Column study of the influence of air humidity on the retention of hydrocarbons on soil

Francisco García-Herruzo *, José M. Rodríguez-Maroto,
Rafael A. García-Delgado, César Gómez-Lahoz, Carlos Vereda-Alonso

Departmento de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga, 29071-Málaga, Spain

Abstract

Inverse gas chromatography (IGC) is used for the analysis of the influence of air relative humidity on the retention of hexane, benzene, toluene and *p*-xylene in a sandy soil under experimental conditions similar to those typical of soil vapor extraction (SVE). The advantages of IGC over other techniques, are (a) an efficient use of lab resources, (b) a high sensitivity to low partitioning coefficients and (c) a closer reproduction of field conditions. In our procedure, experiments with only two samples of different mass are necessary to establish if linear isotherms can be used to describe the retention of the contaminants. This approach gives information necessary for analyzing the feasibility and design of remediation technologies with a laboratory effort significantly smaller than the adsorption/desorption cycle for isotherm determination. The retention coefficients of the contaminants decrease as humidity increases in a similar fashion for all of them, probably because the reduction in the number of the adsorption sites available for the organic compounds due to the presence of water is quite similar for all the contaminants studied. These retention coefficients may be related to those obtained for dry air conditions for all the contaminants through $(R-1)_{\text{RH\%}} = A(R-1)_{\text{dry air}}^{B}$, where the parameter B is found to remain approximately constant (0.90), while the parameter A decreases linearly with the relative moisture. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Understanding the retention of volatile organic compounds (VOCs) onto soils is necessary for a correct performance of risk assessment as well as for the feasibility studies of most of the in situ remediation technologies. Partition between the gaseous and immobile phases in the vadose zone is of special interest to soil vapor extraction (SVE) and thermal enhanced soil vapor extraction (EPA, 1997). The records of decision of the superfund program indicate that the use of SVE is increasing: it has grown from a 33% of the innovative techniques in 1982–1989 (EPA, 1991) to 46% in the 1982–1995 period (EPA, 1996).

Tools are necessary for a fast and economic evaluation of the sorption phenomena under conditions as similar as possible to those typical of SVE field applications. Soil columns can be used to obtain equilibrium information in several ways. For instance, Ruiz et al. (1998) studied the adsorption isotherms by adsorption-desorption cycles which required about 24 h to obtain one point of the equilibrium isotherm of one contaminant.

The use of inverse gas chromatography (IGC) for the study of adsorption phenomena is getting increasing

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* Corresponding author. Tel.: +34-952-131-915; fax: +34-952-132-000.
  E-mail address: Herruzo@uma.es (F. García-Herruzo).

attention. Basically, the technique is the same as the usual gas chromatography. Inverse means that the aim of the study is to measure the properties of the stationary phase and its interactions with a component of the gaseous phase rather than the chromatographic separation itself (Steinberg and Kreamer, 1993; Steinberg et al., 1996; von Meien et al., 1997).

The most important advantages of IGC for adsorption estimation in environmental applications are the following: (a) requires a small time to obtain the adsorption isotherm equations; (b) presents a very high sensitivity to small partition coefficients (which are likely to be found in materials such as sandy soils) and (c) is able to reproduce the dynamic conditions of field applications. Details of a mathematical model for establishing both linear and non-linear isotherms by IGC were presented by Rodríguez-Maroto et al. (1998). This kind of studies can also be used for the calculation of surface free energy of gaseous/solid and gaseous/liquid systems (Goss, 1997) through the evaluation of retention, which ultimately allows the estimation of a whole set of thermodynamic parameters.

Another interesting environmental application of IGC is the evaluation of the amount and location of non-aqueous phase liquids (NAPL) at contaminated sites (Whitley et al., 1999). In some cases, the gaseous stream is not circulated through the soil matrix. Instead, a soil sample is placed as a pellet in a cell with one (Yaşyerli et al., 1999) or more faces (Cabbar et al., 1994) open to a chamber and exposed to the circulating gas. Thus, there is no advective gas transport through the soil matrix. This allows the analysis of the partition coefficient and the effective diffusivity in the pores, relevant for the fate of pollutants in the vadose zone.

Here, we present a study of the influence of relative air humidity on the retention of several contaminants on soil. An important research effort has been made by several authors on this subject and a significant decrease of the adsorption capacity of soil with increasing relative humidity is reported (Chiou and Shoup, 1985; Chen and Wu, 1998). Our work shows how the use of IGC with dynamic conditions similar to SVE operation allows a fast determination of the adsorption isotherm. The results obtained are consistent with those obtained by other authors.

2. Experimental

The experimental system, which is shown in Fig. 1, consists of a stainless steel column of 37 cm length and 2.65 cm i.d. which contains the soil sample. There is also some auxiliary equipment to control the pressure drop, and therefore the volumetric flow, the air relative humidity and the column temperature.

The air humidity control consists of a series of gas washing bottles containing NaOH solutions. The desired air relative humidity is easily obtained by changing the NaOH concentration and the temperature, following the data of Liley et al. (1984). A CO_2 trap is necessary to preserve the first bottle from precipitate formation on the gas diffuser, which could cause changes in the pressure drop. Mists are prevented from reaching the soil column by means of a bed of glass spheres and Raschig rings of 3–5 mm placed in the gas flow path.

Contaminants are injected in the gaseous phase through a septum located at the column top end. A detection system (FID for the contaminants analyzed in this work) allows a continuous measure of the contaminant concentration in the gaseous stream at the column exit. The detector is installed in a gas chromatograph, Perkin–Elmer autosystem GC model. There are no rubber or plastic elements between the injector and the detector. Blanks performed in the system without soil showed that no sorption of the contaminants occurs.

Values for tortuosity and dispersivity are obtained from the injections of tracers as described in Rodríguez-Maroto et al. (1998). The main soil characteristics are shown in Table 1. Further details of soil properties can also be found in the previous paper. Soil column temperature is set at $20.0 \pm 0.1°C$ and a volumetric flow of 0.50 ml/s is used. Values of air relative humidity range from dry air (as obtained from a molecular sieve of 3 nm from Merck) to 80% at 20°C.

Before each series of experiments, the soil sample is dried at 60°C for at least 24 h. The stainless steel column is heated empty at 120°C, so that the soil sample is kept dry during the experimental setup ensemble. The baths are allowed to reach the desired temperatures, and the NaOH solution is prepared and titrated (except for the dry air experiments). 310 g of soil are introduced in the column and settled by vibration to 36.7 cm height. The column is then closed and, while still warm, connected to the installation and introduced in the thermostatic bath. Tightness is checked by pressurizing the system while immersed.

Each Dirac Pulse consists of the injection of 0.1 or 1.0 ml of gas on top of the column. The gas samples are in equilibrium with the contaminant as pure liquid at 20°C. Therefore, the plot of concentration versus time is the response curve. It will be assumed that equilibrium between the soil sample and air humidity has been reached when the response curves from two identical injections of contaminant, separated by 24 h are indistinguishable.

For comparison the results obtained from each injection are normalized so that the response curves are plotted as a normalized concentration of the contaminant in the air stream leaving the column, C, versus a dimensionless residence time, θ. The concentration is normalized by the division of each concentration value
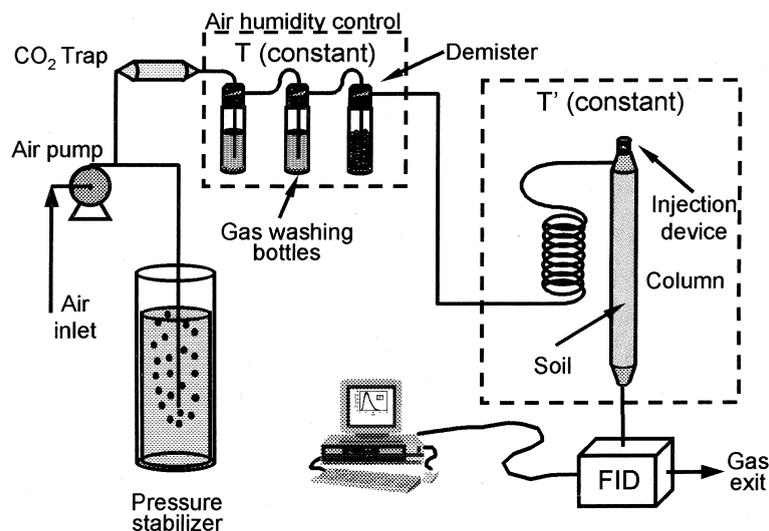
Fig. 1. Experimental setup.

Table 1
Some properties of the soil column

Dry column pneumatic permeability (cm^2 atm^{-1} s^{-1})	2760 ± 150
Soil bulk density, ρ_b (g cm^{-3})	1.57 ± 0.03
Soil density of solids (g cm^{-3})	2.61 ± 0.04
Soil porosity, v (vol./vol.)	0.41 ± 0.02
Tortuosity, as defined by Marsily (1986)	0.72 ± 0.02
Dispersivity (cm)	0.17 ± 0.02
Size distribution:	
Diameter (mm)	*Weight* (%)
>0.50	2.88
0.50–0.20	87.15
0.20–0.10	9.22
<0.10	0.75

by m/V_{void}, where m is the mass of the contaminant injected and V_{void} is the void volume of soil. θ represents the volume of air circulated through the column as number of pore volumes, once the contribution of the dead volumes to the residence time is corrected. Thus, the one-dimensional area below the response curve of any substance is equal to 1.

3. Results and discussion

An example of the influence of the air relative humidity can be observed in Fig. 2. It shows the experimental results obtained from the injection of benzene and p-xylene, for dry air and for a relative humidity of 80%, together with the model results (solid lines). In the figure only from 1/3 to 1/9 of the experimental data points are plotted to allow a better view of the model results.
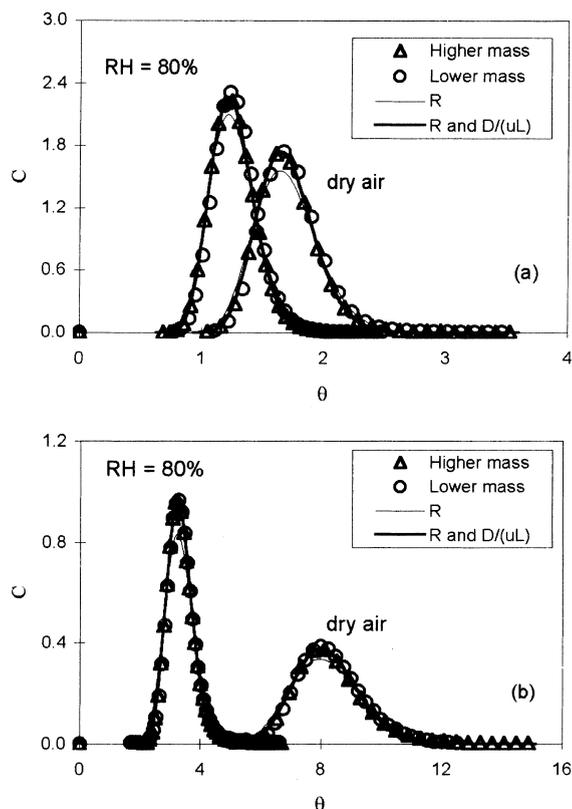
Fig. 2. Experimental and model results for different mass of benzene (a) and p-xylene (b).

In both cases, it can be observed that the experimental results after normalization are independent of the mass injected which indicates that all the phenomena

involved in the retention processes are linear with respect to the mass injected. This includes the adsorption isotherm within the range of concentration values assayed (Jaekel et al., 1996; Rodríguez-Maroto et al., 1998).

Therefore, values for R (retention coefficient) and $D/(uL)$ (dispersion dimensionless number) are obtained by fitting the analytical solution for the response curve to the Dirac pulse and to the experimental results. If C_s is the contaminant concentration (mass/mass) of the solid phase and C_v is the concentration of the gaseous phase (mass/vol.), for a linear isotherm, then the retention coefficient is defined by

$$C_s = KC_v, \qquad R = 1 + \frac{\rho_b}{v}K,$$

and the one-dimensional advective-dispersive transport equation, assuming homogeneous porous medium, local equilibrium and constant gas density, is given by

$$R\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial Z} = \left(\frac{D}{uL}\right)\frac{\partial^2 C}{\partial Z^2}, \quad \theta = \frac{tQ}{V_{\text{void}}}, \ Z = \frac{z}{L},$$
$$C = \frac{C_v}{m/V_{\text{void}}},$$

where Q is the volumetric flow, t and z the temporal and space coordinates and L is the soil bed length. In order to check the local equilibrium hypothesis, some experiments were repeated at a volumetric flow of 0.25 ml/s. These yielded values of the retention coefficient which were within the experimental error of those performed at 0.50 ml/s.

Fig. 2 shows two solid lines for each Dirac pulse, that corresponds to the model results. The first one is obtained using R as the only regression parameter whereas the retention coefficient and the dispersion dimensionless number are used together as fitting parameters in the second case. Results are presented in Table 2.

As can be seen, moderate uncertainties in the effective dispersion coefficient do not affect significantly the value of the retention parameter. This means that, if the effective dispersion coefficient is unknown, then it can be obtained from the experimental results, together with the retention coefficient. The values for the retention coefficient are quite similar to those cases where the

dispersion phenomena were evaluated previously (Rodríguez-Maroto et al., 1998).

Thus, once the soil is equilibrated with the air moisture, the injection of only two samples of different mass of a contaminant are enough to establish whether a linear adsorption isotherm can be used for the range of concentrations used. The value of the retention coefficient (or the isotherm parameter) and the axial dispersion are obtained immediately and can be used for SVE design.

This method is used for the study of the influence of the air relative humidity on the retention of the four contaminants listed above. For all of them and all the moistures assayed, the isotherms are linear as deduced from the normalized response curves to injections of different mass. A summary of the results is presented in Fig. 3, where the retention coefficient is plotted against the relative humidity (RH). Each point in this figure corresponds to the mean value of the retention coefficient obtained from at least three injections. Deviations from the mean value are always below 10%, and typically are about 3%. This reproducibility is obtained for a series of experiments performed in a continuous period. If the column is emptied and all the installation procedure repeated and another series performed, then the deviations between the different series may increase to about 20%. Results obtained for different series are presented as different points in Fig. 3.

The same trend is observed for every contaminant studied: maximum retention for dry air and a sharp decrease of the value of R as the air moisture increases as is found in most soils (Yaşyerli et al., 1999). In all cases, the retention is smaller for the more volatile compounds.

A relationship, similar to the one observed by Steinberg and Kreamer (1993), can be established between the values of $(R-1)$ for all the contaminants at certain relative humidity contents and the corresponding values for dry air condition $(R-1)_{\text{dry}}$. This is shown in Fig. 4, where results for the different contaminants and air humidity contents are plotted against the retention of each contaminant under dry air conditions.

The relationship can be expressed by the following equation applicable to all the contaminants studied:

$$(R-1)_{\text{RH\%}} = A(R-1)_{\text{dry air}}^B.$$

Table 2
Values of the parameters obtained for the results presented in Fig. 2

Compound	Relative humidity (%)	Fitted parameter R		Fitted parameters R and $D/(uL)$	
		R	$D/(uL)$	R	$D/(uL)$
Benzene	80	1.24	0.012	1.24	0.0095
	Dry	1.67	0.012	1.67	0.0095
p-xylene	80	3.27	0.011	3.28	0.0080
	Dry	8.07	0.011	8.11	0.0085

This equation is consistent with the one proposed by Goss (1997), and reviewed and discussed in Goss and Schwarzenbach (1998). As can be deduced from the later paper, the parameter B can change slightly with the value of air humidity and for different families of com-
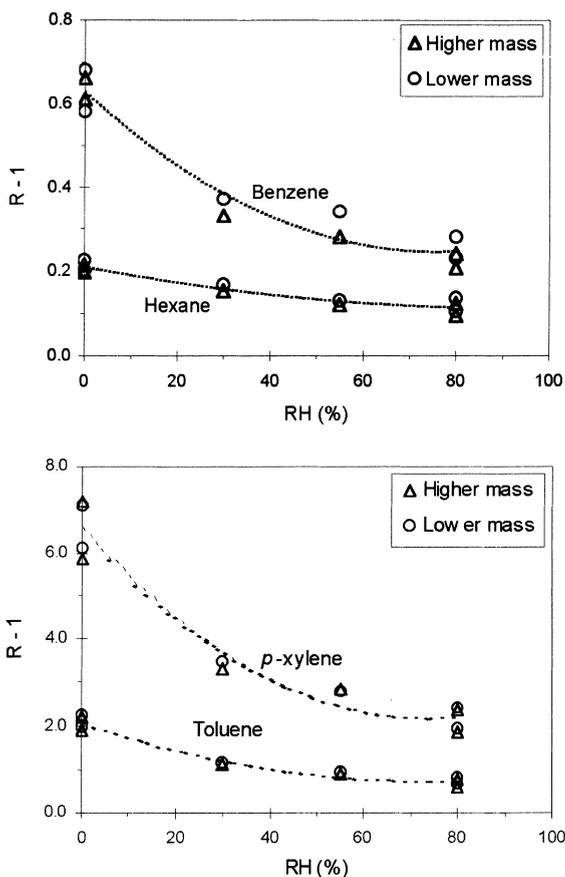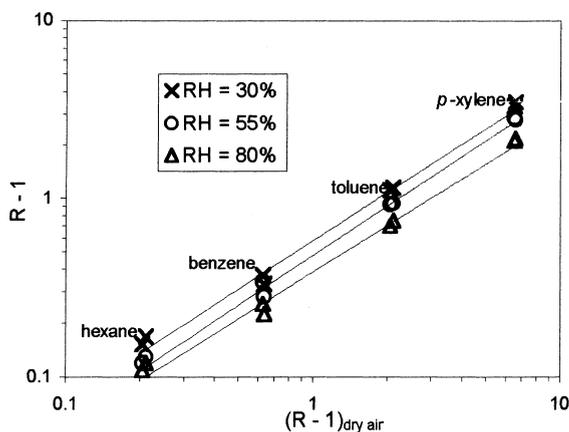
Table 3
Values of A and B for the results presented in Fig. 4

RH (%)	A	B	r^2
30	0.578	0.90	0.994
55	0.478	0.92	0.996
80	0.386	0.87	0.992

pounds. These variations are negligible in the correlation obtained for our results.

The values for A and B are shown in Table 3. The values of the parameter A indicate that higher retentions occur for all the contaminants as the relative humidity decreases. A linear relationship between the value of A and air humidity can be obtained

$$A = 0.692 - 3.84 \times 10^{-3}(\text{RH}\%) \quad (r^2 = 0.9994).$$

Of course, this relationship is only applicable to the intermediate values of air relative moisture. The retention for an extremely dry air would be underestimated ($A = 1$ for RH = 0%), and for very high humidity condensation and dissolution would probably become important.

On the other hand, values of the parameter B show that all the contaminants studied undergo a similar relative reduction of the retention coefficient when the air humidity increases. This indicates that there is a competitive adsorption between each contaminant and water: the reduction of the sorption sites available for the organic compounds, caused by the presence of water, is independent of the nature of the contaminant. These results are in agreement with those obtained by Steinberg et al. (1996) for TCE and benzene.

Thus, if the values of the retention coefficient for dry air conditions of any compound similar to the ones presented here are known, then the retention coefficients for other air humidity contents can be obtained using these correlations. Analogously if a retention coefficient is obtained experimentally for a relative air humidity different to those presented here, then the values for all the other compounds at this humidity may be estimated. Thus, the correlations obtained may be an important help in the study of the possible retention of complex contaminants such as gasoline.

Fig. 3. Summary of the experimental results.

Fig. 4. Comparison between the results at different humidity contents with dry air.

Acknowledgements

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