water partition constant (K_{OC}) has been correlated with the octanol-water partition coefficient (K_{OW}) in linear free energy relationship (Goss and Schwarzenbach, 1998). In addition, the existence of suspended organic solids in liquid can enhance the solubility of VOCs of low water solubility. The sorption of VOCs in activated sludge biomass has been an investigation topic in many studies. The accumulation of some VOCs or hazardous pollutions by live (Smith *et al.*, 1993; Wang and Grady Jr., 1995), dead (Dobbs *et al.*, 1989; Tsezos and Wang, 1991), and pasteurized (Moretti and Neufeld, 1989; Dobbs *et al.*, 1995) microorganisms has been investigated. By the sorption of the biomass, the total VOC contents in the liquor will be raised, that is, the existence of biomass will increase the apparent solubility of VOCs in the liquor.

Many Henry's law constant values of environmental significant compounds in pure water phase have been published (Mackay and Shiu, 1981). Even though these data are important for understanding the fate and transport of VOCs, they could not satisfactorily be used for liquids containing other components such as non-volatile organic compounds or activated sludge. The apparent Henry's law constants of some hydrophobic organic compounds could be changed by dissolved organic carbon concentration in wastewater (David *et al.*, 2000). The apparent Henry's law constant decreases or the apparent solubility increases by increasing the pasteurized biomass concentration in the liquid (Davison *et al.*, 2000; Barton *et al.*, 2003).

Although many studies have investigated the VOC equilibrium change between two phases, little attention has been paid to that in three phase systems. The target of this research was to discuss the partitioning equilibrium migration in gas-deionized water, gas-wastewater, and gas-water-activated sludge systems. This study provides phase equilibrium information for hydrophilic and hydrophobic VOC treatment by bioscrubbers or bubble column.

2 MATERIALS AND METHODS

2.1 Theoretical

The dimensionless Henry's law constant (K_H) have been presented in eq 1 and called as an air-water partition coefficient in the environmental literature:

$$K_H = C_g/C_w \tag{1}$$

where C_g and C_w are the gas- and aqueous-phase VOC concentrations (mg/L), respectively.

A model describing the partitioning of a VOC between vapor, water and dissolved organics has been applied in wastewater system (David *et al.*, 2000). In wastewaters with some dissolved organics, the sorption phenomenon for a specific VOC can be described as eq 2 that the dissolved VOC exists both in the aqueous phase and combined with the dissolved organic carbon (DOC). The partition coefficient (K_{OC}) of VOC between the DOC and the aqueous phases can be expressed as eq 3.

$$C_g \xleftrightarrow{K_H} C_w \xleftrightarrow{K_{OC}} DOC-bound\ VOC \tag{2}$$

$$K_{OC} = \frac{DOC-bound\ VOC}{C_w} = \frac{C_d/S_d}{C_w} \tag{3}$$

where C_d and S_d are the DOC-bound VOC and DOC concentrations, respectively, both based on the liquid-phase volume (mg/L). C_d/S_d represents the mass of VOC bounded to

that of DOC and has a unit of mg VOC/(mg DOC). Equation 3 is based on the concept of partition of VOC between an organic liquid, such as octanol, and water by assuming that the dissolved organics as a pseudo-solvent for nonionic compounds. The physical properties of the dissolved organics control the partition of the dissolved VOC compound in the wastewater (Grathwohl, 1990).

In a liquid containing activated sludge (a mixed liquor), some VOC is adsorbed in the suspended solids (SS) and the partition coefficient (K_p) of the VOC between the solid and the aqueous phases can be expressed similar to eqs 4 and 5:

$$C_g \xleftrightarrow{K_H} C_w \xleftrightarrow{K_P} SS-bound\ VOC \tag{4}$$

$$K_P = \frac{SS-bound\ VOC}{C_w} = \frac{C_S / S_S}{C_w} \tag{5}$$

where C_S and S_S are the SS-bound VOC and suspended-solid (SS) concentrations, both based on the liquid-phase volume (mg/L). C_S/S_S represents the mass of VOC absorbed in and/or adsorbed on the suspended solids and has a unit of mg VOC/(mg SS). Equation 5 was mentioned in literature for calculating the organic biosorption coefficient in activated sludge liquor (Grady Jr. *et al.*, 1997). The total VOC concentration C_T in the wastewater with suspended solids is the sum of that in aqueous, dissolved organic, and suspended solid phases as shown in the following equation:

$$C_T = C_w + C_d + C_S \tag{6}$$

With a system composed of water, DOC and SS, the apparent Henry's law constant K'_H can then be express as:

$$K'_H = \frac{C_g}{C_T} = \frac{C_g}{(C_W + C_d + C_S)} = K_H \frac{1}{1 + K_{OC}S_d + K_P S_S} \tag{7}$$

,and the apparent solubility of the VOC in the liquor can be drawn:

$$C_T = \frac{C_g}{K'_H} = \frac{C_g}{K_H}(1 + K_{OC}S_d + K_P S_S) \tag{8}$$

Equation 8 indicates that C_T varies with both dissolved organics and suspended solids in liquids.

A model similar to eq 7 has been cited in literature for the partitioning of VOCs between gas and liquids containing suspended natural organic matter (SNOM) and suspended inorganic matter (SIM) (Staudinger and Roberts, 1996). As far as the authors' knowledge, no SNOM-water and SIM-water partition coefficient have been published and no model has been proposed for modeling K'_H with the activated sludge concentration.

2.2 Material and method

An aeration tank was used for cultivation of activated sludge for the present study. The seed sludge was obtained from a recycling line of an activated sludge system of a petrochemical wastewater plant of Kaohsiung Refinery, Chinese Petroleum Corp., Taiwan. A mixed liquor suspended solid (MLSS) concentration in the range of 40,000-45,000 mg/L was kept in the laboratory aeration liquor with a pH value in the range of 6.8-7.2. The sludge was fed simultaneously with glucose as carbon sources. A daily organic loading rate of 0.20 kg COD (chemical oxygen demand) per kg MLSS was kept for the whole experimental period. In addition to the organics, urea, potassium dihydrogen phosphate, and ferric iron were added to the activated sludge liquor as supplemental nutrients with a constant ratio of COD:N:P:Fe of 100:5:1:0.5. For supplementing natural nutrients, dried food yeast powder (Taiwan Sugar Co., Taiwan)

was added to the aeration tank at a rate of 0.2 g/L per day. A sludge retention time in the range of 10-15 days was kept by maintaining a proper sludge-wasting rate.

A simplified centrifugation method was used to separate the wastewater from the activated sludge mixed liquor. A fixed volume of the mixed liquor sample was centrifuged in a centrifuge (Universal 30F, Hettich, Germany) operated at 11,000 rpm (15,000 g) for 15 min. The centrifugation efficiently separated the mixed into two parts: activated sludge biomass with bound water and supernatant wastewater (Jin *et al.*, 2003). The supernatant was then filtered through a cellulose acetate membrane (Advantec MFS, USA) with an average pore size of 0.45 μm. The filtrate was then stored at 4 °C for subsequent experiments. Before the sorption experiment, both the activated sludge mixed liquor and the prepared filtrate were pasteurized at 80 °C for 2 hr to inactivate the biomass activity. The pasteurized samples were then diluted with deionized (DI) water (NANOpure, Barnstead, USA) to obtain the desired concentrations. Blank samples of wastewater and mixed liquor were analyzed after pasteurization, no target VOCs appeared in each chromatogram.

The single equilibration technique (SET) has usually been used for water-gas partition analysis (Staudinger and Roberts, 1996; Cheng *et al.*, 2004). The SET measures C_g at an equilibrium of VOC between the aqueous and gas phases with the equilibrium being established within a gas-tight vessel that contains VOC solution of a given initial mass at a constant temperature. By the SET, K'_H in eq 7 can be calculated by the following relationship:

$$K'_H = \frac{C_g}{C_T} = \frac{C_g}{(m_T - C_g V_g)/V_L} = \frac{C_g V_L}{(m_T - C_g V_g)} \tag{9}$$

where V_L is the bulk volume of the liquid phase injected with an initial mass of m_T of the chemical compound to be tested, and V_g is the overhead gas volume.

The standard SET procedures in this study were as follows. Target VOCs were isopropanol, acetone, toluene, and *p*-xylene (analysis ACS grade, Merck, Germany), and the tested temperature was fixed at 298 K (25 °C). In the case of water soluble isopropanol, and acetone, vials of nearly 43 mL (Kimble Glass, USA) were used for the tests. 40 mL of one of the pasteurized deionized water (abbrevaited as DI water), wastewater filtrate (abbrevaited as wastewater), and DI water mixed with a known amount of activated sludge (abbrevaited as mixed liquor) was used for each 43-mL vial with a screw cap and PTFE septa. For much less water-soluble toluene and *p*-xylene, Erlenmeyer flasks (Kimble Glass, USA) with an empty volume of around 310 mL were used. Before the tests, the inner volume of each of the vials or flasks was determined by the water-replacement method. Every liquid sample volume in the vial or flask was obtained by weighting and modified by its density. The flask was filled with 302 mL of one of the experimental liquids before sealed by a screw-fasten cap with a PTFE septum. After sealing of all the vials or flasks, a fixed volume (isopropanol 20 μL, acetone 5 μL, toluene 2 μL and *p*-xylene 2 μL) of each liquid organic compound was injected into a vial by a syringe (Hamilton, USA). The concentration of each VOC in the liquid phase would be fixed. 3-9 replicates were prepared for each compound and each liquid.

The prepared samples were then shaken in a 298 K water-bathed shaker with a rate of 150 rpm for 2 hours, and the shaker turned off for the following 2 hours in order to obtain a phase and temperature equilibrium. After then, 1.0 mL of the overhead gas sample in each vial or flask was extracted using a gas-tight sampling syringe for analyzing the target compound concentration. Notably, the sampling period was kept as short as possible to prevent any possible disturbance of the gas-liquid equilibrium (Staudinger and Roberts, 1996; Cheng *et al.*, 2004). For ensuring the effectiveness of

pasteurization, the chromatogram of the headspace gas sample was also checked if there was any by-product peak except the target VOC.

Total organic carbon (TOC) contents in the collected wastewater samples were measured by a TOC analyzer (Model 700, O. I. Analytical, USA). Suspended solids in the activated sludge liquors were determined by the traditional gravimetric method. For obtaining C_g, each gas sample was analyzed by a gas chromatography (GC-14B, Shimadzu, Japan) equipped with a flame ionization detector (GC-FID). A 30 m x 0.53 mm ID x 5.0 μm film thickness capillary column (AT-1, Alltech, USA) was used in the GC-FID. K'_H for each compound in each liquid was then obtained from eq 9. Statistical analysis was then performed to obtain the mean and standard deviation (SD) of the estimated K'_H. All statistical analyses were carried out with the software SigmaPlot (SPSS, USA) and Microsoft Excel.

3 RESULTS AND DISCUSSION

3.1 K'_H in wastewater and activated sludge mixed liquor

Using the SET method, experimental K'_H data for isopropanol, acetone, toluene and p-xylene in mixed liquor and the synthetic wastewater at 298 K are shown in Figure 1. K'_H corresponding to MLSS = 0 was for compounds partitioning between air and DI water, i.e., $K'_H = K_H$. The maximum MLSS was maintained at around 40,000 mg/L.

K'_H for all the test compounds in the mixed liquor have larger standard deviations than those in the wastewater. These deviations might be attributed to the greater variations of the structure and chemical compositions of the activated sludge biomass than the wastewater. Sludge age might be responsible for the greater variations.

For all the tested hydrophilic compounds, K'_H increased with an increasing of MLSS at the experimental temperature of 298 K and in the MLSS range of 0-40,000 mg/L. At a MLSS of around 40,000 mg/L, K'_H increased up to 21 and 13 % for isopropanol and acetone, respectively, compared with those in DI water. The increase corresponds to a decrease in solubility of the hydrophilic compound in the mixed liquor. Apparently, the hydrophobic biomass in the mixed liquor accounts for the solubility decrease.

In general, biomass like activated sludge is surrounded with organic compounds in the mixed liquor. These extra-cellular polymeric substances (EPS) are composed mainly of proteins, carbohydrates and lipids (Liao *et al.*, 2000). These EPS are much hydrophobic than the low-molecular alcohols and acetone. As the biomass concentration increases, the decrease of the bulk water volumetric fraction decreased the solubility and increases the K'_H of these hydrophilic compounds in the mixed liquors as shown in Figs. 1(a)-1(b).

On the other hand, K'_H decreased with an increase of MLSS for hydrophobic toluene and p-xylene as shown in Figure 1(c). The presence of biomass increased the partition of these compounds to the mixed liquor. At 298 K and a MLSS of 40,000 mg/L, it was observed that the K'_H decreased up to 69 and 86 % for toluene and p-xylene, respectively, as compared with those in DI water. All K'_H decreased significantly with increasing biomass concentration. Compared with DI water, the biomass in the mixed liquors would absorb or adsorb more hydrophobic compounds and increase the apparent solubility of these compounds (Wang *et al.*, 1993). However, K'_H/K_H of toluene in mixed liquors with MLSS = 35,000 mg/L are around 0.41 and 0.52 for unwashed (this work) and DI-washed biomass (Barton *et al.*, 2003), respectively. Higher K'_H/K_H might result from the partial removal of hydrophobic EPS from the biomass.

Somewhat different phenomena were observed for the solubility of organic compounds in biomass-free wastewater with some dissolved organics. As shown in Figure 1, K'_H for all tested compounds decreased with increasing organic content in the wastewater. K'_H of all the test compounds in the wastewater was only 1 to 11% smaller than those in DI water.

The above results indicate that a medium to high concentration of activated sludge can help in enhancing the water solubility of hydrophobic compounds such as benzene, toluene and xylenes (BTX). This solubility increase is essential to the increase in the removal of such compounds from waste air streams that are injected into the activated basin. On the other hand, the solubility increase attributed to the dissolved organics in wastewaters may be negligible as compared with that to the activated sludge biomass.

3.2 Verification of the K'_H model

By referring to eq 7 and with 0 suspended solid concentration ($S_S = 0$) or 0 dissolved organic concentration ($S_d = 0$), K'_H is either related to S_d or S_S by the following equations:

$$K'_H = K_H \frac{1}{1 + K_P S_S} \tag{10}$$

$$K'_H = K_H \frac{1}{1 + K_{OC} S_d} \tag{11}$$

Equation 11 has been reported to describe the variation of K'_H of VOCs to S_d in wastewater (David *et al.*, 2000). In this study, K_{OC} and K_P were estimated from regressions of the experimental data by eqs 11 and 12, respectively, by the software. Data of experimental K_H and calculated K_{OC} and K_P were listed in Table 1. For ensuring the significance of independency of K'_H with K_H on TOC at the tested temperature, the ANOVA was introduced for testing the independency. Result indicated the K'_H was 99% significant than K'_H in the TOC range. The regressed lines were plotted in Figure 1 for all species.

Table 1. Experimental K_H, K_P and K_{OC} of target VOCs at 298K

Compound	Log K_{OW} [a]	K_H		$K_P \times 10^6$ [e]		$K_{OC} \times 10^6$ [f]	
		This work [b]	Literature	(L/mg)	R^2	(L/mg)	R^2
Isopropanol	0.05	$(3.101 \pm 0.013) \times 10^{-4}$	3.23×10^{-4} [c]	-4.26	0.765	11.3	0.832
Acetone	-0.24	$(1.408 \pm 0.016) \times 10^{-3}$	1.59×10^{-4} [c]	-2.66	0.844	17.8	0.806
Toluene	2.73	0.272 ± 0.004	2.24×10^{-1} [d]	46.7	0.959	139.3	0.884
p-Xylene	3.15	0.263 ± 0.005	2.32×10^{-1} [d]	82.9	0.957	191.8	0.895

[a] Recommended value (Sangster, 1989).
[b] Results from data of 9 replicates with standard deviation.
[c] Headspace and aqueous concentration analysis data (Snider and Dawson, 1985).
[d] Experimental value by equilibrium partitioning in closed system (EPICS) technique (Dewulf *et al.*, 1995).
[e] Regressed result of eq 10 with known experimental K_H.
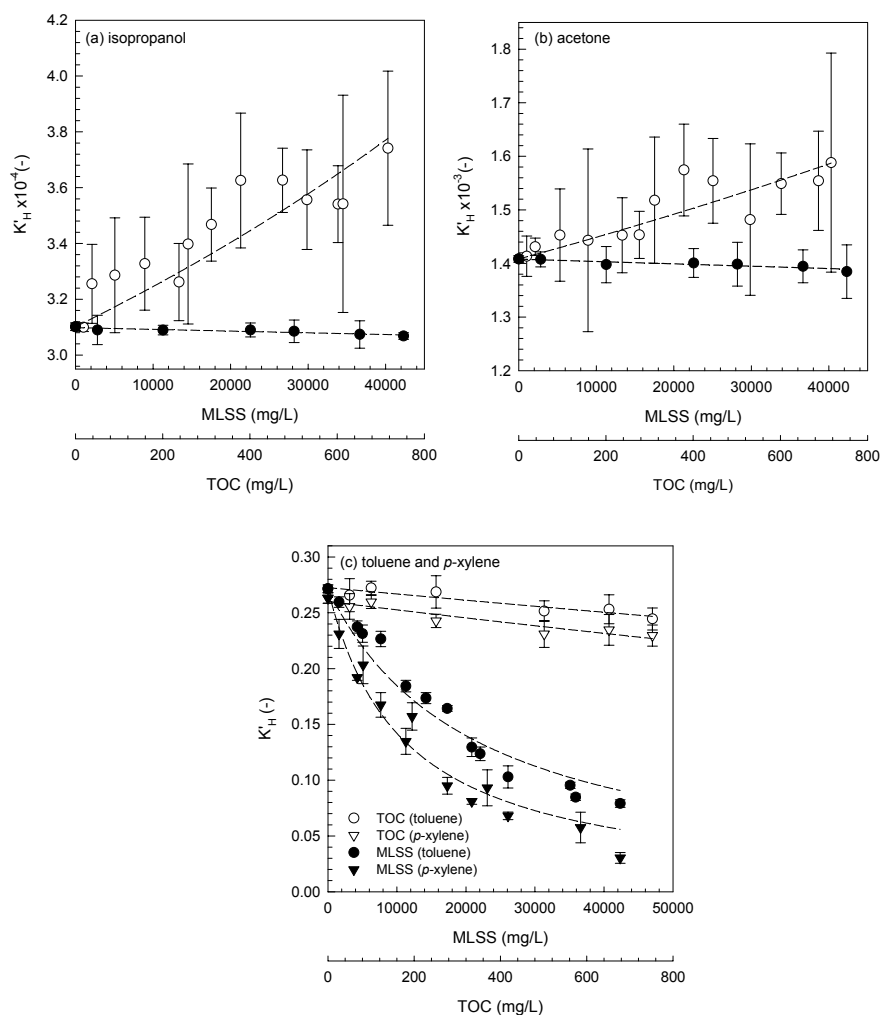[f] Regressed from eq 11 with known experimental K_H.

Figure 1. Variations of K'_H with MLSS and TOC concentrations in wastewater samples at 298 K for (a) isopropanol; (b) acetone; (c) toluene and *p*-xylene.

4 REFERENCES

Barton, J.W., Vodraska, C.D., Flanary, S.A. and Davison, B.H. (2003) Partitioning of BTEX constituents and chloroorganics in high-biomass systems. *Environ. Prog.* 22: 95-102.

Burgess, J.E., Parsons, S.A. and Stuetz, R.M. (2001) Developments in odour control and waste gas treatment biotechnology: a review. *Biotechnol. Adv.* 19: 35-63.

Cheng, W.-H., Chou, M.-S., Perng, C.-H. and Chu, F.-S. (2004) Determining the equilibrium partitioning coefficients of volatile organic compounds at an air-water interface. *Chemosphere.* 54: 935-942.

David, M.D., Fendinger, N.J. and Hand, V.C. (2000) Determination of Henry's law constants for organosilicones in acutal and simulated wastewater. *Environ. Sci. Technol.* 34: 4554-4559.

Davison, B.H., Barton, J.W., Klasson, K.T. and Francisco, A.B. (2000) Influence of high biomass concentrations on alkane solubilites. *Biotechnol. Bioeng.* 68: 279-284.

Dewulf, J., Drijvers, D. and van Langenhove, H. (1995) Measurement of Henry's law constant as function of temperature and salinity for the low temperature range. *Atmos. Environ.* 29: 323-331.

Dobbs, R.A., Shan, Y., Wang, L. and Govind, R. (1995) Sorption on wastewater solids: elimination of biological activity. *Water Environ. Res.* 67: 327-329.

Dobbs, R.A., Wang, L. and Govind, R. (1989) Sorption of toxic organic compounds on wastewater solids: correlation with fundamental properties. *Environ. Sci. Technol.* 23: 1092-1097.

Goss, K.-U. and Schwarzenbach, R.P. (1998) Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. *Environ. Sci. Technol.* 32: 2025-2032.

Grady, C.P.L., Jr., Magbanua, B.S., Jr., Brau, S. and Sanders, R.W., II (1997) A simple technique for estimating the contribution of abiotic mechanisms to the removal of synthetic organic chemicals by completely mixed activated sludge. *Water Environ. Res.* 69: 1232-1237.

Grathwohl, P. (1990) Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations. *Environ. Sci. Technol.* 24: 1687-1693.

Haas, C.N. and Kaplan, B.M. (1985) Toluene-humic acid association equilibria: isopiestic measurements. *Environ. Sci. Technol.* 19: 643-645.

Jin, B., Wilen, B.-M. and Lant, P. (2003) Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge. *Chem. Eng. J.* 98: 115-126.

Liao, B.Q., Allen, D.G., Droppo, I.G., Leppard, G.G. and Liss, S.N. (2000) Bound water content of activated sludge and its relationship to solids retention time, floc structure, and surface properties. *Water Environ. Res.* 72: 722-730.

Mackay, D. and Shiu, W.Y. (1981) Critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data.* 10: 1175-1199.

Moretti, C.J. and Neufeld, R.D. (1989) PAH partitioning mechanisms with activated sludge. *Water Res.* 23: 93-102.

Overcamp, T.J., Chang, H. and Grady, C.P.L., Jr. (1993) An integrated theory for suspended-growth bioscrubbers. *J. Air Waste Manage. Assoc.* 43: 753-759.

Sangster, J. (1989) Octanol-water partition coefficients of simple organic compounds. *J. Phys. Chem. Ref. Data.* 18: 1111-1229.

Smith, J.R., Neuhauser, E.F., Middleton, A.C., Cunningham, J.J., Weightman, R.L. and Linz, D.G. (1993) Treatment of organically contaminated groundwaters in municipal activated sludge systems. *Water Environ. Res.* 65: 804-818.

Snider, J.R. and Dawson, G.A. (1985) Tropospheric light alcohols, carbonyls, and acetonitrile: concentrations in the southwestern united states and Henry's law data. *J. Geophys. Res.* 90: 3797-3805.

Staudinger, J. and Roberts, P.V. (1996) A critical review of Henry's law constants for environmental applications. *Crit. Rev. Environ. Sci. Technol.* 26: 205-297.

Tsezos, M. and Wang, X. (1991) Study on the kinetics of hazardous pollutants adsorption and desorption by biomass: mechanistic considerations. *J. Chem. Technol. Biotechnol.* 50: 507-521.

Wang, L., Govind, R. and Dobbs, R.A. (1993) Sorption of toxic organic compounds on wastewater solids: mechanism and modeling. *Environ. Sci. Technol.* 27: 152-158.

Wang, X. and Grady, C.P.L., Jr. (1995) Effects of biosorption and dissolution on the biodegration of di-n-butyl phthalate. *Water Environ. Res.* 67: 863-871.

Zigmontienė, A. and Baltrėnas, P. (2004) Biological purification of air polluted with volatile organic compounds by using active sludge recirculation. *Journal of Environmental Engineering and Landscape Management.* 12: 45-52.