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Adsorption of Different VOC onto Soil Minerals from Gas Phase: Influence of Mineral, Type of VOC, and Air Humidity

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The adsorption of volatile organic compounds (VOC) onto soils plays an important role in the mobility of these kinds of contaminant through soils. It is therefore of interest to learn more about the mechanisms of interaction between VOC and soil particles. An experimental study has been carried out in order to determine the adsorption isotherms of volatile organic gases of different properties on soil minerals of different characteristics, working in a wide range of compound concentrations. The adsorption of seven organic compounds (*n*-hexane, *n*-heptane, *n*-octane, toluene, xylene, ethylbenzene, and methyl ethyl ketone) and of water vapor on sand, clay, and limestone has been analyzed. The influence of the presence of water on the adsorption of these compounds has also been analyzed, working at levels below the limit of applicability of Henry's law. The levels of relative air humidity used were 20 and 50%. The results show a big difference between the adsorption levels of the three soil minerals and a higher adsorption for polar compounds than for aliphatic and aromatic compounds. The water affects the VOC adsorption by decreasing the retention of these compounds to a greater extent for aromatic and aliphatic compounds than for the polar compound and by linearizing the isotherms. This reduction has been quantified by a simple exponential equation.

Introduction

The knowledge of the interactions between volatile organic compounds (VOC) and soils has been a matter of growing concern due to the increasing appearance of soils contaminated with these kinds of compounds.

The adsorption of volatile organic compounds onto soils plays an important role in the mobility of the contaminant through the soil as has been shown by different authors both experimentally (*1*−*4*) and theoretically (*5, 6*). The adsorption may also affect the removal of the compound from the soil when venting techniques are used for soil remediation (*7*).

The adsorption of organic compounds onto soils from aqueous solutions has been widely studied, and both linear (*8*−*11*) and nonlinear isotherms (*12*−*14*) have been found. The adsorption of organic gases onto soils in the presence of a significant amount of liquid water has also been studied, and this adsorption can be characterized by expressions based on the organic matter content of the soil or by lineal expressions such as Henry's law (*15, 16*).

Some works are also presented in the literature about the direct adsorption of organic gases on mineral surfaces with low organic matter content or in the absence of liquid water. Generally, a small number of compounds or soils have been used. At low VOC concentrations in the gas phase, monocomponent adsorption shows an almost linear isotherm (*17*), but different authors have shown a markedly nonlinear isotherm when increasing the VOC concentration, the isotherms having a downward curvature similar to type II in the original BET classification (*18*−*22*). Under oven dry conditions, a strong relationship between the adsorption capacity of a soil and its specific surface area has also been shown (*20, 23, 24*). It is not clear whether this capacity is influenced to a greater degree by a physical parameter such as surface area or by a chemical parameter such as the mineralogical composition of the soil.

In this context, it has been considered of interest to analyze the adsorption behavior of organic compounds of different properties on soil minerals of different characteristics in order to obtain results for various situations. Compounds of different chemical functional groups have been used, both nonpolar or slightly polar (aliphatic, aromatic) and polar (ketone). These kinds of compounds represent a major problem in soils contaminated by volatile organic compounds (solvents, fuels, etc.). Due to their different chemical functions, they may interact with the soil through different kinds of bonds. To generalize the study, minerals of different chemical compositions and physical properties have been used: sand, clay, and limestone.

In addition, the presence of water in the soil or of water vapor in the gas may affect the adsorption of gases of organic compounds. When the amount of water on the soil reaches a value between four and five molecular layers, Henry's law can be applied to quantify the VOC retention (*25, 26*). For lower amounts of water on the soils, different results have been obtained. A reduction in the adsorption capacity of VOC onto soils in the presence of water has been observed by several authors (*2, 3, 6, 18, 24, 26*−*30*). On the other hand, Shimizu et al. (*17*), working with soils with some organic matter content, found that the presence of water may increase the VOC adsorption. It has therefore been considered useful to carry out a study of the influence of the presence of water at lower water levels below the limit of applicability of Henry's law. The effect of air humidity on the adsorption of different organic compounds on the three soil minerals has accordingly been determined.

Experimental Method

The adsorption isotherm of a volatile organic compound on a given mineral has been determined using a dynamic method working in a wide range of gas concentrations. The experimental system is shown in Figure 1. It basically consists of a preconditioning system for the inlet gas, a column where the mineral sample is held, and a gas analysis system.

The airstream from a compressor is conditioned by being passed through a silica bed in order to remove water and through a granular activated carbon bed to remove any organic compounds. Afterward, the air flow is divided into three streams using three mass flow controllers ranging up to 240 cm^3/min. One of these three flows is conducted to a bubble saturator containing pure liquid VOC, whose temperature is held constant at 273 K by means of an ice bath, and air with a concentration of organic compound, c_{go},

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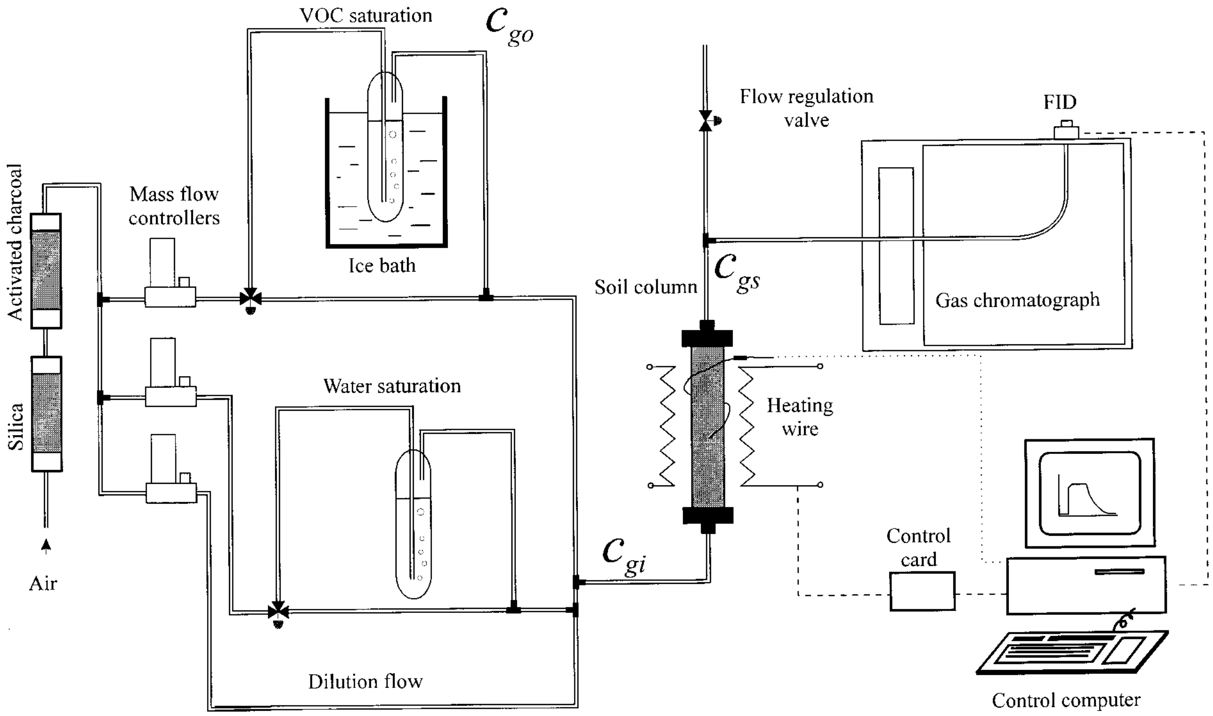

FIGURE 1. Experimental system.

is obtained. The flow from the second controller is sent to a bubble saturator that contains liquid water at room temperature (298 ± 1 K), where it is saturated in water vapor at this temperature. Both air lines are mixed and diluted with the air from the third mass flow controller. The air flow resulting from the three airstreams has a given VOC, c_{gi}, and water vapor concentration.

This air flow is passed through the adsorption section, which consists of a metallic column where the mineral sample is held. Depending on the adsorption capacity of the mineral, two different columns have been used, allowing us to work with more or less mineral sample. The dimensions of these columns are 3.1 cm diameter/19 cm length and 1.1 cm diameter/9 cm length, respectively. The mineral sample is previously prepared by outgassing the water and any possible VOC adsorbed in it by means of heating it up to 403 K, while a dry airstream is passed through it. Once the sample is cool at 298 K, it is conditioned with the desired humidity during 12 h prior to the input of VOC. Afterward the air containing VOC is introduced until the sample is saturated in VOC, then the air flow coming into the bed is replaced with clean air, without VOC but with the specified humidity in order to desorb the VOC retained in the sample. To reduce the operation time, the removal of the retained organic compound is carried out by heating the soil mineral up to 403 K. To ascertain that these heating and cooling cycles have no effect on the adsorption properties of the minerals, several experiments were carried out with the same VOC and water concentrations, showing no significant differences in the amount of VOC adsorbed through several cycles of heating and cooling the minerals.

The air leaving the column is sent directly to a gas chromatograph with a flame ionization detector (FID) that allows the continuous determination of the organic compound concentration, c_{gs}. With these values corresponding to the desorption step, the mass of VOC retained in the mineral and in the system (m_1) has been determined by means

$$m_1 = Q\int_0^{tf} c_{gs}\,dt \tag{1}$$

TABLE 1. Properties of the Three Minerals Chosen

	sand	limestone	clay
density (g/cm^3)	2.53	2.72	2.78
% organic matter	<0.1	<0.1	<0.1
particle diameter (mm)	0.33	1.31	<0.106
BET area (m^2/g)	0.72	0.15	10.91

To take into account the column volume and the amount of VOC retained on the walls and tubes, it has been necessary to carry out experiments with the same gas concentrations but without mineral samples, determining the mass of volatile retained by the experimental system (m_2) by means of a similar expression to eq 1. From this mass, m_2, it is necessary to subtract the volatile mass corresponding to the volume occupied by solid particles in the experiments with a sample ($m_{min}c_{gi}/\rho_{min}$). The final expression to calculate the concentration of VOC adsorbed on soil minerals is

$$c_s = \frac{1}{m_{min}}\left[m_1 - \left(m_2 - \frac{m_{min}}{\rho_{min}}c_{gi}\right)\right] \tag{2}$$

Equation 2 has been used only for the desorption step because the results are considerably more repetitive than for the adsorption step.

Seven volatile organic compounds have been used. The compounds correspond to a nonpolar aliphatic group (*n*-hexane, *n*-heptane, and *n*-octane), a slightly polar aromatic group [toluene, xylene (a mixture of *p* and *m* isomers), and ethylbenzene], and a polar ketone group (methyl ethyl ketone). Three common minerals of soils of different chemical and physical characteristics have been used: quartz sand, limestone (calcite), and a non-expanding clay mineral (muscovite). The properties of these minerals are summarized in Table 1. The BET surface areas were determined with nitrogen as sorbate at 77 K. It was considered useful to use these minerals in the conditions in which they were provided (i.e., untreated). Due to the low adsorption of *n*-hexane on limestone, which falls below the sensitivity limit

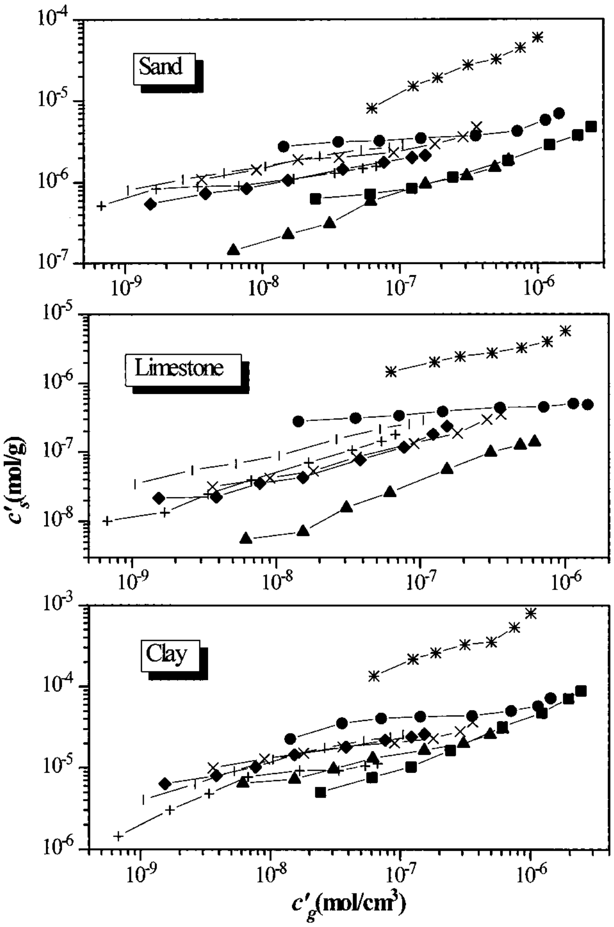

FIGURE 2. Adsorption of VOCs and water onto sand, limestone, and clay: (■) hexane; (▲) heptane; (♦) octane; (×) toluene; (+) xylene; (|) ethylbenzene; (●) methyl ethyl ketone; (*) water.

of the system, the adsorption of this compound has been studied on sand and clay only.

Since water is present in natural soils and may compete with the organic molecules for the adsorption sites, the monocomponent adsorption at room temperature of water vapor in these three minerals has also been studied in addition to the determination of the adsorption isotherms for the seven VOC. Due to the nonsensitivity of the FID detector to water, these isotherms have been determined gravimetrically in a thermobalance.

Results and Discussion

Influence of Type of Soil, Mineral, and VOC. The adsorption isotherms at 298 K of seven different organic compounds and of water vapor on the three dry soil minerals have been determined, working in a wide range of compound concentrations. For VOC, the range of relative concentrations to saturation at 273 K, c_{gi}/c_{go}, was 0.01–1.0, whereas for water the range was 0.05–0.8 relative to the saturation concentration at room temperature (298 K), c_{gi}/c_{gsat}. The results obtained are shown in Figure 2. Using a double logarithmic scale, the molar concentration of adsorbed VOC, c'_s (mol/g), is plotted versus the concentration of VOC in the gas phase, c'_g (mol/cm^3). Molar concentrations are used to take into account the different molecular weights of the compounds studied.

It can be concluded that in general nonlinear isotherms are obtained in the monocomponent adsorption of VOC onto soil minerals, which is in agreement with the results of other authors obtained for oven-dry soils (*18, 19, 21, 22, 24, 26, 31*). The isotherms can be classified as type II in the BET classification, indicating a physical multilayer adsorption. To quantify the adsorption of the VOC and water on the three soil minerals used, the isotherms obtained have been fitted to the nonlineal BET model:

$$c_s = \frac{Bc_m y}{(1 - y)(1 - y + By)} \tag{3}$$

The results of the BET parameters obtained and the correlation factors are shown in Table 2.

In Figure 2, it can also be observed that in general the most polar compounds (water and methyl ethyl ketone) present the highest adsorption on the three minerals [similar results have been reported by Chiou and Shoup (*18*)], followed by the aromatic compounds (toluene, xylene, and ethylbenzene) while the aliphatics (*n*-hexane, *n*-heptane, and *n*-octane) present the weakest adsorption of all the compounds studied. For these compounds, some relationship between the length of the molecule and the adsorption has been observed, because the longer the molecule, the stronger the adsorption of the aliphatics will be. Although for quartz sand, the *n*-hexane adsorption is slightly higher than for *n*-heptane.

To explain these differences between the compounds, it is of interest to take into account the mechanisms of interaction between the adsorption sites of the minerals and the compound molecules (*17, 32*). Considering that the adsorption of VOC is made from the gas phase and not from aqueous solutions, three different mechanisms have been considered: ion–dipole interactions, adsorption by donation of π electrons, and van der Waals–London forces. For aliphatic compounds, the interaction with soils is by means of dispersive forces, such as van der Waals–London forces. These forces are reinforced by mechanisms such as the donation of π electrons for aromatic compounds and through dipole–ion interactions, which are stronger than the others, for polar compounds.

A significant difference has also been observed in the adsorption capacity of the three minerals. In all cases, the highest adsorption capacity corresponds to the clay, being approximately 1 order of magnitude higher than the sand capacity and 2 magnitudes higher than limestone. These

TABLE 2. BET Parameters for VOCs and Water in the Three Soil Minerals

	sand			limestone			clay		
	B	c_m	r^2	*B*	c_m	r^2	*B*	c_m	r^2
n-hexane	21.88	2.90×10^{-4}	0.96				12.51	5.89×10^{-3}	0.94
n-heptane	25.66	1.46×10^{-4}	0.98	10.27	1.38×10^{-5}	0.96	53.80	2.25×10^{-3}	0.98
n-octane	98.24	2.00×10^{-4}	0.99	7.09	3.11×10^{-5}	0.87	103.00	2.44×10^{-3}	0.99
toluene	390	2.01×10^{-4}	0.99	12.02	2.98×10^{-5}	0.93	322	1.84×10^{-3}	0.99
xylene	167.63	1.37×10^{-4}	0.99	17.79	1.76×10^{-5}	0.95	119.29	1.00×10^{-3}	0.99
ethylbenzene	131.95	2.52×10^{-4}	0.99	22.14	2.90×10^{-5}	0.99	77.82	2.28×10^{-3}	0.99
methyl ethyl ketone	1094	2.50×10^{-4}	1.00	741	2.88×10^{-5}	1.00	430	3.29×10^{-3}	0.99
water	7.11	5.24×10^{-4}	0.99	36.29	4.12×10^{-5}	0.99	16.13	5.28×10^{-3}	0.99

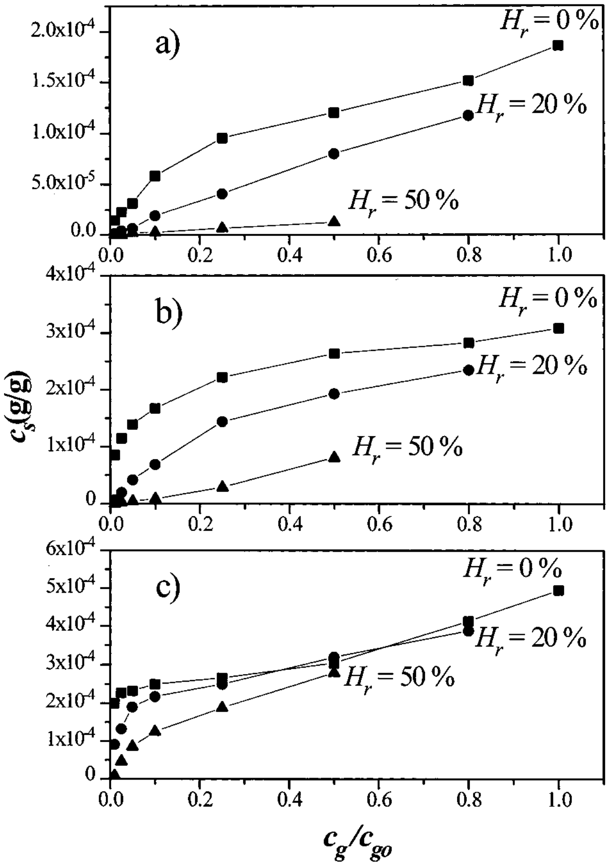

FIGURE 3. Adsorption of VOCs onto sand at different air humidities: (a) *n*-heptane, (b) ethylbenzene, (c) methyl ethyl ketone.

differences between the minerals can be observed for all the VOCs and also for water, and they maintain approximately the same ratio over the whole range of gas concentrations studied. The different adsorption observed in the three soil minerals could be due to the mineralogical composition and their physical properties (particle size, density, porosity, etc). Taking into account that the adsorption is carried out on the active sites of the soil surface coming into contact with the organic gas, the influence of the physical properties can be lumped using the surface area. If the adsorption isotherms of the VOC onto the three soil minerals are normalized dividing them by the BET surface area, a clear decrease in the differences of adsorption capacity is observed, and even a change in the sorption capacity of the aromatic compounds that show a higher level of normalized adsorption onto sand instead of clay is shown. These results suggest that a physical parameter such as surface area determines to a significant degree the adsorption capacity of VOC gases in a wide range of compound concentrations (*20, 23, 24*), although a chemical parameter such as the soil's mineralogical composition plays an important role in the VOC adsorption, as has been stated by other authors such as Petersen et al. (*26*).

Influence of Air Humidity. The influence of the presence of water has been analyzed carrying out experiments with relative humidities of air of 20% and 50%. Due to the configuration of the experimental system, the maximum relative concentration of VOC, c_{gi}/c_{go}, was 0.8 at 20% relative humidity and 0.5 for the experiments at 50% relative humidity. As examples, the adsorption isotherms obtained with *n*-heptane, ethylbenzene, and methyl ethyl ketone on sand are shown in Figure 3.

A remarkable reduction is observed in the adsorption capacity of gases of aromatic and aliphatic compounds as the air humidity increases. From the analysis of the results with methyl ethyl ketone, it can be deduced that at a low VOC concentration there is also a reduction in the adsorption as the air humidity increases; but at a high VOC concentration, the adsorption is similar for the three levels of humidity. Similar results have also been observed for clay and limestone.

To explain the reduction observed in the adsorption of VOC gases onto minerals in the presence of water in the gas phase and the differences in behavior between the compounds, it is useful to take into account the mechanisms of the interactions (mentioned above) between the organic molecules and the water molecules with the mineral surfaces. The organic molecules compete with water molecules for the adsorption sites, and due to the strong dipole interactions of the polar molecule of water, this displaces the nonpolar organic molecules of the aliphatics and aromatics studied from these sites, reducing the adsorption of VOC. In the case of polar compounds such as methyl ethyl ketone, the interactions with the adsorption sites of the minerals are of the same intensity as of water, and the reduction in adsorption is significant only at low VOC concentrations.

A progressive linealization of the adsorption isotherms is also observed as the air humidity increases. Again, the behavior of the polar compounds in the presence of water is somewhat different from the aliphatic and aromatic compounds, since for polar compounds the linearizing effect of water in the adsorption isotherm is less significant. This effect has been described in some works (*1, 18, 19*), while Thibaud et al. (*22*) observed a change in the curvature of the isotherms from downward to upward, which would correspond to a change in the exponent of the Freundlich equation from less to more than unity. This upward curvature may be observed to some degree in the adsorption of toluene and ethylbenzene onto sand and clay at 50% relative humidity.

Despite the significance of the water presence in the adsorption of VOC gases onto soils, only a few works have been presented quantifying the relationship between the adsorption capacity and the water presence (*5, 26–28*). With this aim, the adsorption isotherms obtained with the seven organic compounds on the three soil minerals at different air humidities have been compared. Because the shape of the isotherms varies from nonlinear to almost linear, we have determined the slope of the isotherms at low VOC concentrations, where the isotherms are almost linear. This simplifies the treatment of the experimental data by working with only one parameter, the slope of the isotherm at low gas concentrations, K_r, which can be interpreted as a partition coefficient between the gas phase and the solid.

$$c_s = K_r c_g \tag{4}$$

To determine the value of the slope or the partition coefficient, the isotherms have been fitted to the BET model, which predicts a linear behavior at low gas concentrations and can be approximated at these low gas concentrations as

$$c_s = \frac{Bc_m}{c_{gsat}} c_g \tag{5}$$

then

$$K_r = \frac{Bc_m}{c_{gsat}} \tag{6}$$

The values of K_r versus the relative humidity are shown in Figure 4 in a semilog scale. An approximately linear relationship can be observed between log K_r and the relative humidity of the air, which mathematically can be expressed as

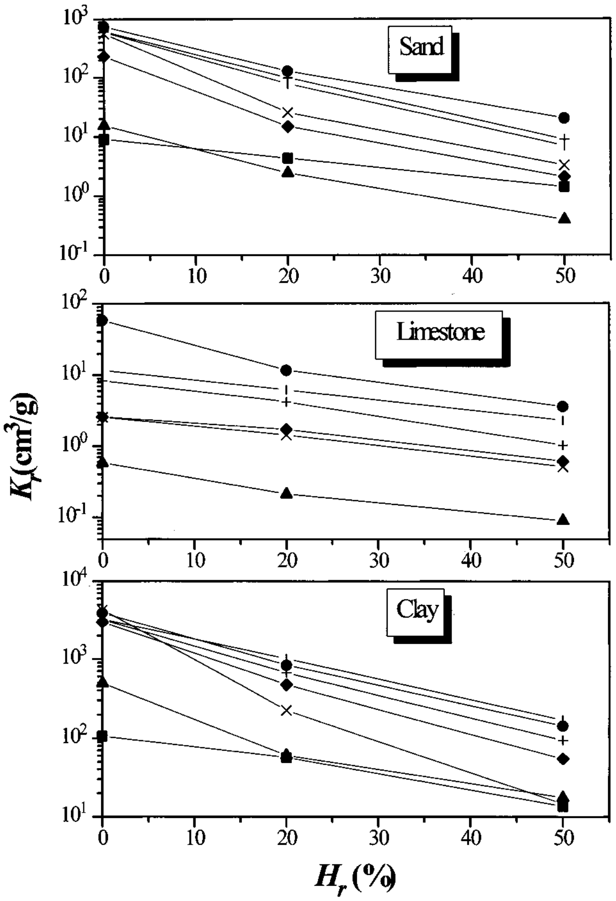

FIGURE 4. Air−soil minerals partition coefficient for VOC at different relative humidities: (■) hexane; (▲) heptane; (♦) octane; (×) toluene; (+) xylene; (|) ethylbenzene; (●) methyl ethyl ketone.

TABLE 3. Values of a_H (eq 7) for the Seven VOC and the Three Soil Minerals

	a_H		
	sand	limestone	clay
n-hexane	3.70		4.16
n-heptane	7.17	3.76	6.49
n-octane	9.16	2.93	7.92
toluene	10.00	3.25	11.17
xylene	8.40	4.23	7.00
ethylbenzene	8.81	3.25	5.87
methyl ethyl ketone	7.14	5.45	6.52

$$K_r = K_{ro} e^{-a_H H_r} \qquad (7)$$

This simple relationship is similar to that used by Goss (*27, 28*). In these works, the temperatures of the experiments were relatively high (50−100 °C), and the range of validity of eq 7 was for relative humidity higher than 30%. In the present work, the exponential relationship can be fitted over the range of 0−50% of relative air humidity at room temperature.

To ascertain whether the reduction in the adsorption capacity of minerals in the presence of water is independent of the mineralogical composition, the partition coefficient (K_r) values for the seven compounds and the three soil minerals have been fitted to eq 7. The values of the constants a_H corresponding to sand, clay, and limestone are presented in Table 3. If the reduction in adsorption capacity were independent of the mineralogical composition of the soil minerals, the values of a_H would be the same, independent of the sorbent. This is to some extent the case for clay and sand, but the values for limestone differ from the other two minerals. From this it can be concluded that the reduction in the adsorption capacity of VOC onto minerals in the presence of water is a phenomenon dependent on the mineralogical composition.

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Notation

a_H	constant of eq 7 (nondimensional)
B	constant of the BET equation (nondimensional)
c_g	concentration in the gas phase (g/cm^3)
c_{gi}	VOC concentration in the gas phase at the inlet of the mineral sample (g/cm^3)
c_{go}	VOC saturation concentration in the gas phase at 273 K (g/cm^3)
c_{gs}	VOC concentration in the gas leaving the mineral sample (g/cm^3)
c_{gsat}	saturation concentration in the gas phase at room temperature (g/cm^3)
c'_g	VOC concentration in the gas phase, expressed as mol/cm^3
c_m	adsorbed concentration corresponding to the formation of a monolayer over the surface of the mineral (g of volatile/g of mineral)
c_s	adsorbed concentration of volatile onto mineral (g of volatile/g of mineral)
c'_s	adsorbed concentration of volatile onto mineral, expressed as mol of volatile/g of mineral
H_r	relative humidity of the air (%)
K_r	partition coefficient between air and mineral (cm^3 of gas/g of solid)
K_{ro}	partition coefficient between air and dry mineral (cm^3 of gas/g of solid)
m_1	VOC mass adsorbed on the column with mineral sample (g)
m_2	VOC mass retained by the column without mineral sample (g)
m_{min}	mass of mineral sample (g)
Q	air flow rate (cm^3/min)
t	time (min)
t_f	time necessary to remove all the volatile adsorbed on the mineral (min)
y	relative concentration to saturation concentration (c_g/c_{gsat})

Greek Symbols

ρ_{min}	specific density of the mineral particles (g/cm^3)

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