Edinburgh Research Archive

Müller, B. and Heal, M. R. (2001) The Henry's law coefficient for 2-nitrophenol in the temperature range 278-303 K, *Chemosphere* **45,** 309-314

The Henry's law coefficient of 2-nitrophenol over the temperature range 278–303 K

B. Müller and M. R. Heal,

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Abstract

Although 2-nitrophenol has been identified as an important environmental chemical there is scarcity in the literature regarding the temperature dependence of its Henry's law coefficient, H. Here a bubble purge method was used to measure H for 2-nitrophenol over the temperature range 278–303 K. A novel approach in the data treatment allowed correction of the data for non-equilibrium partitioning in the apparatus to obtain the true equilibrium H value. The experimentally derived temperature-dependent expression for H of 2-nitrophenol is $\ln H$ (M atm^{-1})=(6290/T (K))-16.6. The standard enthalpy and entropy of gas-to-liquid transfer for 2-nitrophenol in aqueous solution are -52.3 ± 8.1 kJmol^{-1} and -138 ± 28 Jmol^{-1} K^{-1}, respectively. (Errors are 95% confidence intervals.)

Author Keywords: 2-Nitrophenol; Gas-to-liquid partitioning; Bubble column

1. Introduction

The Henry's law coefficient, H, is a fundamental physical property that relates the concentration of a solute i in a dilute aqueous solution, *[i]aq*, to its concentration in the gas phase at equilibrium. Knowledge of gas–liquid partitioning not only predicts the concentration ratio at equilibrium but can also be used in deriving the direction and rate of transfer for systems evolving towards equilibrium. Such data are needed for modelling the environmental fate of pollutants as well as for the development of wastewater treatment strategies.

Phenols and nitrated phenols have become the focus of research following the recognition of their toxicity, even at trace levels. These compounds have been identified in air in the ngm^{-3} range and from levels of μgl^{-1} up to the mgl^{-1} range in rain and fog water (Leuenberger and Leuenberger; Herterich and Herrmann, 1990; Levsen et al., 1990; Richartz et al., 1990; Grosjean, 1991; Tremp et al., 1993; L and L), which makes them one of the most abundant classes of organic compounds in rainwater. This is of consequence for drinking water supplies and for the protection of aqueous organisms (Hart et al., 1993, and references therein). Environmental concern has also arisen from the phytotoxic properties of the nitrophenols and it has been suggested that they may be one factor for the observed forest decline in Europe and northern America (Rippen et al., 1987).

Although the importance of phenols has been recognised, experimental data on their Henry's law coefficient are scarce. Only Tremp et al. (1993) have determined the

Henry's law coefficient of various phenols and nitrophenols experimentally. Leuenberger et al. (1985) have presented a compilation of Henry's law coefficients of a number of phenols based on literature vapour pressure and solubility data. Lüttke and Levsen (1997) have studied phase partitioning of phenol and nitrophenols, but their observed value for 2-nitrophenol is about six times higher than the temperature-corrected value calculated from aqueous solubility and vapour pressure. It has been suggested that organic compounds can be enriched in small droplets in excess of that predicted by Henry's law due to additional adsorption at the air–water interface. However, different models used to describe this adsorption behaviour and based mainly on the octanol–water partitioning coefficient and/or the solubility fail to provide a satisfactory explanation in the case of 2-nitrophenol. More data regarding the physical properties of 2-nitrophenol are needed to interpret these findings satisfactorily. Other reported Henry's law coefficients of 2-nitrophenol have been mainly estimated from vapour pressure and solubility (Rippen et al., 1987; Schwarzenbach et al., 1988; Staudinger and Roberts, 1996) or limiting activity coefficients (Benes and Dohnal, 1999) and are limited to a particular temperature only. Since H is usually a strong function of temperature, it is important to know accurately the temperature dependence of H over an environmentally relevant temperature range.

Using a bubble purge technique the Henry's law coefficient of 2-nitrophenol is measured for the first time over an extended ambient temperature range of 278–303 K. Data analysis has been further developed to correct for potential non-attainment of equilibrium in the bubble column in order to derive the true equilibrium Henry's law coefficient.

2. Experimental

The design of the bubble column apparatus was similar to that of Mackay et al. (1979) (Fig. 1). Helium gas (BOC) was bubbled through the aqueous solution containing 2-nitrophenol which was stripped from the solution into the gas phase. The Henry's law coefficient was calculated from the rate of decrease in aqueous concentration.
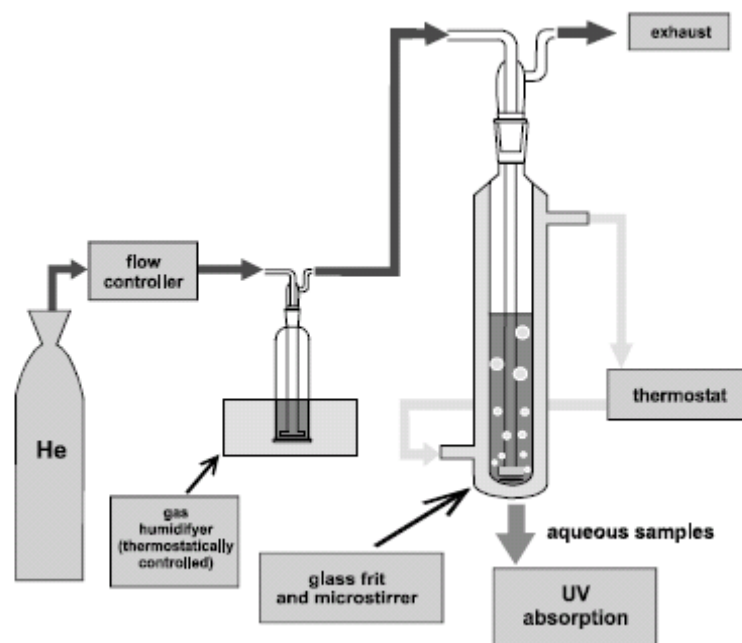
Fig. 1. The bubble column apparatus.

The Pyrex glass bubble column was 51 cm high with an internal diameter of 2.4 cm. Gas was introduced into the bottom of the column through a sintered glass disk (Pyrex 2, 40–100 μm). The liquid temperature was kept constant by a coolant flowing through the jacket surrounding the bubble column. Experiments were conducted at 5 K intervals between 278 and 303 K. A powerful magnetic micro-stirrer ensured vigorous mixing of the liquid in the bubble column; random tests confirmed a uniform liquid concentration over the whole column height. The gas flow was controlled by calibrated mass flow controllers (Tylan, FC 280 SA) and varied between 100 and 1000 cm3 min^{-1} (STP). Volumetric gas flows were corrected to prevailing temperature and pressure. The gas was humidified prior to entering the bubble column, to prevent water evaporation from the purging column, by passing the flow through a vessel containing deionised water (10 MΩ cm, Whatman, Analyst 25). This vessel was immersed in a water bath at the same temperature as the bubble column. No change of liquid volume was noted, even after purging for several hours.

Dilute aqueous solutions (10^{-5}–10^{-4} moll^{-1}) of 2-nitrophenol (BDH) were prepared in 10 MΩ cm deionised water. The concentration in the liquid phase was measured using UV absorption spectroscopy at 278 nm (Shimadzu, UV 160A double beam spectrometer). Liquid samples were taken at intervals of 5–25 min during an experimental run (from 30 min to 2 h), depending on gas flow rate and liquid volume. The gas flow was temporarily stopped for the duration of each absorbance measurement. Care was taken to ensure loss-free transfer of each aliquot. No diminution of volume was detected. At least four absorption measurements were taken for each of about eight different liquid depths in the bubble column for each temperature.

3. Data analysis

The mass balance for the stripping process is

$$-\frac{\mathrm{d}n^{\mathrm{aq}}}{\mathrm{d}t} = +\frac{\mathrm{d}n^{\mathrm{gas}}}{\mathrm{d}t},$$

(1)

where naq and ngas are the molar amounts of species in the aqueous and gas phases, respectively. Substitution for naq=Vaq[i]aq and ngas=F[i]gast (F is the gas flow rate) and integration gives

$$\ln\left(\frac{[i]_0^{\mathrm{aq}}}{[i]_t^{\mathrm{aq}}}\right) = \frac{F}{H^{\mathrm{non\text{-}equi}}RTV^{\mathrm{aq}}}t,$$

(2)

where Hnon-equi represents the apparent Henry's law coefficients as the gas exits the bubble column. Eq. (2) is commonly used in bubble purge experiments to derive Henry's law coefficient with the implicit assumption that equilibrium has been established between gas and liquid in the bubble column.

Mackay et al. (1979) have derived an expression for the mass transfer rate for the general case when the partial pressure in the gas at the exit, pnon-equi, is assumed not to be in equilibrium with the liquid. The derivation assumes that the solution is well mixed (i.e. [i]aq is vertically constant) and that the solute partial pressure in the gas rises by dpi during exposure to a bubble interfacial area increment of dAr. The resulting expression for the non-equilibrium partial pressure at the exit of the column is (Mackay et al. (1979))

$$p_i^{\mathrm{non\text{-}equi}} = \frac{[i]^{\mathrm{aq}}}{H^{\mathrm{equi}}}\left(1 - \exp\left(-\frac{K_{\mathrm{OL}}H^{\mathrm{equi}}RTA_{\mathrm{r}}}{F}\right)\right),$$

(3)

where KOL is a liquid phase mass transfer coefficient and Ar is the total interfacial area between gas and liquid in the column. The non-equilibrium partial pressure can be written in terms of the measured, non-equilibrium, Henry's law coefficient through

$$p_i^{\mathrm{non\text{-}equi}} = \frac{[i]^{\mathrm{aq}}}{H^{\mathrm{non\text{-}equi}}}.$$

(4)

Therefore, from (3) and (4) it follows that the relationship between the measured Henry's law coefficient and the true equilibrium value, Hequi, is

$$H^{\text{non-equi}} = \frac{H^{\text{equi}}}{\left(1 - \exp\left(-\frac{K_{OL}H^{\text{equi}}RTA_r}{F}\right)\right)}.$$

(5)

Since the interfacial area between gas and liquid is proportional to liquid depth, z,

$$A_r = k_z z,$$

(6)

where kz is a constant, the expression that links Hnon-equi,Hequi and z is

$$H^{\text{non-equi}} = \frac{H^{\text{equi}}}{\left(1 - \exp\left(-\frac{K_{OL}k_z RTH^{\text{equi}}z}{F}\right)\right)}.$$

(7)

Substitution from Eq. (2) for the experimentally derived Hnon-equi value and noting that Vaq=Srz (where Sr is the cross-sectional area of the bubble column) yields finally,

$$\frac{\ln\left(\frac{[i]_0^{\text{aq}}}{[i]_t^{\text{aq}}}\right)}{t} = \frac{B}{H^{\text{equi}}}\frac{(1 - \exp(-AH^{\text{equi}}z))}{z}.$$

(8)

The parameters A(=KOLkzRT/F) and B(=F/(RTSr)) are short-hand notation for collections of constants. Thus, when the change in aqueous phase concentration with time is plotted against liquid depth, z, the equilibrium value of Henry's law, Hequi, is obtained by fitting Eq. (8) to the data using Hequi and A as adjustable parameters. All values of B are known. It is important to note that in order to apply Eq. (8), the measured values of Hnon-equi must be obtained from experiments in which the gas flow, F, is kept constant.

4. Results and discussion

Fig. 2 shows plots of ln([i]0aq/[i]taq)/t as a function of liquid depth for 2-nitrophenol for six temperatures between 278 and 303 K. The true equilibrium Henry's law coefficients, Hequi, for 2-nitrophenol at each temperature were derived from the fit of Eq. (8) to each set of data and are given in Table 1. The table also shows the corresponding value of Henry's law coefficient, Hnon-equi, obtained from the

(incorrect) direct application of Eq. (2) to the data (which implicitly assumes that equilibrium is attained in the bubble column). These latter values are, of course, not uniquely defined since they are a function of column depth, which Eq. (2) does not take into account. Whilst agreement between the two sets of data is good at higher temperatures (lower values of H) there is significant systematic discrepancy at the lowest temperatures measured. The discrepancy demonstrates the importance of undertaking the correction procedure outlined above for non-attainment of equilibrium partitioning in the apparatus when values of H exceed a few 100 Matm−1.
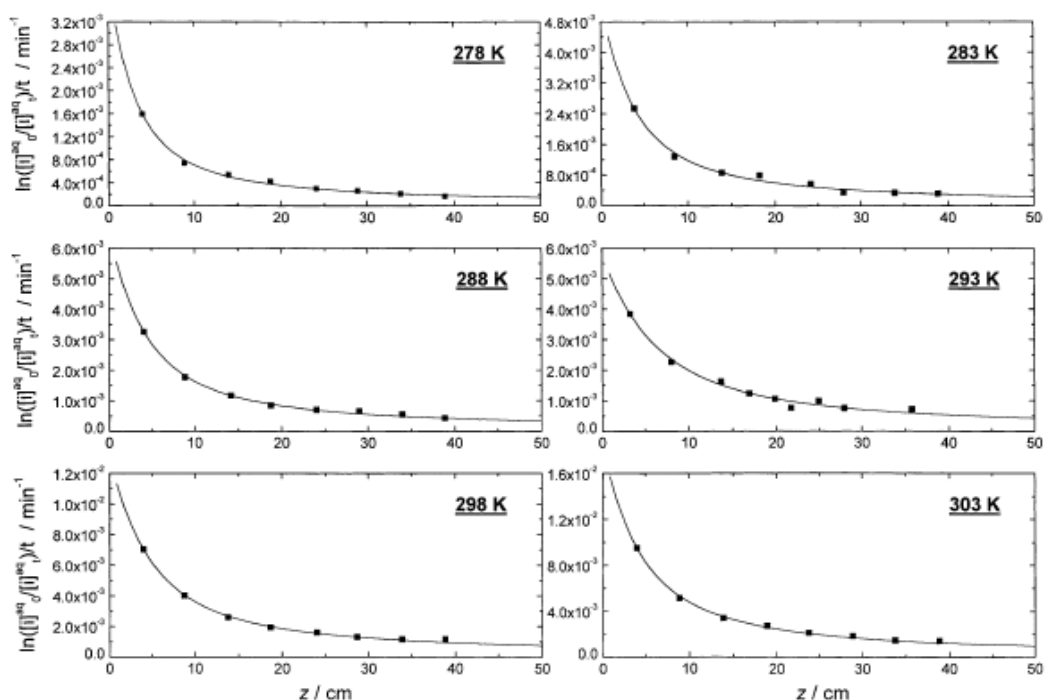

Fig. 2. Plots of ln([i]0aq/[i]taq)/t vs. liquid depth z for six temperatures. The solid lines are fits of Eq. (8) to the data with A and Hequi as adjustable parameters. The value of parameter B is known.

T (K)	$H^{\text{non-equi}}$ (M atm^{-1})	H^{equi} (M atm^{-1})
278	370 ± 13	419 ± 33
283	229 ± 12	248 ± 29
288	169 ± 5	178 ± 10
293	158 ± 19	142 ± 14
298	80 ± 5	81 ± 4
303	60 ± 2	63 ± 3

Table 1. Comparison between Henry's law coefficients obtained from (2) and (8)

The Henry's law coefficients for 2-nitrophenol obtained in this work are compared with values previously reported in the literature in Fig. 3. The agreement between this work and literature data is generally good. The main exception is at T = 278 K, where there is a large difference between the experimental value (H=1359 Matm−1) and the calculated value (H=197 Matm−1) of Lüttke and Levsen (1997). These authors could not provide a satisfactory explanation for their observed enrichment of 2-nitrophenol in the liquid phase. Since the work carried out here represents the first systematic

measurement of the Henry's law coefficient of 2-nitrophenol over the ambient temperature range, it appears that the value of H=1359 Matm−1 at 278 K reported by Lüttke and Levsen (1997) is a considerable overestimate.
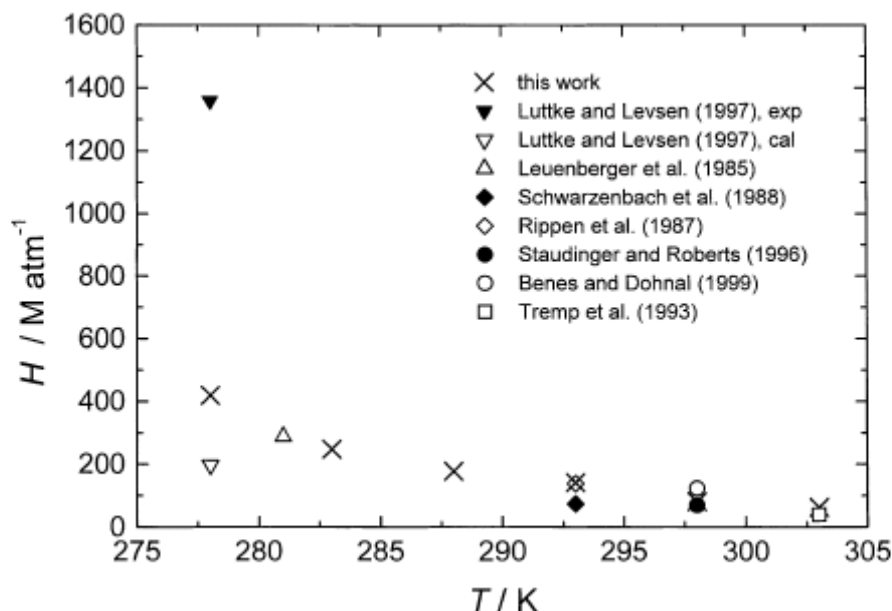

Fig. 3. Comparison between Henry's law coefficients of 2-nitrophenol measured in this work and values reported in the literature. For clarity, error bars on values from this work are omitted.

The Henry's law coefficient can be related to the free energy change of the process igas→iaq through (Kames and Schurath, 1992)

$$H = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right),$$

(9)

where ΔG° is the free energy of gas to liquid transfer in solution, and ΔH° is the enthalpy and ΔS° the entropy of this transfer. The enthalpy and entropy for gas-to-liquid transfer of 2-nitrophenol are determined by plotting lnH vs. 1/T (Fig. 4), if these quantities are assumed invariant over the considered temperature interval. The good linear fit confirms that this is the case. The gradient and intercept of the fitted line yield values for ΔH° and ΔS° of −52.3±8.1 kJmol−1 and −138±28 Jmol−1 K−1, respectively. (Errors are 95% confidence intervals from the fit to the data in Fig. 4.) On the basis of the measured temperature dependence the following expression is therefore recommended for the Henry's law coefficient of 2-nitrophenol between 278 and 303 K,

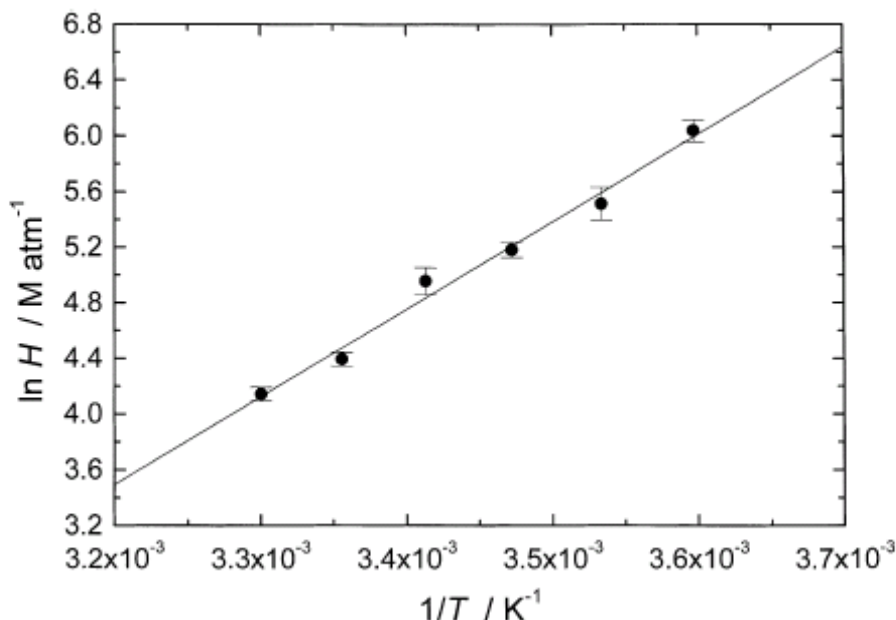$$\ln H \ (\text{M atm}^{-1}) = \frac{6290}{T \ (K)} - 16.6.$$

(10)

Fig. 4. Plot of lnH vs. 1/T for 2-nitrophenol. Error bars are 95% confidence intervals calculated from the statistical fits shown in Fig. 2.

As shown in Fig. 4, this expression reproduces all but one of the six measured H values (to within the 95% confidence intervals given in Table 1). It should also be noted that uncertainty in the measured values may be slightly larger than quoted in the table due to other sources of measurement error.

The Henry's law coefficient for 2-nitrophenol predicts an equilibrium partitioning of 1% into the aqueous phase (at 280 K) for a typical tropospheric cloud water volume fraction of 10^{-6}. Although the H value is comparatively small, 2-nitrophenol is a reactive species and reaction with OH and NO3 radicals in the aqueous phase will considerably enhance the removal of 2-nitrophenol from the troposphere via the heterogeneous phase. Using typical tropospheric OH and NO3 concentrations and published kinetic data (Atkinson et al., 1992), the half-life of 2-nitrophenol due to gas phase reactions is of the order of 12–24 h. However, preliminary modelling studies using a simplified kinetic scheme incorporating gas phase removal of 2-nitrophenol, and parallel gas-to-liquid uptake with liquid phase reactions and typical values of liquid phase OH concentrations (Lelieveld and Crutzen, 1990; Herrmann et al., 1999) indicate that the rate of partitioning and loss of 2-nitrophenol via the tropospheric aqueous phase is comparable with, or greater than, rate of loss in the gas phase.

References

Atkinson, R., Aschmann, S.M. and Arey, J., 1992. Reactions of OH and NO3 radicals with phenol cresols and 2- nitrophenol at 296 K ± 2 K. Environ. Sci. Technol. 26, pp. 1397–1403.

Benes, M. and Dohnal, V., 1999. Limiting activity coefficients of some aromatic and aliphatic nitro compounds in water. J. Chem. Eng. Data 44, pp. 1097–1102.

Grosjean, D., 1991. Atmospheric fate of toxic aromatic compounds. Sci. Total Environ. 100, pp. 367–414.

Hart, K.M., Tremp, J., Molnar, E. and Giger, W., 1993. The occurrence and the fate of organic pollutants in the atmosphere. Water Air Soil Pollut. 68, pp. 91–112.

Herrmann, H., Ervens, B., Nowacki, P., Wolke, R. and Zellner, R., 1999. A chemical aqueous phase radical mechanism for tropospheric chemistry. Chemosphere 38, pp. 1223–1232.

Herterich, R. and Herrmann, R., 1990. Comparing the distribution of nitrated phenols in the atmosphere of 2 German hill sites. Environ. Technol. 11, pp. 961–972.

Kames, J. and Schurath, U., 1992. Alkyl nitrates and bifunctional nitrates of atmospheric interest: Henry's law constants and their temperature dependencies. J. Atmos. Chem. 15, pp. 79–95.

Lelieveld, J. and Crutzen, P.J., 1990. Influences of cloud photochemical processes on tropospheric ozone. Nature 343, pp. 227–233.

Leuenberger, C., Czuczwa, J., Tremp, J. and Giger, W., 1988. Nitrated phenols in rain: atmospheric occurrence of phytotoxic pollutants. Chemosphere 17, pp. 511–515.

Leuenberger, C., Ligocki, M.P. and Pankow, J.F., 1985. Trace organic compounds in rain: 4. Identities, concentrations, and scavenging mechanisms for phenols in urban air and rain. Environ. Sci. Technol. 19, pp. 1053–1058.

Levsen, K., Behnert, S., Prieß, B., Svoboda, M., Winkeler, H.D. and Zietlow, J., 1990. Organic compounds in precipitation. Chemosphere 21, pp. 1037–1061.

Lüttke, J. and Levsen, K., 1997. Phase partitioning of phenol and nitrophenols in clouds. Atmos. Environ. 31, pp. 2649–2655.
Lüttke, J., Levsen, K., Acker, K., Wieprecht, W. and Möller, D., 1999. Phenols and nitrated phenols in clouds at Mount Brocken. Int. J. Environ. Anal. Chem. 74, pp. 69–89.

Lüttke, J., Scheer, V., Levsen, K., Wünsch, G., Cape, J.N., Hargreaves, K.J., Storeton-West, R.L., Acker, K., Wieprecht, W. and Jones, B., 1997. Occurrence and formation of nitrated phenols in and out of cloud. Atmos. Environ. 31, pp. 2637–2648.

Mackay, D., Shiu, W.Y. and Sutherland, R.P., 1979. Determination of air–water Henry's law constants for hydrophobic pollutants. Environ. Sci. Technol. 13, pp. 333–337.

Richartz, H., Reischl, A., Trautner, F. and Hutzinger, O., 1990. Nitrated phenols in fog. Atmos. Environ. 24, pp. 3067–3071.

Rippen, G., Zietz, E., Frank, R., Knacker, T. and Klöpffer, W., 1987. Do airborne nitrophenols contribute to forest decline?. Environ. Technol. Lett. 8, pp. 475–482.

Schwarzenbach, R.P., Stierli, R., Folsom, B.R. and Zeyer, J., 1988. Compound properties relevant for assessing the environmental partitioning of nitrophenols. Environ. Sci. Technol. 22, pp. 83–92.

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

Tremp, J., Mattrel, P., Fingler, S. and Giger, W., 1993. Phenols and nitrophenols as tropospheric pollutants – emissions from automobile exhausts and phase-transfer in the atmosphere. Water Air Soil Pollut. 68, pp. 113–123.