

Analysis of adsorption equilibrium of volatile chlorinated organic compounds to dry soil

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Abstract

Adsorption is one of the main mechanisms of soil contamination by hazardous volatile chlorinated organic compounds. The adsorption equilibriums of six volatile organic chlorinated compounds to three dry soils were investigated using batch adsorption experiments. The adsorption equilibriums for the dry soils could be expressed by the Dubinin–Astakhov equation. The equation's parameters were analyzed with the characteristic values of the soils and compounds. No correlation between the values of the affinity coefficients, β , and the molecular volume, M_v , was found. W_0 could be expressed by the functions of a pore volume of less than 10 nm, $V_{<10\text{nm}}$, or the specific surface area, S . The adsorbed amount could be estimated using equations relating E_0 , $V_{<10\text{nm}}$ (or S), and β . The predicted amounts agreed well with the measured data.
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1. Introduction

Recently, soil pollution by hazardous volatile chlorinated organic compounds (VCOCs) such as tetrachloroethylene and trichloroethylene has become a serious problem. Adsorption is one of the main mechanisms in soil pollution. The adsorption characteristic of these hazardous compounds in soil must be clarified to understand the extent of the contamination and to select an effective cleanup method. However, there have been few reports on the adsorption to soil from the gas phase.

In some reports, the adsorption isotherms from the gas phase to wet soil were represented by the Freundlich equation [1,2]. Moreover, in other reports, the adsorption to wet soil could be expressed by the Henry equation [3–5]. The adsorbed amounts could be estimated using equations relating the organic content and the water content of each soil, and the *n*-octanol/water partition coefficient and Henry's constant for the gas–water equilibrium of each compound.

However, near the soil surface, the water content decreased and a different adsorption mechanism for surface

dry soil was observed. In some reports, the amount adsorbed by dry soil increases in comparison with wet soil [4–8]. For the adsorption of trichloroethylene to dry soil, the surface area correlated with the soil–gas equilibrium constant. A few reports conducted a qualitative analysis; however, the correlations between the adsorbed amounts and the characteristic values of the soils and compounds have not been sufficiently analyzed.

Concerning the adsorption isotherms of porous materials, the Langmuir Eq. (1) is assumed to be monolayer adsorption, and the BET Eq. (2) is assumed to be multilayer adsorption. The gas adsorption by micropore adsorbents such as activated carbon was represented by the Dubinin–Astakhov Eqs. (3) and (4). Confirming the type of adsorption isotherm that can be applied to dry soil is necessary. Here, for the Langmuir equation's parameters, C_S (mg/kg dry soil) is the equilibrium adsorbed weight per unit dry weight of soil, and C_G (mg/m³) is the concentration of the adsorbate in gas. Moreover, a and b are the parameters of the Langmuir equation. In the BET equation, v and v_m (ml/kg dry soil) are the equilibrium adsorbed volume and the monolayer adsorbed volume per unit dry weight of soil. x is the relative pressure p/p_0 . In the Dubinin–Astakhov equation, W (ml/kg dry soil) is the adsorbed volume per unit dry weight of soil. W_0 is the limiting adsorbed volume. E (kJ/mol) is the specific

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adsorption energy. E_0 is the E value of a standard compound. A (J/mol) is the adsorption potential. n is the parameter of the adsorption isotherm. β is the affinity coefficient. R (J/mol) is the gas constant. T (K) is the experimental temperature.

Langmuir equation:

$$C_S = \frac{abC_G}{1 + aC_G} \quad (1)$$

BET equation:

$$v = \frac{v_m Cx}{(1-x)(1-x+Cx)}, \quad x = \frac{p}{p_0} \quad (2)$$

Dubinin–Astakhov equation:

$$W = W_0 \exp \left[- \left(\frac{A}{E} \right)^n \right] = W_0 \exp \left[- \left(\frac{A}{\beta E_0} \right)^n \right] \\ = W_0 \exp \left[- \left(\frac{1}{E_0} \right)^n \left(\frac{A}{\beta} \right)^n \right] \quad (3)$$

$$A = RT \ln \left(\frac{p_0}{p} \right) \quad (4)$$

In this study, we confirmed the type of adsorption isotherm that can be applied to the adsorption of VCOCs to dry soils. Moreover, the adsorption isotherm's parameters were analyzed by the relations between the characteristic values of

the compounds and the soils. The adsorption mechanism of VCOCs to dry soils and a prediction method of the adsorbed amount were considered.

2. Materials and methods

Tetrachloroethylene (PCE), trichloroethylene (TCE), *cis*-1,2-dichloroethylene (*cis*-1,2-DCE), 1,1,1-trichloroethane (MC), 1,1,2-trichloroethane (1,1,2-TCA), and 1,2-dichloroethane (1,2-DCA) were employed in this study. Three types of dry soils were used after sieving under 2 mm, and dried at 105 °C for 24 h. The surface areas, the organic carbon contents, the water contents of the sampling time and the true densities of the soil samples are summarized in Table 1. Moreover, the pore volume distributions of the soils are shown in Fig. 1.

Based on batch tests, the amount of these compounds adsorbed on the container was not negligible for the low adsorptive wet soils. However, since the dry soils adsorbed many VCOCs, the adsorption on the container was ignored, and a batch type adsorption apparatus was used in this study.

About 2–20 g soil samples were put into 100 ml (internal volume 125 ml) vials. The vials were sealed with teflon-faced butyl-rubber septa and placed in a constant temperature water bath. The test compounds were injected through each septum using a syringe. The injected weight

Table 1
Properties of soil samples

	Sampling site	Water content a (%)	True density ρ_{DS} (g dry soil/ml)	Organic carbon content α (g C/g dry soil)	Surface area S (m ² /g dry soil)	Pore volume (<0.1 mm) (cm ³ /g dry soil)	Effective diameter D_{10} (μ m)	Uniformity coefficient D_{60}/D_{10} [–]
Sand A	Hiratuka city	7.3	2.5	0.0022	15	0.028	26	8.2
Kanto loam A	Yokohama city	45	2.5	0.013	180	0.19	2.2	18
Black soil A	Yokohama city	40	2.0	0.078	51	0.057	4.2	9.7

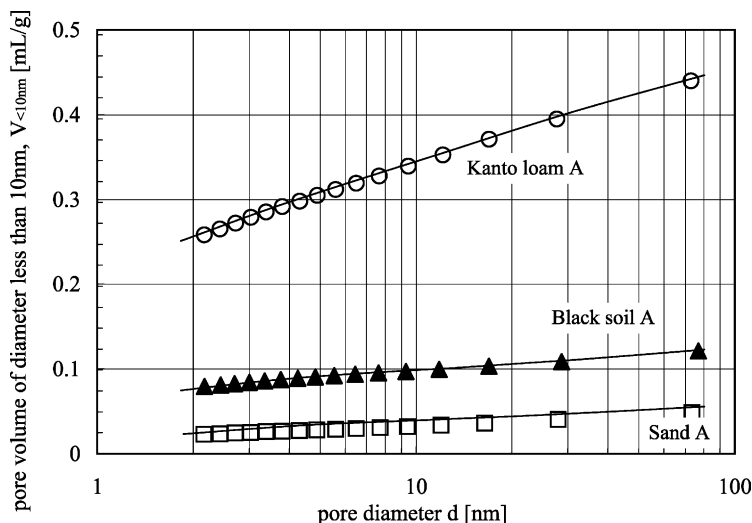


Fig. 1. Pore volume distribution of soil samples.

M (μg) was calculated by the difference in the syringe weights before and after the injection.

After more than 48 h and until the gas concentration stabilized not change, the vials were placed in a water bath at 15°C . The headspace gas concentration, C_G (mg/m^3 air), was analyzed by a gas chromatograph (Shimadzu model GC-14A) with an electron capture detector (ECD). A 25 m, 0.2 mm i.d. fused silica 5% phenyl–methylsilicone phase capillary column (Shimadzu, CBP-5) was used. The equilibrium adsorbed amount, C_S (mg/kg dry soil), was calculated by Eq. (5).

$$C_S = \frac{M - (125 - W_S/D_S) \times 1000 \times C_G}{W_S} \quad (5)$$

Here, W_S (g dry soil) is the dry soil weight and D_S (g dry soil/ml) is the true density of the dry soil.

3. Results and discussion

3.1. Adsorption isotherm equation to dry soil

Three major adsorption isotherms, the Langmuir equation, the BET equation and the Dubinin–Astakhov equation, were examined to determine which one of these best represents the adsorption of VOCs to dry soil. The results are shown in Figs. 2–4, respectively. The equilibrium adsorbed amount could not be expressed well by the Langmuir equation or by the BET equation. These results were similar for all the soil samples and all the compounds. However, in Figs. 2–4, the equilibrium adsorbed volumes were expressed very well by the Dubinin–Astakhov equation, an equal linear line with a limiting adsorbed volume for all compounds. Therefore, the adsorption potential theory, filled up from a pore volume of high absorption potential, was applicable. Here, when the

Table 2
 β with standard compound PCE for each volatile organic chlorinated compound

	β [–]
PCE	1
TCE	1.14
MC	1.40
<i>cis</i> -1,2-DCE	1.35
1,2-DCA	1.75
1,1,2-TCA	1.40

value of n was 1.5, the linear line was the best fit. The values of the major activated carbons were between 1.5 and 2.3, and the value of a small pore activated carbon was 3.0. Abe et al. [9] reported that the value of n decreased with an increase in the pore diameter. Because the pore diameter of soils is bigger than that of the activated carbons, the value of n was comparatively small. Furthermore, the adsorption isotherms to *S* and *A* and Kanto loam *A* were expressed by one equation with the same β value when PCE was a standard compound ($\beta = 1$). However, the adsorption isotherms to black soil *A* were represented by two lines. The intercept values of W_0 were equal, and the slopes were different in chloroethylenes and chloroethanes. The values of E_0 were calculated from the slopes of the adsorption isotherms. β is summarized in Table 2. W_0 and E_0 are summarized in Table 3.

3.2. Analysis of relation between parameters of adsorption isotherm and the characteristic values of the soils and compounds

The adsorption isotherm parameters in Tables 2 and 3 were analyzed. First, the β values were analyzed. Dubinin and Tomofeyev [10], and Wood [11,12] reported that the β values of the adsorption for activated carbon have a posi-

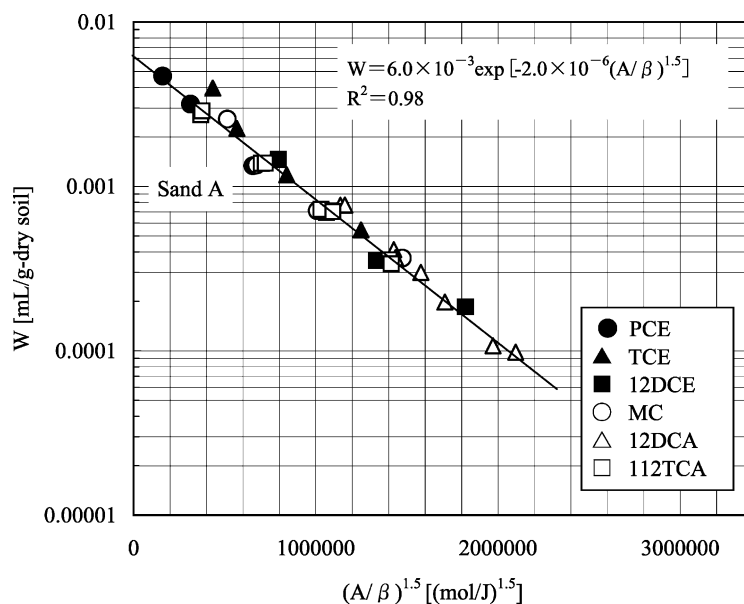


Fig. 2. Application of the Dubinin–Astakhov equation (sand A).

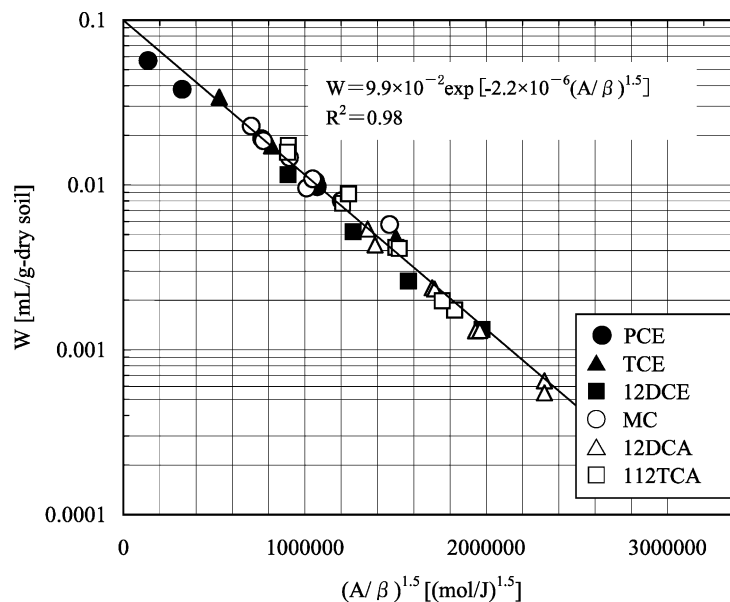


Fig. 3. Application of the Dubinin–Astakhov equation (Kanto loam A).

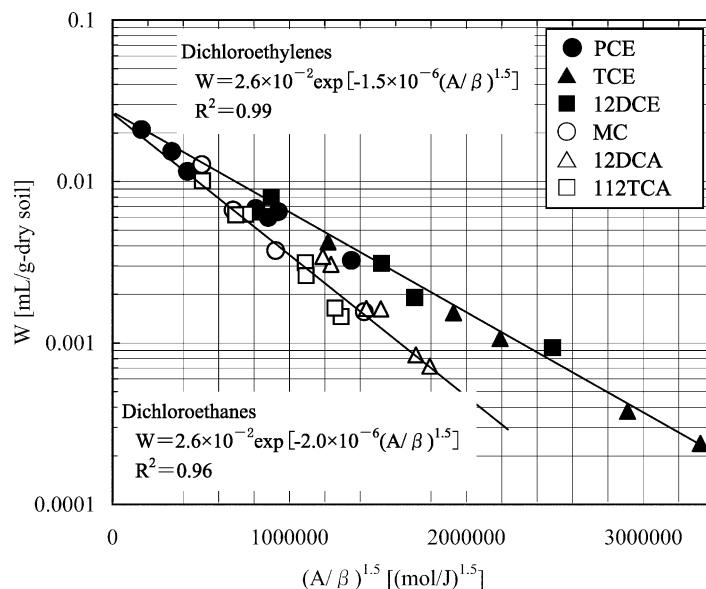


Fig. 4. Application of the Dubinin–Astakhov (black soil A).

tive correlation with the molecular volume M_v . In this study, such a result is not observed in Fig. 5. However, the β values in this study were in the range of the correlation dispersion of the above reports. Moreover, the β values of the

chloroethanes were significantly higher than the values of the chloroethylenes. Because the soil surface was hydrophilic, the polar compounds were easily adsorbed on the soil surface, and the β values increased.

Table 3
 W_0 , E_0 and physical properties of soil samples

	W_0 (ml/g dry soil)	E_0 (J/mol)	Surface area S (m^2/g dry soil)	Pore volume (ml/g dry soil)		
				<75 nm	<10 nm	<2 nm
Sand A	6.0E-03	6.4E+03	15	0.048	0.032	0.022
Kanto loam A	9.9E-02	6.0E+03	182	0.44	0.34	0.25
Black soil A (chloroethylenes)	2.6E-02	7.8E+03	51	0.12	0.098	0.077
Black soil A (chloroethanes)	2.6E-02	6.3E+03	51	0.12	0.098	0.077

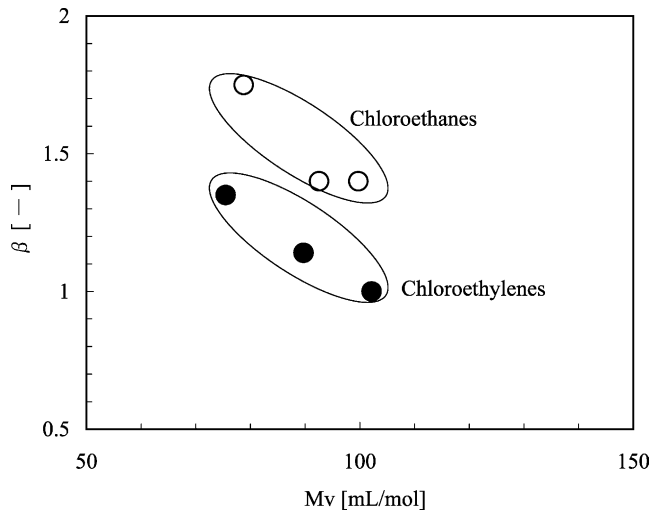


Fig. 5. Relationship between the molecular volume M_v and β .

Secondly, the E_0 values in Table 3 were analyzed. The E_0 values of each soil had similar behavior at $(6.0\text{--}6.4) \times 10^3$; however, the E_0 value of black soil A for chloroethylenes was 7.8×10^3 . This means that dichloroethylenes, with low polarity and high affinity for soil organic substances, adsorb more easily in comparison with the dichloroethanes, because black soil A had a high organic carbon content. Though it is necessary to examine the relation between the organic carbon content and the E_0 values of the high organic carbon content soils in more detail, the E_0 values for the low organic carbon content soils were about 6.2×10^3 .

Third, the W_0 values were analyzed. The relations between W_0 and $V_{<10\text{nm}}$ are shown in Fig. 6. The relation between W_0 and S is shown in Fig. 7. Though the data is limited, W_0 had a good positive correlation with $V_{<10\text{nm}}$ or S . In the range of $V_{<2\text{nm}}\text{--}V_{<75\text{nm}}$ for the pore diameter, when we checked for the correlation between W_0 and pore volume, a good correlation of more than $R^2 = 0.99$ was found. In this study, $V_{<10\text{nm}}$ with the best correlation ($R^2 = 1.00$) was employed as the correlation equation. In addition, the volume ratios of W_0 for $V_{<2\text{nm}}$ and $V_{<10\text{nm}}$ were 27

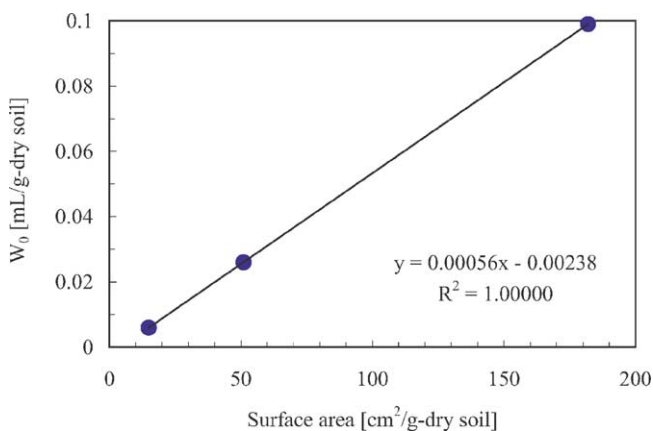


Fig. 6. Relationship between the surface area S and W_0 .

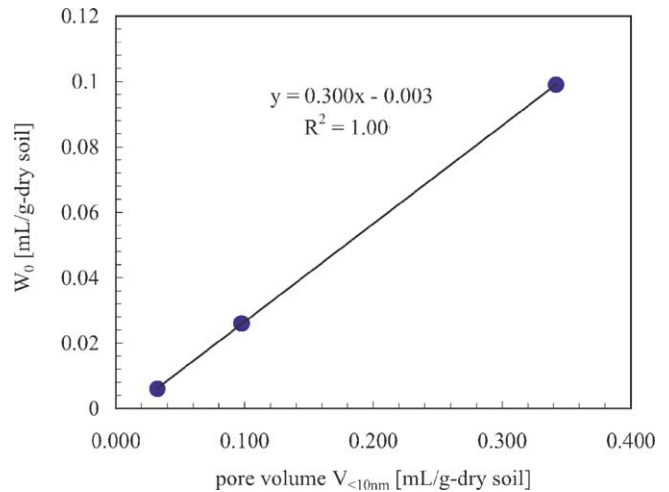


Fig. 7. Relationship between the pore volume $V_{<10\text{nm}}$ and W_0 .

and 12% for sand A, 40 and 23% for Kanto loam A, and 34 and 22% for black soil A. Therefore, all the micropores were not filled up because there are very small micropores through which VCOCs do not pass. From the above results, W_0 could be estimated using Eq. (6) or Eq. (7).

$$W_0 = 0.000553 \times S - 0.00261 \quad R^2 = 1.00 \quad (6)$$

$$W_0 = 0.298 \times V_{<10\text{nm}} - 0.00378 \quad R^2 = 1.00 \quad (7)$$

Here, $V_{<10\text{nm}}$ (cm^3/g dry soil) was the pore volume with a diameter of less than 10 nm.

3.3. Prediction of adsorbed amounts to dry soil from characteristic values of compounds and soils

W_0 could be expressed by the characteristic values of the soils using Eq. (6) or Eq. (7). The values of β and E_0 could be expressed using the experimental constant values summarized in Tables 2 and 3. From Eqs. (3) and (6), the equilibrium adsorbed volumes to dry soil, W , could be estimated by Eq. (8). Therefore, C_S could be expressed by Eq. (9).

$$W = (5.53 \times 10^{-4} \times S - 0.00261) \times \exp \left[- \left(\frac{RT \ln(p_0/p)}{\beta E_0} \right)^{1.5} \right] \quad (8)$$

$$C_S = (5.53 \times 10^{-4} \times S - 0.00261) \times \exp \left[- \left(\frac{RT \ln(p_0/p)}{\beta E_0} \right)^{1.5} \right] \times \rho_L \quad (9)$$

The predicted adsorbed amounts using Eq. (9) are compared with the measured data in Figs. 8 and 9. For black soil A, the E_0 value was the experimental value. Both values for the 90% data agree well within $\pm 30\%$. Therefore, the equilibrium adsorbed amounts of the dry soil could be predicted using Eq. (8).

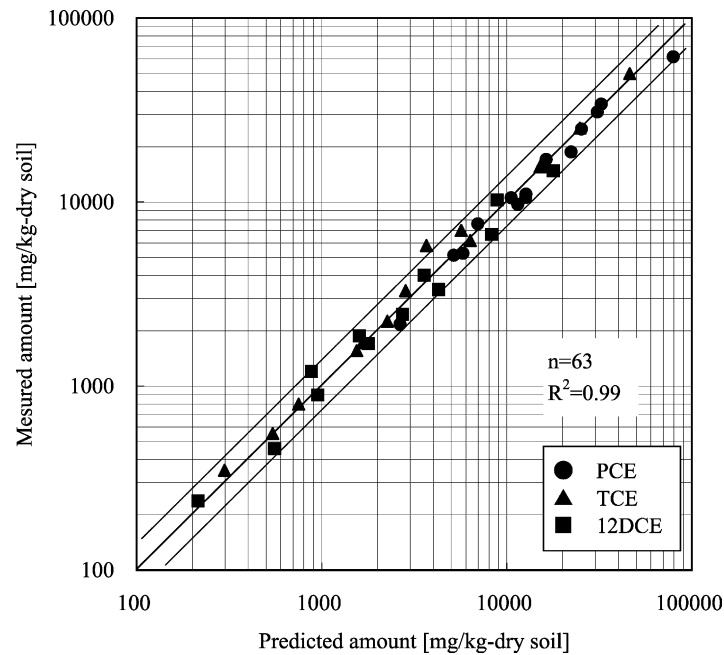


Fig. 8. Comparison of the estimated amounts with the measured amounts (chloroethylenes).

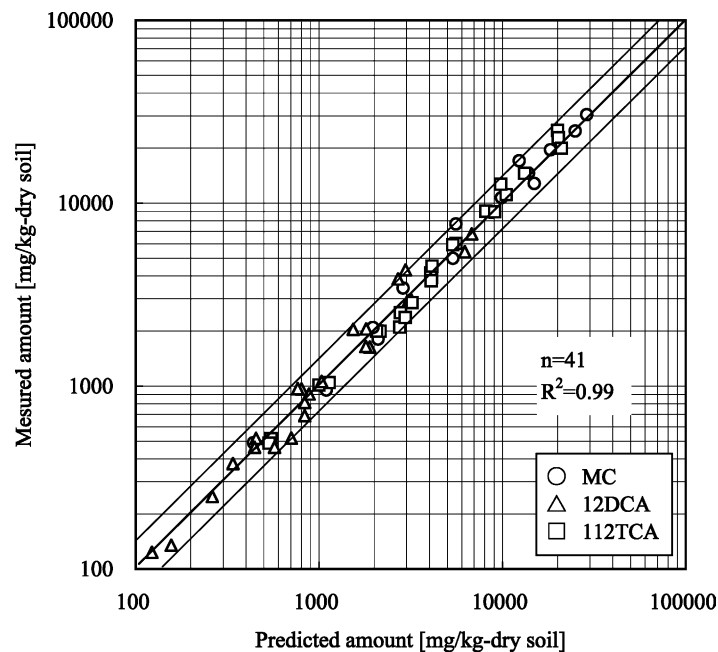


Fig. 9. Comparison of the estimated amounts with the measured amounts (chloroethanes).

4. Conclusion

Adsorption is one of the main mechanisms in soil contamination by hazardous volatile chlorinated organic compounds. We determined the adsorption isotherms of six volatile chlorinated organic compounds (VCOCs) to three types of dry soil as a basic study to analyze soil pollution with VCOCs. The adsorption isotherm parameters were estimated by the relations between the characteristic values of the soils and the compounds. The adsorption mechanism to

dry soils and the prediction method of the adsorbed amount were discussed.

- (1) The adsorption equilibriums of the VCOCs for the dry soil could be expressed by the Dubinin–Astakhov Eq. (3).
- (2) A correlation between the values of β and the molecular volume M_v was not found, but the values of β were characteristic values of the compounds. The values of E_0 for almost all the soils were ca. 6.2×10^3 , though

the value of black soil A for the chloroethylenes was 7.8×10^3 .

- (3) The values of W_0 could be expressed by the functions of the pore volume of pores smaller than 10 nm, $V_{<10\text{nm}}$ or the specific surface area S . Therefore, the micropores of the soil mainly contribute to the absorption.
- (4) The adsorbed amount, C_{ST} , could be predicted by Eq. (9) from the specific adsorption energy of a standard compound, E_0 , and the pore volume, $V_{<10\text{nm}}$, or the surface area, S , and the affinity coefficient, β . It was also confirmed that the predicted amounts agreed well with the measured data.

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