



Effect of aggregate structure on VOC gas adsorption onto volcanic ash soil

Shoichiro Hamamoto^{a,*}, Katsutoshi Seki^b, Tsuyoshi Miyazaki^{c,1}

^a Division of Environmental Science and Infrastructure Engineering, Graduate School of Science and Engineering, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570, Saitama University, Japan

^b Department of Accounting and Finance, Faculty of Business Administration, 5-28-20, Hakusan, Bunkyo-ku, Tokyo 112-8606, Toyo University, Japan

^c Department of Biological and Environmental Engineering, 1-1-1 Yayoi Bunkyo-ku, Tokyo 113-8657, Graduate School of Agricultural and Life Science, The University of Tokyo, Japan

ARTICLE INFO

Article history:

Received 22 April 2008

Received in revised form

13 September 2008

Accepted 6 November 2008

Available online 14 November 2008

Keywords:

Volatile organic compound

Adsorption

Gas

Aggregated soil

Organic matter

ABSTRACT

The understanding of the gaseous adsorption process and the parameters of volatile organic compounds such as organic solvents or fuels onto soils is very important in the analysis of the transport or fate of these chemicals in soils. Batch adsorption experiments with six different treatments were conducted to determine the adsorption of isohexane, a gaseous aliphatic, onto volcanic ash soil (Tachikawa loam). The measured gas adsorption coefficient for samples of Tachikawa loam used in the first three treatments, Control, AD (aggregate destroyed), and AD-OMR (aggregate destroyed and organic matter removed), implied that the aggregate structure of volcanic ash soil as well as organic matter strongly enhanced gas adsorption under the dry condition, whereas under the wet condition, the aggregate structure played an important role in gas adsorption regardless of the insolubility of isohexane. In the gas adsorption experiments for the last three treatments, soils were sieved in different sizes of mesh and were separated into three different aggregate or particle size fractions (2.0–1.0 mm, 1.0–0.5 mm, and less than 0.5 mm). Tachikawa loam with a larger size fraction showed higher gas adsorption coefficient, suggesting the higher contributions of macroaggregates to isohexane gas adsorption under dry and wet conditions.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The understanding of the interaction between soils and volatile organic compounds (VOC) such as organic solvents or fuels has been a matter of growing concern due to increasing soil contamination [29]. Several field studies have shown that gas-phase contaminants can arrive at the water table ahead of a liquid contaminant plume [13,34]. The sorption of VOC gas strongly affects its transport and the amount that is retained in soil [27]. Therefore, it is important to understand the sorption process and the parameters that control transport in terms of the remediation of contaminants or risk assessment [26].

Several researchers have reported that VOC gas is strongly sorbed directly onto soil minerals under dry conditions [2,23,26]. At dry conditions, gas sorption is strongly affected by the soil-water content where an increase in soil-water content causes a rapid decrease in VOC gas adsorption capacity [23,24,26,32]. On the other hand, under the wet condition, VOC gas sorption is mainly dominated by dissolution to soil water, as expressed by Henry's

law, and the gas adsorption capacity slightly increases as the soil-water content increases [24,26]. To date, the sorption of VOC gas, especially chlorinated organic compounds such as trichloroethylene (TCE) and toluene, has been studied with various soils and soil minerals at different soil-water contents [24,26,27]. However, few studies regarding gas sorption phenomena such as the aliphatic and aromatic phenomena of petroleum chemicals have been reported [29]. These petroleum chemicals are distinguished typically as a light nonaqueous phase liquid (LNAPL) and are less dense than water. As the water table fluctuates, LNAPL tends to be redistributed upward and downward over the vertical extent of the water table's rise and fall [13]. Hence, the high mobility of these petroleum chemicals near the soil surface has a significant impact on human health and the environment. In Japan, increasing concern about contaminated soils by petroleum chemicals [15] necessitates a better understanding of the physical and chemical interactions between these chemicals and soils.

Volcanic ash soils, which are widely distributed in Japan and account for one-sixth of the total land area [8], exhibit unique soil properties such as high water retention, large total porosity due to noncrystalline materials such as allophane, and good drainage, all of which are favorable for plant root growth [33,18]. Using the results of N₂ gas adsorption tests, Bartoli et al. [3] showed that the total micropore and meso-specific surface areas of volcanic ash soils

* Corresponding author. Tel.: +81 48 858 3116; fax: +81 48 858 3116.

E-mail address: s07de004@mail.saitama-u.ac.jp (S. Hamamoto).

¹ Tel.: +81 3 5841 5350; fax: +81 3 5841 8877.

increased as the soils became more allophanic. They also indicated that the soil surface became more hydrophobic when more soil allophanes were coated by organic matter, resulting in smaller specific surface areas. Due to its high clay content, the texture of volcanic soils is often classified as light clay (LiC) or clay loam (CL) [9]. These unique soil properties are closely related to a well-developed soil structure with aggregates [33]. The gas adsorption coefficients (K_g) for aggregated soils under dry conditions are four to five orders higher than those for glass beads and sands [20]. Despite the unique properties, possible high gas adsorption capacity, and wide distribution of volcanic ash soil, there have been few investigations of VOC gas adsorption onto volcanic ash soil. It is reasonable to believe that the aggregate structure affects VOC gas adsorption because the inter- or intra-aggregate pore structure and the soil-water retention characteristics of volcanic ash soils are closely related to gas adsorption sites.

In this paper, we report the results of adsorption experiments of isohexane, an aliphatic gas, onto volcanic ash soils in Japan. We investigated the effect of the aggregate structure and the organic matter content on gas adsorption by using six different treatments of volcanic ash soils.

2. Materials and methods

2.1. Soil samples

Two soil samples, Tachikawa loam (Andisols) and Toyoura sand, were used in this study. Tachikawa loam was collected at a depth of 70 cm on an experimental farm at the Field Production Science Center of The University of Tokyo at Nishitokyo, Tokyo. Both soils were sieved with a 2.0 mm mesh screen. To investigate the effect of the aggregate structure and organic matter on gas adsorption onto Tachikawa loam, the following three treatments were performed: the aggregate structure was destroyed (AD), the aggregate structure was destroyed and organic matter was removed (AD-OMR), and no treatment was applied (Control). AD samples were prepared by mixing the rewetted soil samples following the same procedure as those used in the measurement of the liquid limit of soil [19]. For AD-OMR samples, the organic matter was removed by treatment with hydrogen peroxide, H_2O_2 [6] after the aggregate structure of the soil samples was destroyed in the same way as that of the AD samples. Both the AD and the AD-OMR samples were sieved in a 0.5 mm mesh after being oven dried. In a separate experiment aimed at investigating the effect of aggregate size on gas adsorption, oven-dried Tachikawa loam was sieved with 2.0 mm, 1.0 mm, and 0.5 mm mesh. Three different aggregate or particle size fractions, (1) 2.0–1.0 mm, (2) 1.0–0.5 mm, and (3) less than 0.5 mm, were prepared for treatment in the gas adsorption experiments.

The soil-water retention curves of Tachikawa loam, repacked in a cylindrical stainless core 5.0 cm wide and 2.0 cm long with a bulk density of 0.50 Mg m^{-3} , were measured by the water hanging method from -10 to $-100 \text{ cm H}_2\text{O}$ [4] and by the pressure plate method from -10 to $-1.0 \times 10^4 \text{ cm H}_2\text{O}$ [5]. The water potentials of the air-dried soil samples of Tachikawa loam with three different soil-water contents (0.60, 0.43, and $0.3 \text{ g H}_2\text{O g}^{-1}$ soil) were measured with a Dewpoint Potential Meter (WP4; Decagon Devices, Inc., USA). The particle size distributions for AD-OMR samples of Tachikawa loam were measured by the hydrometer method [10]. In addition, the aggregate size distributions for Control samples of Tachikawa loam were measured by sieving the dried samples with different sizes of mesh [21]. The specific surface areas of all the treatments in Tachikawa loam and Toyoura sand were determined by the ethylene glycol monoethyl ether (EGME) method [25]. Pre-treatments to remove organic matter and saturation with Ca^{2+} were omitted, as suggested by Petersen et al. [23]. The organic carbon

Table 1

Chemical properties of isohexane (2-methylpentane).

| Chemical formula | C_6H_{14} |
|--|---------------------------|
| Molecular weight (g mol^{-1}) | 86.18 |
| Vapor pressure (mmHg) | 211 |
| Dimensionless Henry Coefficient ^a | 71.8 |

^a Hine and Mookerjee [12].

and the nitrogen contents of the soil samples were also measured with a CN analyzer (Sumigraph NC-90A; Sumika Chemical Analysis Service, Ltd., Japan).

2.2. Gas sample

Isohexane (2-methylpentane) was used as a model VOC gas in this study. Isohexane is an aliphatic hydrocarbon and a solvent for vegetable oils, glues, coatings, and paints. It is also found in gasoline and has been used as an intermediate for chemicals [1]. Table 1 presents the chemical properties of isohexane. The solubility of isohexane in water was investigated in a preliminary experiment. The dissolution of isohexane in water was not detectable and therefore was neglected in this study.

2.3. Measurement of adsorption isotherms

The adsorption isotherms of isohexane to Tachikawa loam and Toyoura sand were determined by the Equilibrium Partitioning In Closed Systems (EPICS) method [24]. EPICS is a mass-balance technique which measures the gas concentration in the headspaces of two sealed glass bottles: a bottle with a known amount of sorbent, i.e., a soil sample, and a bottle without any sorbent.

The sorbent was introduced into the 50 mL bottle, which was then sealed with a Teflon cap. The adsorbing VOC gas, isohexane (2-methylpentane), was introduced into both bottles (with and without the sorbent) by replacing a 1.0 mL volume of air with an equivalent volume of saturated gas. After that, the bottles were shaken for 36 h at 20°C to reach equilibrium; preliminary experiments showed that equilibrium was reached after this period. The equilibrated gas in the headspace was sampled with a gas-tight syringe of 1.0 mL and analyzed by a gas chromatograph equipped with a flame-ionization detector (GC-14B; Shimadzu Corporation). As the amounts of the introduced gas in both bottles were the same, the following equation was obtained:

$$V_B C_B = V_S C_S + MQ, \quad (1)$$

where V_B (cm^3) and C_B (g cm^{-3}), respectively, are the gas volume and the concentration in the bottle without the sorbent, V_S (cm^3) and C_S (g cm^{-3}), respectively, are the gas volume and concentration in the bottle with the sorbent, M (g) is the mass of the sorbent, and Q (g g^{-1} soil) is the amount of sorbent adsorbed per mass of soil. By assuming that Henry's law is valid [23],

$$Q = K_g C_S, \quad (2)$$

where K_g ($\text{cm}^3 \text{ g}^{-1}$) is the adsorption coefficient. From Eqs. (1) and (2), the following equation was obtained:

$$\frac{V_B C_B}{V_S C_S} - 1 = K_g \frac{M}{V_S}. \quad (3)$$

Therefore, by making multiple measurements with different masses of sorbent (M), the adsorption coefficient, K_g ($\text{cm}^3 \text{ g}^{-1}$), was determined as the slope of a linear adsorption isotherm obtained from plotting the left-hand side of Eq. (3) against M/V_S [22,24]. Five different sorbent masses (M) ranging from 1.0 to 15 g with two replicates, i.e., a total of ten measurements, were used to draw an adsorption isotherm.

Table 2
Physical properties of soils used in this study.

| | Tachikawa loam (volcanic) | Toyoura sand (sand) |
|--|---------------------------|-------------------------|
| Texture (%) | | |
| Sand | 32.9 | 99.4 |
| Silt | 38.6 | 0.6 |
| Clay | 28.5 | 0.0 |
| Soil class | Clay loam | Sand |
| Soil particle density (g cm ⁻³) | 2.70 | 2.65 |
| Bulk density (g cm ⁻³) | 0.50 | 1.50 |
| Total porosity (cm ³ cm ⁻³) | 0.81 | 0.43 |
| Saturated hydraulic conductivity (cm s ⁻¹) | 5.38 × 10 ⁻⁴ | 1.13 × 10 ⁻² |

For each soil, Tachikawa loam (six treatments) and Toyoura sand, adsorption isotherms were determined for several different water contents. Those of the Control samples of Tachikawa loam were obtained by air drying soil samples taken under natural conditions (drying process) and by adding water to oven-dried soil samples for Toyoura sand, AD, AD-OMR, 2.0–1.0 mm, 1.0–0.5 mm, and <0.5 mm samples (wetting process).

3. Results and discussion

3.1. Soil properties

The physical properties of the soil samples are shown in Table 2. Fig. 1 shows the measured water retention curve of Tachikawa loam and a fitting curve with a bimodal lognormal pore-size distribution model [31]:

$$\theta = \theta_r + (\theta_s - \theta_r) \sum_{i=1}^2 w_i Q \left[\frac{\ln(h_i/h_{mi})}{\sigma_i} \right] \quad w_1 + w_2 = 1, \quad (4)$$

where h_i (cm H₂O) is the suction head; h_{mi} , σ_i , and w_i are parameters; $Q(x)$ is the complementary cumulative normal distribution function; θ (cm³ cm⁻³) is the volumetric water content; θ_s (cm³ cm⁻³) is the saturated water content; and θ_r (cm³ cm⁻³) is the residual water content, assumed to be 0.

The pore-size density (PSD), defined as the derivative of the water content versus pF, where pF equals $\log(-h$ in cm H₂O), was calculated by

$$\text{PSD} = [\log_e(10)] h \sum_{i=1}^2 w_i \left(\frac{\theta_s - \theta_r}{\sqrt{2\pi}\sigma_i r} \exp \left[-\frac{[\ln(h/h_{mi})]^2}{2\sigma_i^2} \right] \right) \quad (5)$$

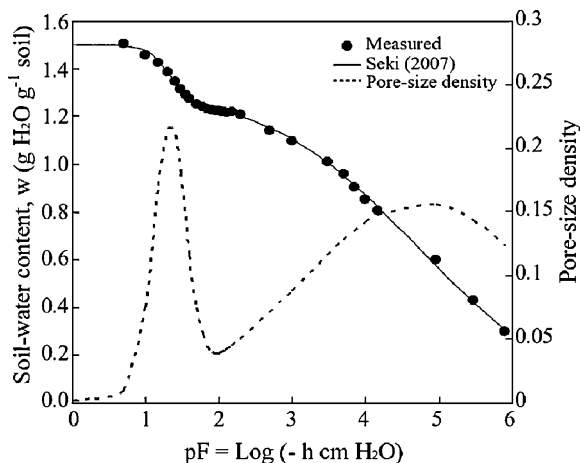


Fig. 1. Water retention curve (solid line) and pore-size density (dashed line) for Tachikawa loam. pF equals $\log(-h$ in cm H₂O), where h is the suction head.

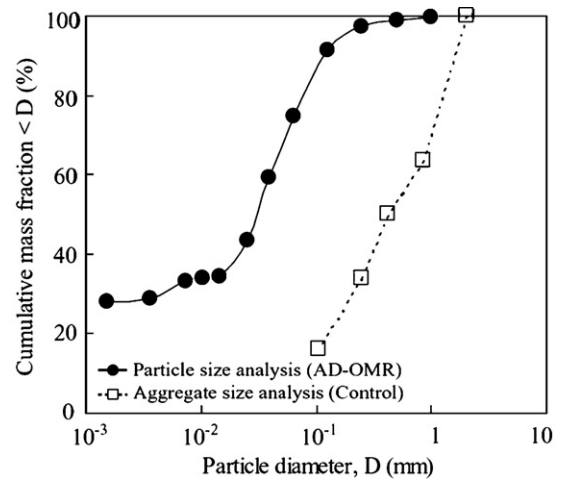


Fig. 2. Particle size analysis (solid line) and aggregate size analysis (dashed line) for Tachikawa loam.

The pore-size density of Tachikawa loam showed two peaks at pF = 1.3 and pF = 4.8. The bimodality came from the aggregate structure of Tachikawa loam [17]. The pore-size distribution curve can be well separated at pF = 2 (soil-water content 1.2 g H₂O g⁻¹ soil), corresponding to the pore radius of 15 μm; the intra-aggregate or textural pores are responsible for the first mode at pF > 2 (pore radius > 15 μm), whereas the inter-aggregate or structural pores are represented by the second mode at pF < 2 (pore radius < 15 μm). Fig. 2 shows the particle size distribution for AD-OMR samples and the aggregate size distribution for Control samples. By destroying the aggregate structure, the aggregates were fragmented, resulting in a smaller average particle size and a wider particle size distribution.

3.2. Specific surface area and CN contents

Table 3 shows the specific surface area and the organic carbon and nitrogen contents of soil samples. The specific surface areas after all the treatments of Tachikawa loam (between 335 m² g⁻¹ and 414 m² g⁻¹) were higher than that of Toyoura sand (6.45 m² g⁻¹). The higher specific surface area of Tachikawa loam was attributed to noncrystalline materials such as allophane, which is the dominant constituent of many volcanic ash soils [18].

The organic carbon and the nitrogen contents of AD-OMR samples were significantly lower than those of the Control and AD samples, which was attributed to the decrease in organic matter by treatment with hydrogen peroxide (H₂O₂). On the other hand, the specific surface area of AD-OMR samples was higher than those of the Control and AD samples, perhaps because the existence of organic matter in the Control and AD samples prevented EGME gas

Table 3

Specific surface area and organic nitrogen and carbon contents of soils used in this study. Means followed by the same letter are not significantly different at $P = 0.05$ by the Tukey–Kramer test.

| Sample | Specific surface area (m ² g ⁻¹) | N (%) | C (%) |
|----------------|---|-------------------|-------------------|
| Toyoura sand | | 6.45 | |
| Control | 364.7 ^a | 0.20 ^a | 2.56 ^a |
| AD | 357.8 ^a | 0.20 ^a | 2.55 ^a |
| AD-OMR | 413.6 ^b | 0.13 ^b | 0.68 ^b |
| Tachikawa loam | | | |
| 2.0–1.0 mm | 377.9 ^a | 0.19 ^a | 2.40 ^a |
| 1.0–0.5 mm | 358.9 ^b | 0.20 ^a | 2.48 ^a |
| <0.5 mm | 334.5 ^c | 0.22 ^b | 2.67 ^b |

adsorption onto soils and the specific surface areas of the samples were underestimated.

Higher organic carbon and nitrogen contents and a lower specific surface area were observed in smaller particle or aggregate fractions (Table 3), which could be explained by the differences in the organic matter constituents of aggregates of different sizes. Organic matter such as root exudates and the continual death of roots, particularly root hairs, usually plays an important role in the formation of soil aggregates [16]. In addition, adjacent aggregates in the field often adhere to one another and form macroaggregates [11], which are usually assemblages of smaller groupings, or microaggregates. Six et al. [30] showed that no-till soil management led to increased stabilization of carbon in a small, stable microagggregate structure. Referring to experimental data, Tisdall and Oades [35] and De Gryze et al. [7] insisted that microaggregates are held together by persistent binding agents whereas macroaggregate binding agents are naturally more transient. The differences in the organic carbon and nitrogen contents of <0.5 mm compared to the 2.0–1.0 mm and 1.0–0.5 mm soil samples could be the result of the different organic matter properties of binding agents of macro- or microaggregates, leading to the different specific surface areas in these soil samples.

3.3. Adsorption isotherms

Fig. 3 shows the linear adsorption isotherms measured by the EPICS method for isohexane on Control samples of Tachikawa loam at soil-water contents (w) of 0.23 and 0.67 ($\text{g H}_2\text{O g}^{-1}$ soil) and Toyoura sand at $w=0.00$ and 0.15 ($\text{g H}_2\text{O g}^{-1}$ soil). All adsorption isotherms for Tachikawa loam (Control, AD, AD-OMR, 2.0–1.0 mm, 1.0–0.5 mm, and <0.5 mm) and Toyoura sand were linear at all soil-water contents. The calculated regression coefficient (R^2) for all samples was more than 0.96. Hence, the validity of Henry's law for the adsorption of isohexane gas to soil was confirmed, and the adsorption coefficients were determined by the slope of the linear adsorption isotherms (Fig. 3).

Fig. 4 shows the adsorption coefficients (K_g) for Toyoura sand at different soil-water contents. As the soil-water contents increased, the K_g values drastically decreased. This trend agreed with the results of other investigations into K_g for trichloroethylene or toluene measured by the same method [23,24,27]. However, the absolute value of K_g of isohexane was very different from that of TCE. Poulsen et al. [27] measured the adsorption isotherm of TCE by the EPICS method and reported that the K_g value of Lundgaard (sandy soil), with a specific surface area of $10.8 \text{ m}^2 \text{ g}^{-1}$, was around $50 \text{ cm}^3 \text{ g}^{-1}$ under the oven-dried condition ($w=0.00 \text{ g H}_2\text{O g}^{-1}$ soil)

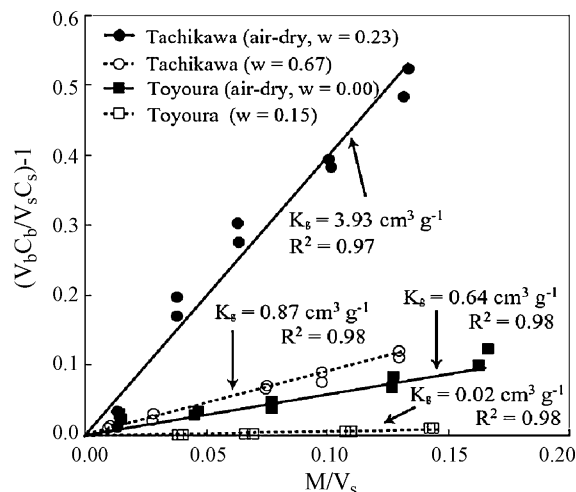


Fig. 3. Adsorption isotherms for isohexane on Tachikawa loam at soil-water content of 0.23 and 0.67 ($\text{g H}_2\text{O g}^{-1}$ soil) and on Toyoura sand at soil-water content of 0.00 and 0.15 ($\text{g H}_2\text{O g}^{-1}$ soil).

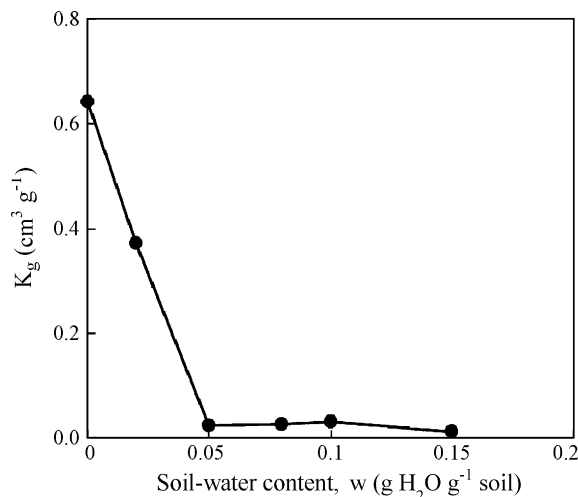


Fig. 4. Change of adsorption coefficient K_g of isohexane for Toyoura sand.

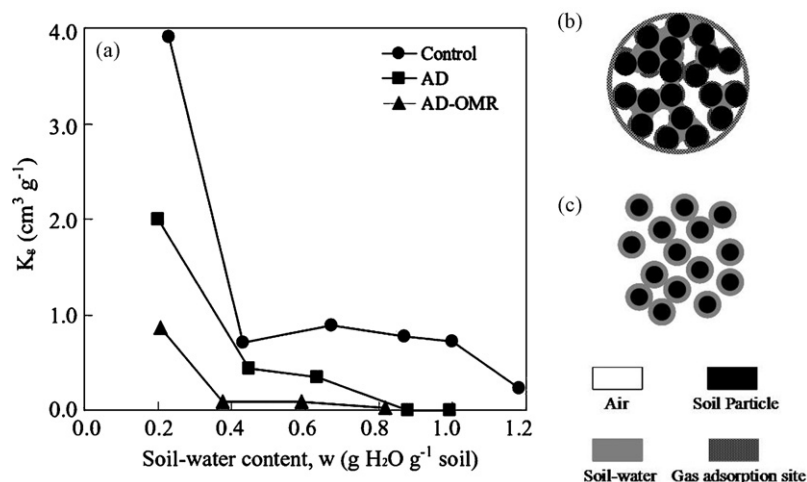


Fig. 5. (a) Change of adsorption coefficient K_g of isohexane for Tachikawa loam with different treatments for the aggregate structure and organic matter. Schematic description of gas adsorption sites for (b) Control samples and (c) AD samples.

and was maintained at around $0.5 \text{ cm}^3 \text{ g}^{-1}$ under the wet condition above $w=0.02$. However, in this study, the K_g value of oven-dried Toyoura sand was $0.64 \text{ cm}^3 \text{ g}^{-1}$ and was maintained at around $0.02 \text{ cm}^3 \text{ g}^{-1}$ above $w=0.05$. The lower K_g values of the isohexane in the total soil-water content may be attributed to the nonpolarity of isohexane implied based on a very high dimensionless Henry's coefficient of isohexane (71.8) compared to that of TCE (0.40) [12]. A dipole interaction between the water molecules and the polar surface of the soil particle inhibited the isohexane gas adsorption because aliphatics such as isohexane are typically nonpolar chemicals and the gas adsorption was caused by relatively weak van der Waals forces [23,28,29]. The lower K_g values of isohexane gas may indicate the higher mobility of a gaseous aliphatic than of TCE or toluene in soil, and the lower polarity of isohexane may indicate the importance of soil-water conditions for the management of contaminated soils by petroleum chemicals such as aliphatic.

3.4. The effect of aggregate structure and organic matter on gas adsorption

The K_g values of the three treatments (Control, AD, and AD-OMR) on Tachikawa loam are shown in Fig. 5a. The K_g values of Control samples were significantly higher than those for Toyoura sand (Fig. 3) in the whole range of soil-water content because Tachikawa loam has more gas adsorption sites due to the existence of allophane, a highly porous mineral with a high specific surface area (Table 3).

The K_g values of Control samples exhibited three stages of change with an increase in soil-water content. The values drastically decreased to a soil-water content (w) of $0.4 \text{ g H}_2\text{O g}^{-1}$ soil (Stage 1), was maintained at around $0.70 \text{ cm}^3 \text{ g}^{-1}$ from $w=0.4$ – 1.0 (Stage 2), and then decreased again from $w=1.0$ – 1.2 (Stage 3). At lower soil-water content levels, the soil-air interfaces in both intra- and inter-aggregate pore spaces acted as adsorption sites of isohexane gas, resulting in significantly higher K_g values in Stage 1. As the soil-water content increased, the isohexane gas adsorption within the intra-aggregate pore spaces was reduced since the intra-aggregate pores were filled with water. However, at Stage 2, the soil-air interfaces in inter-aggregate pore spaces might still have acted as the main adsorption sites, leading to relatively constant K_g values. Fig. 1 shows that the intra-aggregate pores of Tachikawa loam start to be filled with water above $w=1.2$. Therefore, the decrease in K_g values in Stage 3 (Fig. 5a) might be due to the water filling the inter-aggregate pores. The observed three stages of the change in K_g is a unique phenomenon which was not observed with Toyoura sand (Fig. 4) or chlorinated organic compound gases such as TCE or toluene [23,24,27] and may represent chemical properties of isohexane, including nonpolarity, and physical soil properties, including the aggregate structure of Tachikawa loam.

Petersen et al. [23,24] and Poulsen et al. [27] reported that the K_g values of TCE or toluene increased linearly at high soil-water contents due to the dissolution of chemicals in soil water. Poulsen et al. [27] reported that toluene adsorption to soil was caused by strong vapor-solid sorption below the wilting point (at a soil-water potential of $\text{pF}=4.2$) and by dissolution to soil water above the wilting point. In this study, strong vapor-solid sorption was observed below $w=0.4$, corresponding to a pF of around 5.5, not at the wilting point of $\text{pF}=4.2$. Petersen et al. [24] and Ong and Lion [22] showed that TCE adsorption drastically decreased to a soil-water content corresponding to three to five molecular layers of water. In this study, a soil-water content of $0.4 \text{ g H}_2\text{O g}^{-1}$ soil of Tachikawa loam corresponds to three molecular layers of water, as calculated based on the total specific surface area of Tachikawa loam ($364.7 \text{ m}^2 \text{ g}^{-1}$, Table 3) and assuming that a water molecule occupies an area of $10.8 \times 10^{-20} \text{ m}^2$ [14].

The K_g values of the AD and AD-OMR samples were smaller than those of the Control samples (Fig. 5a). Under the air-dry condition ($w=0.2$), the K_g value of the Control samples was around two times higher than those of AD samples and four times higher than those of AD-OMR samples. All three samples (Control, AD, and AD-OMR) showed a remarkable decrease in K_g at a soil-water content of 0.4, but they all showed different patterns of K_g changes at $w=0.4$ – 1.2 . At $w=0.8$, the K_g values of AD and AD-OMR samples approached zero, although the value of the Control samples at $w=1.2$ was $0.2 \text{ cm}^3 \text{ g}^{-1}$. Higher K_g values of aggregate soil with widely different soil-water contents might be related to the aggregate structure (Figs. 1 and 2), conceptually illustrated in Fig. 5b. Higher water retention in intra-aggregate pores caused a greater likelihood of isohexane gas adsorption onto the outer walls of the aggregates. By the fragmentation of the aggregates (AD and AD-OMR samples), the pore structure of Tachikawa loam disaggregated, as illustrated in Fig. 5c. The increase in the thickness of the water film around each soil particle compared with that shown in Fig. 5b decreased the gas adsorption site and the K_g values. In addition to the effect of the aggregate structure, the difference between the AD and AD-OMR samples indicated that the existence of organic matter contributed to increased gaseous adsorption onto soils (Fig. 5a).

3.5. Effect of aggregate size on gas adsorption

Fig. 6 shows the adsorption coefficients of three different aggregate or particle size ranges (2.0–1.0 mm, 1.0–0.5 mm, and <0.5 mm) of Tachikawa loam. The K_g values of all the treatments remarkably decreased from $w=0.2$ to 0.4. The larger the aggregate size of the soil samples, the higher the observed K_g values in the overall soil-water content range. Under the dry condition ($w=0.2 \text{ g H}_2\text{O g}^{-1}$ soil), the K_g values of 2.0–1.0 mm samples were around two-and-a-half times and five times higher than those of 1.0–0.5 mm and <0.5 mm samples, respectively. In addition, the K_g values of 1.0–0.5 mm and <0.5 mm soil samples approached zero at $w=0.4$ and 0.8, respectively, while those of 2.0–1.0 mm soil samples were maintained at $0.44 \text{ cm}^3 \text{ g}^{-1}$ at $w=1.2$. These results implied that the existence of macroaggregates larger than 1.0 mm affected isohexane gas adsorption to Tachikawa loam even under the wet condition. The different specific surface areas of different sizes of fractions of aggregates (Table 3) alone cannot fully explain such large differences in the adsorption coefficients. The different characteristics of binding agents and the stability of macro- and microaggregates [7,35] might be one cause of the different

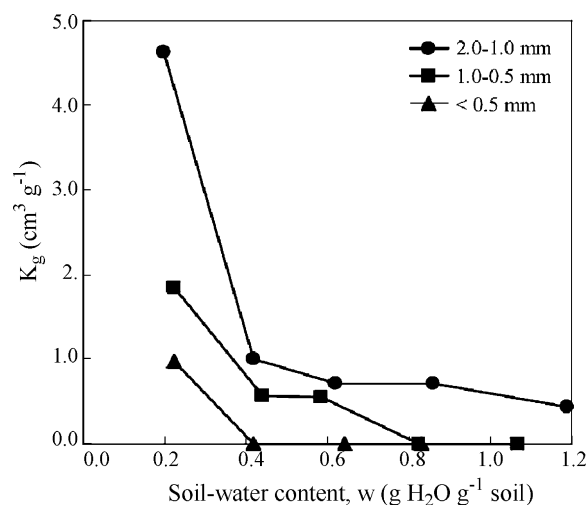


Fig. 6. Change of adsorption coefficient K_g of isohexane for Tachikawa loam with different aggregate sizes.

adsorption characteristics of soil samples with different aggregate sizes, and the more persistent binding agent and higher stability of microaggregates might reduce the diffusion of isohexane gas into intra-aggregate pore spaces, resulting in decreased gas adsorption. However, the role of the binding agent in gas adsorption capacity is not clear at this stage.

4. Conclusions

Based on gas adsorption experiments for Toyoura sand, a lower gas adsorption capacity onto soil of isohexane, a gaseous aliphatic, than that of a chlorinated organic compound gas such as TCE or toluene was observed. This result has been attributed to the lower polarity of isohexane. The lower K_g values of isohexane gas may indicate the higher mobility of gaseous aliphatic in soil than that of TCE or toluene, and the lower polarity of isohexane may indicate the importance of soil-water conditions for the management of contaminated soils by petroleum chemicals such as aliphatic.

The gas adsorption capacity of Tachikawa loam (volcanic ash soil) was significantly higher than that of Toyoura sand due to the existence of a highly porous mineral such as allophane. The aggregate structure of volcanic ash soil as well as organic matter strongly enhanced gas adsorption onto volcanic ash soil. Regardless of the insolubility of isohexane, the effect of the aggregate structure on gas adsorption was strong under the wet condition. In addition, a larger particle or aggregate size contributed to stronger gas adsorption onto volcanic ash soil under dry and wet conditions, suggesting a contribution of macroaggregates to gas adsorption. As the role of macroaggregates in gas adsorption is not fully understood, more experimental and theoretical investigations into gas adsorption to volcanic ash soil are needed for a better understanding of gas movement, risk assessment, and the cleaning of contaminated soils by VOC, including petroleum chemicals.

References

- [1] ACGIH (American Conference of Governmental Industrial Hygienists), Documentation of the Threshold Limit Values and Biological Exposure Indices, 6th ed., ACGIH, Cincinnati, OH, 1991.
- [2] S. Amali, L.W. Petersen, D.E. Rolston, P. Moldrup, Modeling multicomponent volatile organic and water vapor adsorption on soils, *J. Hazard. Mater.* 36 (1994) 89–108.
- [3] F. Bartoli, A.J. Poulencard, B.E. Schouller, Influence of allophane and organic matter contents on surface properties of Andosols, *Eur. J. Soil Sci.* 58 (2007) 450–464.
- [4] J.H. Dane, J.W. Hopmans, Hanging water column, in: J.H. Dane, G.C. Topp (Eds.), *Methods of Soil Analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 680–683.
- [5] J.H. Dane, J.W. Hopmans, Pressure cell, in: J.H. Dane, G.C. Topp (Eds.), *Methods of Soil Analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 684–688.
- [6] P.R. Day, Particle fractionation and particle size analysis, in: *Method of Soil Analysis, Monograph No. 9, Am. Soc. Agron, Madison, WI, 1965*, pp. 545–567.
- [7] S. De Gryze, J. Six, R. Merckx, Quantifying water-stable soil aggregate turnover and its implication for soil organic matter dynamics in a model study, *Eur. J. Soil Sci.* 57 (5) (2006) 693–707.
- [8] K. Egashira, Y. Kaetsu, K. Takuma, Aggregate stability as an index of erodibility of ando soils, *Soil Sci. Plant Nutr.* 29 (1983) 473–481.
- [9] T. Fujikawa, T. Miyazaki, Effects of bulk density on the gas diffusion coefficient in repacked and undisturbed soils, *Soil Sci.* 170 (2005) 892–901.
- [10] G.W. Gee, D. Or, Particle-size analysis, in: J.H. Dane, G.C. Topp (Eds.), *Methods of soil analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 255–293.
- [11] D. Hillel, Soil structure and aggregation, *Environ. Soil Phys.* (1998) 101–125 (Part II, Chapter 5).
- [12] J. Hine, P.K. Mookerjee, The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions, *J. Org. Chem.* 40 (1975) 292–298.
- [13] L.C. Hull, Soil gas surveying techniques and interpretation, in: Paper presented at the in situ characterization and monitoring technique workshop, Idaho Falls, Idaho, June 7–9, 1988.
- [14] H.F. Livingston, The cross-sectional areas of molecules adsorbed on solid surfaces, *J. Colloid Sci.* 4 (1949) 447–458.
- [15] MOE, Property owners considerations for the control of oil odor and floating oil films caused by oil contaminated soil, in: *Guidelines on the control of oil contamination, Soil Environment Management Division Environmental Management Bureau Ministry of the Environment Government of Japan, 2006*.
- [16] F.B. Metting Jr. (Ed.), *Soil Microbial Ecology: Applications in Agricultural and Environmental Management*, Marcel Dekker, New York, 1993.
- [17] T. Miyamaoto, T. Annaka, J. Chikushi, Soil aggregate structure effects on dielectric permittivity of an andisol measured by time domain reflectometry, *Vadose Zone J.* 2 (2003) 90–97.
- [18] P. Moldrup, S. Yoshikawa, T. Olesen, T. Komatsu, D.E. Rolston, Air permeability in undisturbed volcanic ash soils: predictive model test and soil structure fingerprint, *Soil Sci. Soc. Am. J.* 67 (2003) 32–40.
- [19] R.A. McBride, Atterberg limits, in: J.H. Dane, G.C. Topp (Eds.), *Methods of soil analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 389–398.
- [20] K. Muraoka, J. Yamauchi, K. Ishiuchi, Relationship between soil structure and mechanics of vapor sorption, *J. Environ. Syst. Eng.* 678 (19) (2001) 21–30 (in Japanese with English summary).
- [21] J.R. Nimmo, K.S. Perkins, Aggregate stability and size distribution, in: J.H. Dane, G.C. Topp (Eds.), *Methods of soil analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 317–328.
- [22] S.K. Ong, L.W. Lion, Effects of soil properties and moisture on the sorption of trichloroethylene vapor, *Water Res.* 25 (1991) 1031–1037.
- [23] L.W. Petersen, D.E. Rolston, P. Moldrup, T. Yamaguchi, Volatile vapor diffusion and adsorption in soils, *J. Environ. Qual.* 23 (1994) 799–805.
- [24] L.W. Petersen, P. Moldrup, Y.H. El-Farhan, O.H. Jacobsen, T. Yamaguchi, D.E. Rolston, The effect of moisture and soil texture on the adsorption of organic vapors, *J. Environ. Qual.* 24 (1995) 752–759.
- [25] K.D. Pennell, Specific surface area, in: J.H. Dane, G.C. Topp (Eds.), *Methods of soil analysis. Part 4. SSSA Book Ser. 5, SSSA, Madison, WI, 2002*, pp. 295–315.
- [26] T.G. Poulsen, P. Moldrup, T. Yamaguchi, J.W. Massmann, J.A. Hansen, VOC vapor sorption in soil: Soil type dependent model and implications for vapor extraction, *J. Environ. Eng.* 124 (1998) 146–155.
- [27] T.G. Poulsen, T. Yamaguchi, P. Moldrup, L.W. de Jonge, D.E. Rolston, Predicting volatile organic vapor sorption from soil specific surface area and texture, *J. Environ. Qual.* 29 (2000) 1642–1649.
- [28] P.S.C. Rao, R.A. Ogwada, R.D. Rhue, Adsorption of volatile organic compounds on anhydrous and hydrated sorbents: equilibrium adsorption and energetics, *Chemosphere* 18 (1989) 2177–2191.
- [29] J. Ruiz, R. Bilbao, M.B. Murillo, Adsorption of different VOC onto soil minerals from gas phase: Influence of mineral, type of VOC, and air humidity, *Environ Sci Technol.* 32 (1998) 1079–1084.
- [30] J. Six, E.T. Elliott, K. Paustian, J.W. Doran, Aggregation and soil organic matter dynamics under conventional and no-tillage systems, *Soil Sci. Soc. Am. J.* 49 (1998) 645–651.
- [31] K. Seki, SWRC fit—a nonlinear fitting program with a water retention curve for soils having unimodal and bimodal pore structure, *Hydrol. Earth Syst. Sci. Discuss.* 4 (2007) 407–437.
- [32] Y. Shimizu, N. Takei, Y. Terashiima, Sorption of organic pollutants from vapor phase: the effects of natural solid characteristics and water content, *Water Sci. Technol.* 26 (1992) 79–87.
- [33] S. Shoji, M. Nanzyo, R. Dahlgren, Volcanic ash soils: genesis, properties and utilization Developments in Soil Science, vol. 21, Elsevier, Amsterdam, 1993.
- [34] B.E. Sleep, J.F. Sykes, Modeling the transport of volatile organics in variably saturated media, *Water Resour. Res.* 25 (1989) 81–92.
- [35] J.M. Tisdall, J.M. Oades, Organic matter and water-stable aggregates in soils, *J. Soil Sci.* 62 (1982) 141–163.