Effect of soil organic carbon on the quantification of jet-fuels in soil using partitioning tracer method

Sungsu Rhee [a], Seunghak Lee [b], Junboum Park [c],*

[a] Seoul National University Engineering Research Institute, San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-742, Republic of Korea
[b] Water Environment Center, Environment Division, Korean Institute of Science and Technology, Seoul 136-791, Republic of Korea
[c] Department of Civil and Environmental Engineering, Seoul National University, San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-742, Republic of Korea

ABSTRACT

Partitioning tracer method has been studied as an effective technique for estimating the light nonaqueous-phase liquid (LNAPL) contamination in the subsurface. This study is for investigating the effect of soil organic contents on the LNAPL quantification using partitioning tracer method. The sorption characteristics of alcohol tracers to the soils having different organic carbon contents were evaluated by sorption isotherm experiments. In the column tests, the soils were contaminated with jet-fuel and the average saturations of residual jet-fuel were estimated by partitioning tracer method and compared with that by the volume measurement. The sorption results indicated that considerable amount of 4-methyl-2-pentanol and hexanol could be sorbed to the soils and the sorption amount of 2-ethyl-1-butanol was relatively smaller than those of the other alcohol tracers. The column experiments demonstrated that the accuracy of quantification for the jet-fuel by partitioning tracer method should decrease with increasing the soil organic carbon contents. However, the accuracy could be enhanced by considering the sorption of tracer to the soils, especially for the tracer of 2-ethyl-1-butanol.

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1. Introduction

Subsurface contamination by spills and leaks of petroleum-based liquids has become an issue of great concern and importance in recent years [1,2]. Petroleum hydrocarbons including gasoline, fuel oil and jet-fuel are called as light nonaqueous-phase liquids (light NAPLs, LNAPLs) since their densities are less than that of water ($1 \, g/cm^3$). Once LNAPL is released into the subsurface, it tends to float along the top of the capillary fringe and usually stays in the unsaturated zone, or is left behind in the saturated zone due to the variation of groundwater table [3–5].

Remediation of the LNAPL-contaminated sites could be divided as the source zone control and the treatment of contaminants dissolved in groundwater. Successful source control largely depends on the accurate delineation for the volume of LNAPLs in the targeted sites [6]. However, the conventional methods based on the point analysis like soil coring, cone penetrometer testing, soil gas analysis, aqueous-phase sampling, etc., are not effective for quantifying the LNAPL contamination because these methods could not estimate the residual state of LNAPL beyond the sampling point [7–9]. A major weakness of these methods is that they could provide data only at the discrete points and cover relatively small aquifer volumes [1,8]. The partitioning tracer method has been studied as an alternative, non-invasive method for locating and quantifying NAPL saturation in the subsurface.

The partitioning tracer method has been studied as an effective technique for estimating the contamination with nonaqueous-phase liquids (NAPLs) in the subsurface by previous researchers [3,6,8–15]. In this method, the partitioning tracer is reversibly retained by NAPL while the nonpartitioning tracer stays in the water phase, which should consequently cause the difference in the flowing velocities of two tracers in the subsurface. The average saturation of residual NAPL, S_n, within the swept pore volume can be calculated by the following equation [3]:

$$R = \frac{\bar{t}_p}{\bar{t}_n} = 1 + \left(\frac{\rho_b}{\theta_w}\right) K_d + \left[\frac{S_n}{1 - S_n}\right] K_{nw} \tag{1}$$

where R is for the retardation factor, $\bar{t}_p$ for the travel time of the partitioning tracer, $\bar{t}_n$ for the travel time of the nonpartitioning tracer, ρ_b for the bulk density of porous media, θ_w for the water-filled porosity, K_d for the water-aquifer solids partition coefficient, and K_{nw} for the NAPL–water partition coefficient. Eq. (1) has been generally adopted in the partitioning tracer method characterizing the NAPL contamination within the saturated aquifer. It assumes that the nonpartitioning tracer partitions into neither the NAPL phase nor the soil matrix, while the partitioning tracer partitions linearly into the NAPL phase and the soil matrix in equilibrium without

* Corresponding author. Tel.: +82 2 880 1438; fax: +82 2 875 6933.
E-mail address: junbpark@snu.ac.kr (J. Park).

other types of partitioning such as the water–NAPL interface or the water-gas partitioning.

The second term on the right-hand side of Eq. (1), could be neglected when there is negligible sorption of the tracer by the soil matrix [1,3,16,17]. However, sorption of the partitioning tracer to the soil matrix may increase the retardation of the partitioning tracer and affect the accuracy of the partitioning tracer method. Jin et al. [18] suggested that there is a potential for interference due to sorption of tracers to immobile sedimentary organic carbon and/or mineral surfaces at low residual NAPL saturation. And Schwartz and Zhang [19] have reported that the range of organic carbon contents in geologic materials could be extremely variable. Therefore, if the aquifer has the high organic carbon contents in the soil, the quantification of NAPL by partitioning tracer method could be inaccurate due to the sorption of partitioning tracer to soil organic matter.

The purpose of this study is to investigate the effect of soil organic carbon on the LNAPL quantification in the partitioning tracer method. Soils having different organic carbon contents were contaminated with the jet-fuel. The average saturations of residual jet-fuel in the soils were estimated by partitioning tracer method and compared with those by the method of volume measurement.

2. Experimental methods

2.1. Materials

Jumunjin sand, the silica sand commercially available in Korea, was used for representing the alluvial aquifer material having no significant amount of soil organic matter. The weathered granite soil collected from the vicinity of Seoul National University was used for representing the materials in weathered granite aquifer which is commonly found in Korea. Soil properties of Jumunjin sand and weathered granite soil are summarized in Table 1, and chemical and mineralogical constituents of Jumunjin sand and weathered granite soil are summarized in Table 2, which were estimated by XRF (Shimadzu XRF-1700, Japan) and XRD (Rigaku D/Max 2200, Japan), respectively.

Commercial organic fertilizer, passing through No. 10 sieve (2 mm opening size) and retained by No. 40 sieve (0.420 mm opening size), was used to represent the organic matter in soil matrix. The main components of the organic fertilizer were rice straw and poultry wastes and the effective particle size of the organic fertilizer was 1.61 mm. Table 2 shows the chemical and mineralogical constituents of the organic fertilizer. Jumunjin sand was mixed with organic fertilizer to prepare three soil mixtures of MIX A, MIX B and MIX C having different organic carbon contents. The mixing ratios

of Jumunjin sand to organic fertilizer were 19:1 (MIX A), 9:1 (MIX B), and 4:1 (MIX C) by weight.

Chloride (Sigma–Aldrich, USA), 4-methyl-2-pentanol (Sigma–Aldrich, USA), 2-ethyl-1-butanol (Sigma–Aldrich, USA) and hexanol (Sigma–Aldrich, USA) were employed as tracers in this study. Chloride was generally known as a non-reactive and ideal tracer [20] and chosen as a conservative and nonpartitioning tracer. The alcohol tracers were chosen as a partitioning tracer showing good separations in tracer response curves during partitioning tracer test. Three alcohols having the same molecular weight (102.2 g/mol) were selected to consider the general effect of the molecular structure on partitioning of alcohols between jet-fuel and water.

Commercial jet-fuel was used for representing the petroleum hydrocarbons of LNAPL in soil matrix, and the conductivity and the density of the jet-fuel at 15 °C were 224 ps/m and 0.7919 g/cm^3, respectively. The jet-fuel was dyed with Sudan IV (Sigma–Aldrich, USA) at a concentration of 0.1 g/L for visual identification of the jet-fuel phase. The dyed jet-fuel was filtered with 0.45 μm membrane filter to remove any insoluble dye. Although the addition of Sudan IV probably had some effect on the partition coefficient of tracers, these were expected to be negligible for the very low molar fraction that Sudan IV represents in NAPL [21]. The dyed jet-fuel was used in both of the batch-partitioning experiment and the column studies.

2.2. Partitioning of tracer between jet-fuel and water

Partitioning of alcohol tracers between water and the dyed jet-fuel (with Sudan IV) was estimated by batch experiments. Ten mL of alcohol tracer solutions having the concentration of 100–600 mg/L were placed in 20 mL vials with the same volumes of dyed jet-fuel, and sealed with Teflon-lined screw cap leaving minimum

Table 1
Soil properties of Jumunjin sand and weathered granite soil.

	Jumunjin sand	Weathered granite soil
Specific gravity	2.64	2.60
Plasticity index	NP[a]	NP
Coefficient of gradation	1.0	1.4
Uniformity gradation	1.5	8.4
Effective particle size	0.57 mm	0.32 mm
Unified soil classification system	SP[b]	SW[c]
Percentage passing sieve No. 200	0%	7.6%
Hydraulic conductivity (cm/s)	9.3×10^{-3}	8.2×10^{-4}

[a] Non-plastic.
[b] Poorly graded sand.
[c] Well graded sand.

Table 2
Chemical and mineralogical constituents of Jumunjin sand, weathered granite soil and organic fertilizer.

Chemical constituents (wt%)				Mineralogical constituents (wt%)			
Constituents	JS[a]	WGS[b]	OF[c]	Constituents	JS	WGS	OF
SiO$_2$	88.50	69.90	60.00	Quartz	74.7	21.7	43.8
Al$_2$O$_3$	6.59	16.00	11.80	Plagioclase	7.2	50.8	7.7
TiO$_2$	0.08	0.15	0.57	K-feldspar	18.1	16.1	14.1
Fe$_2$O$_3$	0.04	1.48	6.55	Muscovite	0.0	11.4	16.4
MgO	0.02	0.16	1.98	Calcite	0.0	0.0	2.7
CaO	0.21	0.39	7.34	Goethite	0.0	0.0	15.1
Na$_2$O	0.12	2.52	0.54				
K$_2$O	3.81	5.70	3.78				
MnO	0.03	0.07	0.37				
P$_2$O$_5$	0.02	0.03	1.33				
LoI[d]	0.50	2.59	5.35				

[a] Jumunjin sand.
[b] Weathered granite soil.
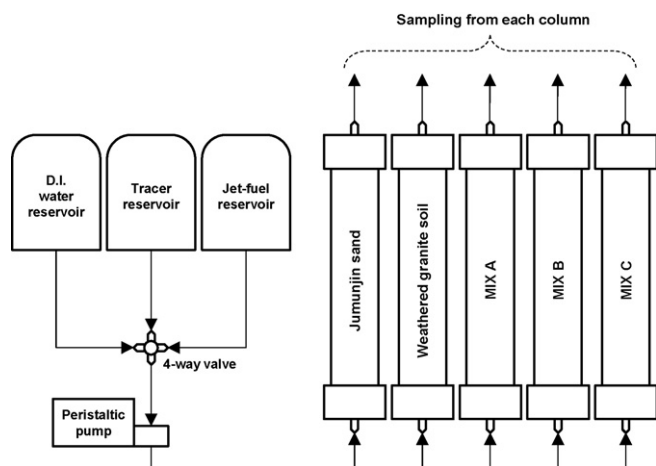[c] Organic fertilizer.
[d] Loss-on-ignition.

Fig. 1. Schematic diagram of column system.

headspace. The vials were placed on rotary shaker for 24 h to reach at equilibrium under room temperature (about 20 °C). After shaking, the vials were kept for 1 h to allow the separation of tracer solution and dyed jet-fuel, and centrifuged for 5 min to achieve complete separation. Samples were collected with a syringe from lower water layer and analyzed for the tracer concentration using gas chromatography (GC, HP-6890, USA). Partition coefficients of tracers between dyed jet-fuel and water were calculated as follows (Eq. (2)):

$$K_{nw} = \frac{c_n}{c_w} \tag{2}$$

where c_n is for the concentration of the tracer in the NAPL phase (mg/L) and c_w for the concentration of the tracer in the water phase (mg/L). c_n was calculated by subtracting c_w from the initial tracer concentration in water.

2.3. Sorption characteristic of tracer to soil

Sorption isotherm experiments were conducted to evaluate the sorption characteristics of alcohol tracers to the test soils. Four grams of test soils were placed in 20 mL vials and the tracer solutions having the concentration of 100–600 mg/L were filled without headspace. The vials were sealed with Teflon-lined screw cap. The vials were placed on a rotary shaker for 24 h to reach at equilibrium under room temperature (about 20 °C). After shaking, the vials were centrifuged for 40 min at 3800 rpm and the supernatant was analyzed for the tracer concentration by GC.

2.4. The effect of soil organic carbon on partitioning tracer test

Partitioning tracer experiments were performed with five columns having different amounts of organic carbon contents in the soils to estimate the effect of soil organic carbon. The schematic diagram of column system is shown in Fig. 1. The columns were made of glass having 3.5 cm diameter and 40 cm length. Each column was dry-packed with Jumunjin sand, weathered granite soil, MIX A, MIX B or MIX C, respectively, by gently tapping the column wall. Column ends were stopped with acrylic cap and the porous stones were placed between the soil and the cap. Dry-packed columns were initially purged with CO_2 gas and then slowly saturated with deionized water at a constant flow rate of 0.15 mL/min for 48 h to remove the trapped air in the soil column. Preliminary tests showed that the soil column was fully saturated with water within 48 h since there was negligible change of the column weight after 48 h of water injection. Ten mM of sodium azide (NaN$_3$, Sigma, USA)

solution was firstly injected into the saturated columns to minimize the bacterial reactivity against alcohol tracer and petroleum. Jet-fuel dyed with Sudan IV was injected into saturated column for 1 pore volume and the residual saturation of jet-fuel was induced by continuously injecting deionized water over 5 pore volumes until no movement of dyed jet-fuel was observed in the column.

Partitioning tracer experiments were repeated with and without the jet-fuel contamination in soil columns. The chloride was used as a nonpartitioning tracer while 4-methyl-2-pentanol, 2-ethyl-1-butanol and hexanol as partitioning tracers. The concentrations of 4-methyl-2-pentanol, 2-ethyl-1-butanol and hexanol were 600 mg/L, respectively, and 100 mg/L for chloride. Tracer solution containing four tracers was injected into the soil columns at a flow rate of 0.14–0.16 mL/min for 0.2 pore volumes followed by the injection of deionized water. Two mL of column effluent samples were collected at every 30 min and analyzed for alcohol tracers and chloride by GC and ion chromatography (IC, Water IC-Pac 432, Korea). The residual saturation of jet-fuel dyed with Sudan IV (S_n) in soil columns was calculated by the following Eq. (3), which has been generally adopted in the previous partitioning tracer test using the method of moments [11]:

$$S_n = \frac{\bar{t}_p - \bar{t}_n}{(K_{nw} - 1)\bar{t}_n + \bar{t}_p} = \frac{R - 1}{K_{nw} + R - 1} \tag{3}$$

The average saturation of residual jet-fuel estimated by partitioning tracer experiment was compared with that by the method of volume measurement. In the method of volume measurement, the residual volume of jet-fuel in the column was calculated by subtracting the volume of jet-fuel produced during the water flood from the volume of jet-fuel initially injected. The average saturation of residual jet-fuel was obtained by dividing the residual jet-fuel volume with the pore volume of the column. The errors of the volumetric measurement were generally resulted from the water solubility and the volatility of jet-fuel, and these possible errors were considered to be minimized during column experiments.

2.5. Analytical method

GC (HP-6890, USA) was equipped with DB-1 fused-silica column (30 m × 0.25 mm i.d., film thickness 0.25 μm, J & W Scientific Inc., USA) and a flame ionization detector (FID). The FID signal was acquired and integrated with a personal computer (PC) using HP Chemstation software (Agilent Technologies, USA). IC (Water IC-Pac 432, Korea) was equipped with IC-Pak anion column (4.6 mm × 5 cm) and operated with the diluted solution of sodium borate/gluconate concentrate as the mobile phase at the flow rate of 1.2 mL/min.

3. Results and discussion

3.1. Partitioning of alcohols between jet-fuel and water

Partitioning of alcohols between water and the dyed jet-fuel is shown in Fig. 2. Results indicated that partitioning of the alcohol between water and the dyed jet-fuel was linear with respect to alcohol concentrations employed in this study. Measured partition coefficients, reflected as the slope of the linear trend, were constant with increasing alcohol concentration in water. Based on these measurements, the partition coefficients for 4-methyl-2-pentanol, 2-ethyl-1-butanol and hexanol between water and the dyed jet-fuel were calculated to be 2.56, 2.73 and 4.03, respectively. The values of partition coefficients for the alcohol tracers having the same molecular weight tended to increase as their molecular structure became simpler. It may imply that the alcohol tracers can possibly show the different partitioning characteristics as a result of their molecular structure as long as they have the same molec-
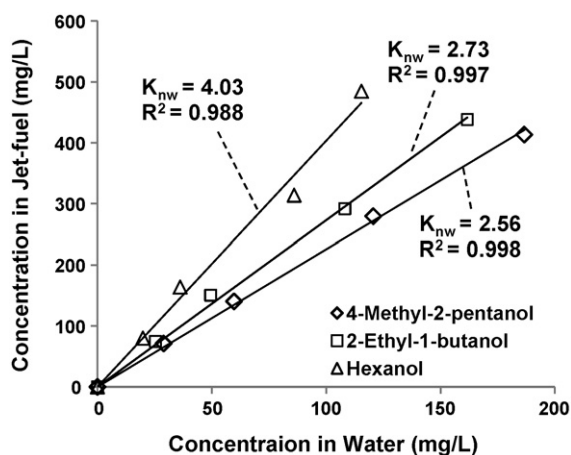
Fig. 2. Partitioning of alcohols between jet-fuel and water.

ular weight. These alcohols might show the different partitioning behaviors toward the jet-fuel and thus present the different shapes of response curves in the partitioning tracer experiment.

3.2. Sorption characteristics of tracers to soils

Sorption isotherm experiments were performed to evaluate the sorption characteristics of different alcohols to the soils having different organic carbon contents without jet-fuel contamination. The data from sorption isotherm experiments were fitted with the linear, Freundlich and Langmuir isotherm models, and the best agreement was found with Freundlich model having the highest R^2 value. Since the sorption term of Eq. (1) considered the linear sorption of tracer between water and soil, the quantification of jet-fuel by Eq. (1) may not be accurate in the cases of the alcohol tracers employed in this study. Alcohol sorptions to the soils are shown in Fig. 3 with the fitting of Freundlich isotherm model [22], and the Freundlich constants are summarized in Table 3.

In the most cases, the amounts of 4-methyl-2-pentanol and hexanol sorbed to the soils were larger than that of 2-ethyl-2-butanol and the sorption amount of 4-methyl-2-pentanol was exponentially increased with the equilibrium concentrations in aqueous phase. The sorption amounts of 2-ethyl-1-butanol to

Table 3
Freundlich isotherm constants for alcohols on test soils.

Test soils	Freundlich constants	4M2P[a]	2E1B[b]	HEX[c]
Jumunjin sand	K_f	0.002	1.169	4.123
	n	0.4643	1.2111	1.2872
	R^2	0.9943	0.9807	0.9526
Weathered granite soil	K_f	52.674	0.077	185.055
	n	2.1911	0.7500	3.6470
	R^2	0.9462	0.9049	0.9555
MIX A	K_f	0.036	1.551	1.326
	n	0.6119	1.0655	1.0043
	R^2	0.9500	0.9989	0.9058
MIX B	K_f	0.002	0.690	14.184
	n	0.4754	0.8939	1.8195
	R^2	0.9979	0.9916	0.9471
MIX C	K_f	0.098	6.872	5.317
	n	0.6871	1.4571	1.2194
	R^2	0.9834	0.9984	0.9982

Freundlich isotherm model used in this study: $S = K_f C_e^{1/n}$ (S is the mass of solute sorbed per dry unit weight of solid (mg/kg), C_e is the concentration of the solute in solution in equilibrium with the mass of the solute sorbed onto the solid (mg/L), K_f is the Freundlich isotherm constant, and n is the Freundlich exponent constant).
[a] 4-Methyl-2-pentanol.
[b] 2-Ethyl-1-butanol.
[c] Hexanol.

most of the soils were smaller than the other alcohol tracers. This indicates that considerable amounts of 4-methyl-2-pentanol and hexanol can be sorbed to the soils and thus the quantitative analysis of the jet-fuel by the partitioning tracer test using 4-methyl-2-pentanol and hexanol can be largely affected by the soil organic carbon. In contrast, the effect of sorption to the soils could be minimized in the tracer test using 2-ethyl-1-butanol. In the case of weathered granite soil (Fig. 3b), the shapes of sorption isotherms were dissimilar to results from the other test soils since the chemical and mineralogical constituents of weathered granite soil were different from Jumunjin sand.

The organic carbon contents in Jumunjin sand, weathered granite soil, and MIX A to C were determined by the loss-on-ignition method [23] and were found to be 0, 0.56, 1.53, 3.07 and 6.10% by weight, respectively. Although, the effect of sorption to the soils could be minimized using 2-ethyl-1-butanol among the test alcohol tracers, the variation of the Freundlich constants (K_f and n) may

Table 4
Retardation factors for alcohols with and without the jet-fuel contamination.

Test soils	Organic carbon contents (wt%)	Tracers	R_{uct} [a]	RR_{uct} [b]	R_{ct} [c]	RR_{ct} [d]
Jumunjin sand	0.00	4-Methyl-2-pentanol	1.05	1.0	1.33	0.9
		2-Ethyl-1-butanol	1.02	0.9	1.47	1.0
		Hexanol	1.05	0.8	1.57	1.0
Weathered granite soil	0.56	4-Methyl-2-pentanol	1.01	1.0	1.15	1.0
		2-Ethyl-1-butanol	1.03	1.0	1.26	1.0
		Hexanol	1.03	0.9	1.28	0.9
MIX A	1.53	4-Methyl-2-pentanol	1.15	1.0	1.47	1.0
		2-Ethyl-1-butanol	1.21	1.0	1.69	1.0
		Hexanol	1.29	0.9	1.97	0.8
MIX B	3.07	4-Methyl-2-pentanol	1.16	0.8	1.57	1.0
		2-Ethyl-1-butanol	1.30	1.0	1.88	0.9
		Hexanol	1.35	0.8	2.21	0.8
MIX C	6.10	4-Methyl-2-pentanol	1.40	1.0	1.63	1.0
		2-Ethyl-1-butanol	1.57	0.8	2.07	1.0
		Hexanol	1.79	0.7	2.43	0.7

[a] Retardation factor of alcohol without jet-fuel contamination.
[b] Recovery ratio of alcohol without jet-fuel contamination.
[c] Retardation factor of alcohol with jet-fuel contamination.
[d] Recovery ratio of alcohol with jet-fuel contamination.
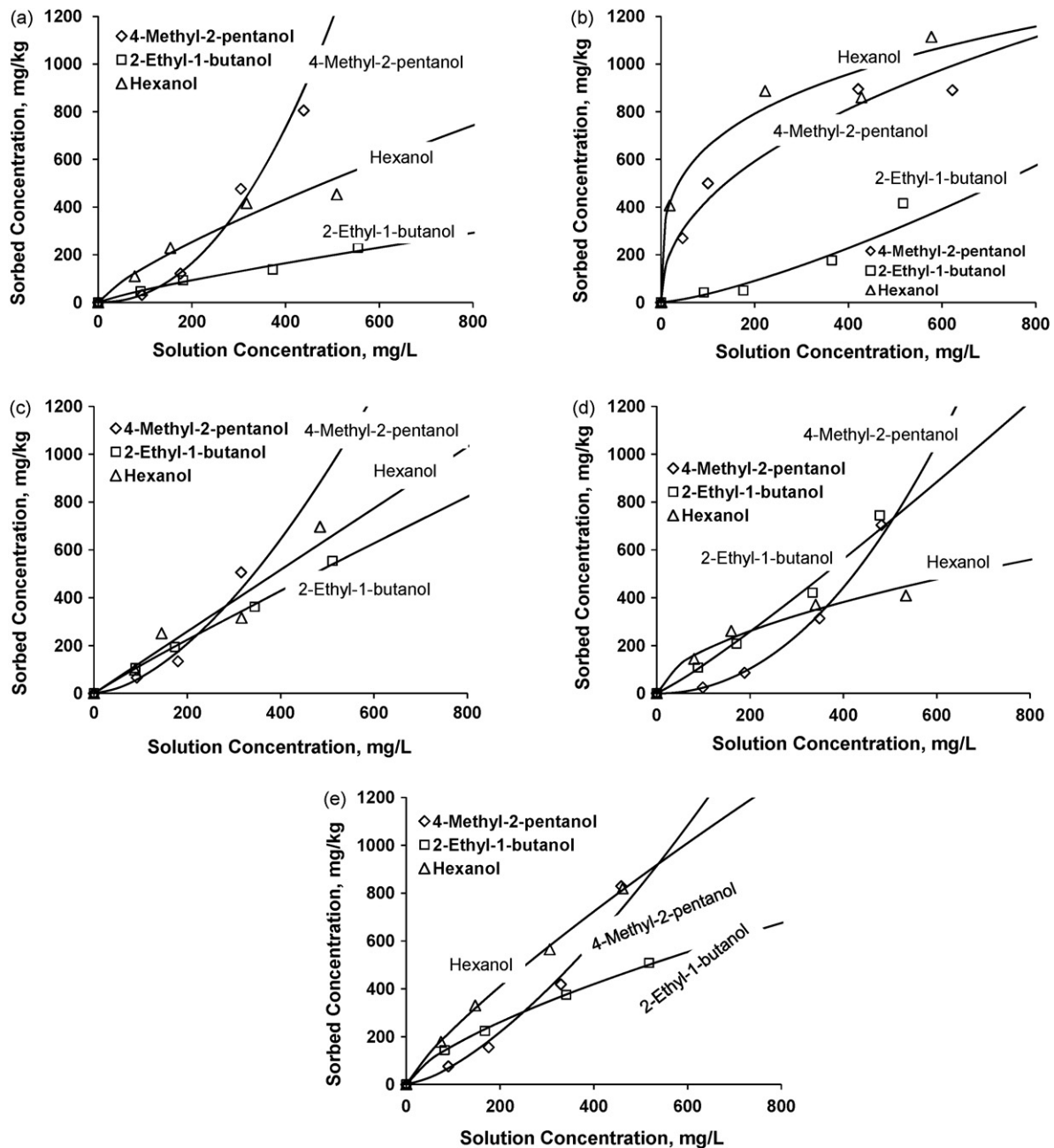
Fig. 3. Sorption isotherms of alcohols on test soils of (a) Jumunjin sand, (b) weathered granite soil, (c) MIX A, (d) MIX B and (e) MIX C.

not be correlated quantitatively with that of the organic carbon contents in the test soils possibly due to the volume of organic fertilizer causing the different solid to liquid ratios in each vial.

3.3. Effect of soil organic carbon on partitioning tracer method

Recovery ratio of tracer, which was the zeroth order moment (the area of breakthrough curve) of injected tracer divided by that of recovered tracers from the soil columns, was calculated and shown in Table 4. All tracers appeared to recover an acceptable amount of the injected tracers.

The effluent concentrations of tracers from the soil columns without the jet-fuel contamination are shown in Fig. 4. The reason why the pore volumes of Fig. 4d and e were larger than the others is that the particle sizes of soil mixtures in MIX A to B were different, though this study used the same size columns for Fig. 4.

Particle size of the organic fertilizer was about 3 times bigger than that of Jumunjin sand. For this reason, the pore volume of the soil column tended to increase with the amount of organic fertilizer in the soil mixture.

The separations between alcohols and chloride could be represented with the retardation factor of alcohol in the uncontaminated soil (R_{uct}) in Table 4. R_{uct} is the travel time of alcohol divided by that of chloride. The separation percentage between the alcohol and chloride can be calculated by the following equation (Eq. (4)):

$$\text{Separation}(\%) = |1 - R_{uct}| \times 100 \tag{4}$$

In Fig. 4 and Table 4, no significant separations of tracers (e.g. less than 5% separation of tracers for Jumunjin sand and less than 3% for weathered granite soil) were observed in the uncontaminated columns even though the soils were found to sorb measurable amount of alcohol tracers in the sorption experiments. The alco-
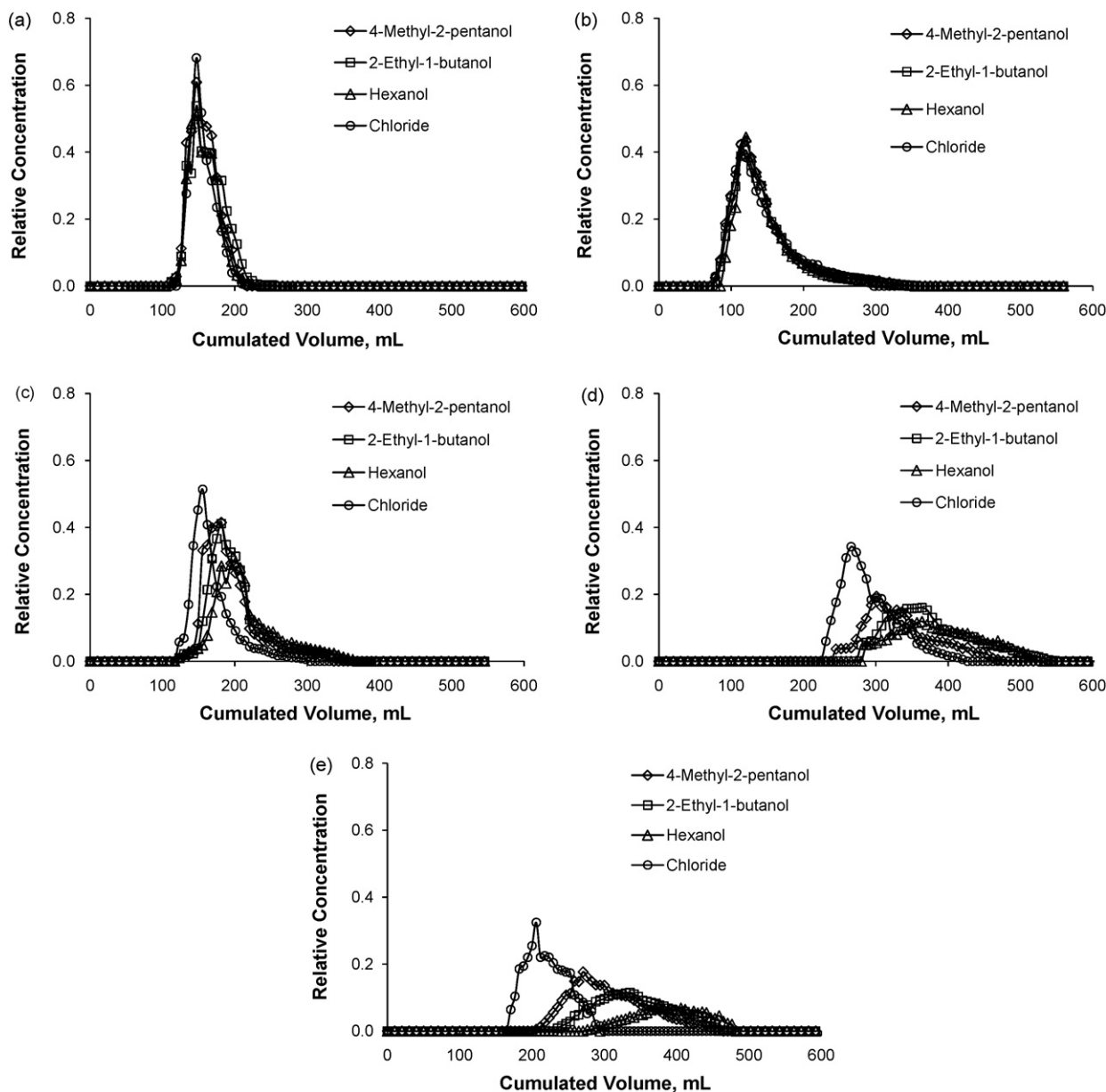
Fig. 4. The effluent concentrations of tracers in uncontaminated soils of (a) Jumunjin sand, (b) weathered granite soil, (c) MIX A, (d) MIX B and (e) MIX C.

hol tracers injected in Jumunjin sand and weathered granite soil without jet-fuel contamination can be possibly considered as non-partitioning and conservative tracers in this system like chloride. Based on the differences of retardation factors ranging from 1 to 5% between the alcohol tracers and chloride, it could be confirmed that the effect of chloride sorption to soils and the retardation of chloride is negligible. These results also indicate that the tracer tests may not be significantly affected by soil organic carbon when the carbon content is less than 0.56% under our test condition.

However, the separation degree of alcohols increased with organic carbon contents in the columns of MIX A to C (Fig. 4). In Fig. 5, it is shown that the separation percentage between alcohols and chloride appears to have a linear relationship with the organic carbon content in the soil. These results indicate that the partitioning tracer method will not necessarily be less accurate, only if the sorption effect is ignored.

The results from the column experiments using MIX A to C were likely different from those of the batch sorption experiments. The retardation factors of 4-methyl-2-pentanol for MIX A to C from the
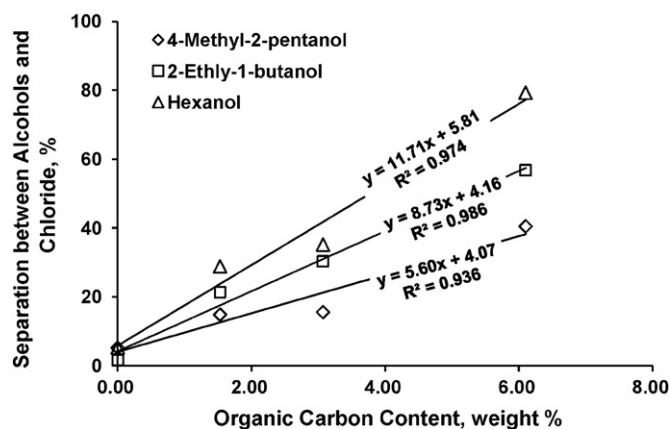

Fig. 5. Separation percentage between alcohols and chloride as a function of the organic carbon content (wt%) in uncontaminated Jumunjin sand and MIX A to C.
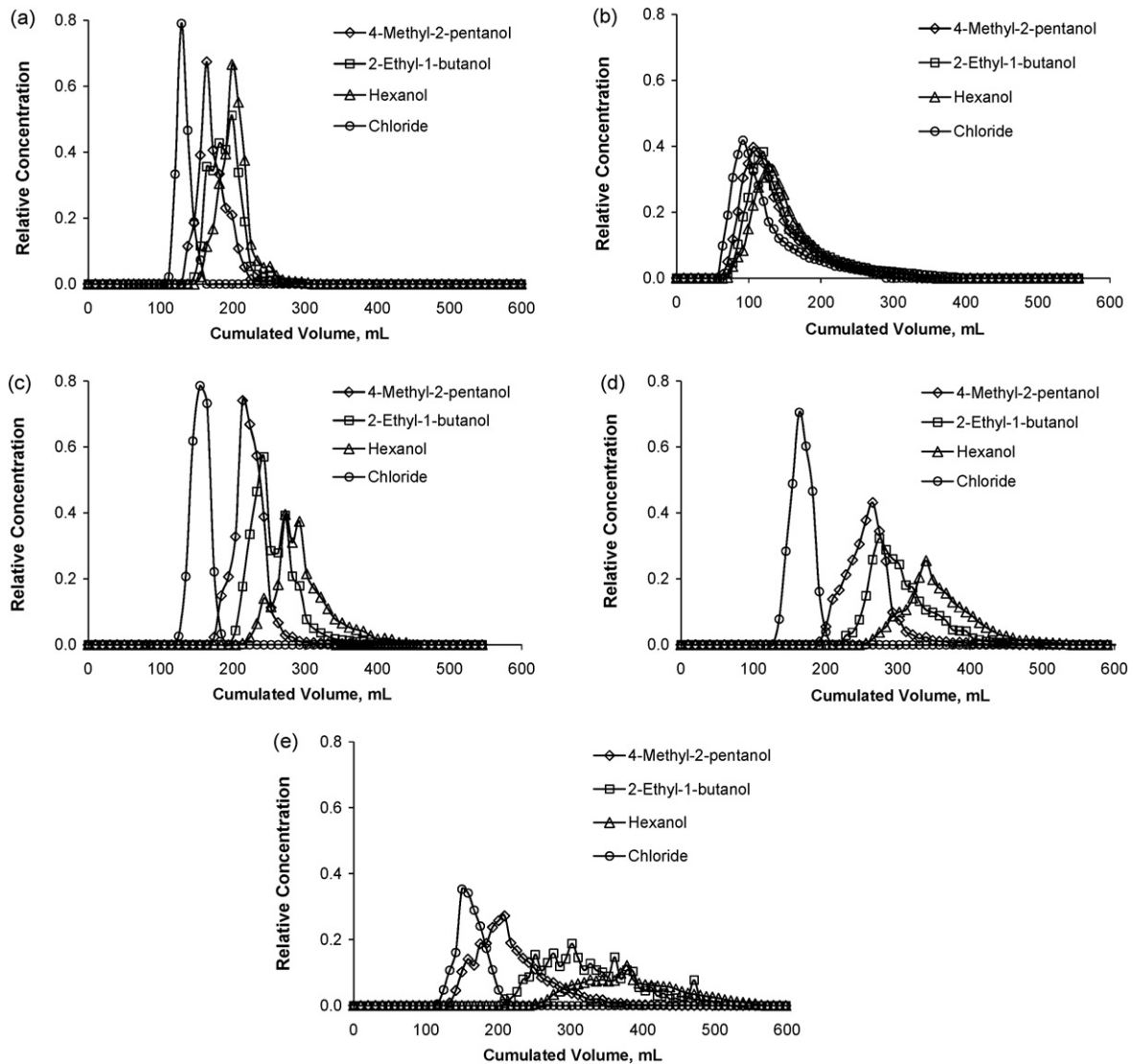
Fig. 6. The effluent concentration of tracers in soils with jet-fuel contamination of (a) Jumunjin sand, (b) weathered granite soil, (c) MIX A, (d) MIX B and (e) MIX C.

column experiments were smaller than those of the other tracers and this implies that the sorption affinity of 4-methyl-2-pentanol onto the soil organic contents in the soil mixtures was weaker than those of the other alcohol tracers. In the cases of the batch sorption experiments, however, the sorption amount of 2-ethyl-1-butanol was smaller than those of the other alcohol tracers. These opposite conclusions from the column experiments and the batch sorption experiments could be explained by considering the alcohol concentrations employed in the column experiments were different from those in the batch sorption experiments. Injected concentrations of the alcohol tracers into the soil columns were about 600 mg/L each and the maximum peak concentrations of the alcohol tracers in MIX A, MIX B and MIX C were about 250, 120 and 105 mg/L, respectively. Therefore, 4-methyl-2-pentanol had the lowest sorption affinity toward the soil mixtures at the range of alcohol concentration employed in the column experiments even though the batch sorption experiments showed that the highest sorption amount was found with 4-methyl-2-pentanol at the alcohol concentration over than 600 mg/L.

The effluent concentrations of tracers from the soil columns with jet-fuel contamination are shown in Fig. 6, and those values were higher than those without jet-fuel contamination (Fig. 4) possibly due to less dispersion of tracer caused by smaller water-filled pore

space in the jet-fuel column. The retardation of Fig. 4 was mainly affected by tracer sorption onto the test soil, while that of Fig. 6 was affected by both of tracer sorption onto the soil and partitioning into jet-fuel. Therefore, the retardation of Fig. 4 was different with that of Fig. 6 even though water–solid retardation was same. The retardation factors of alcohols with jet-fuel contamination are summarized in Table 4. The average saturations of residual jet-fuel in the soils estimated by the method of volume measurement (S_n^{mea}) are summarized in Table 5. For Jumunjin sand (Fig. 6a) and weathered granite soil (Fig. 6b), the separations between alcohols and chloride were mainly affected by the existence of the residual jet-fuel since no separations were occurred in the columns without jet-fuel contamination (Fig. 4a and b). Although the field application of the partitioning tracer method should consider many potential field conditions, these results from lab-scale experiment may support that the jet-fuel in the saturated soil having no significant amount of organic carbon contents could be quantified using the partitioning tracer method. For MIX A (Fig. 6c), MIX B (Fig. 6d) and MIX C (Fig. 6e), however, the retardation of alcohols was caused by both of jet-fuel contamination and soil organic carbon. It could be concluded that the organic carbon in the soils might cause the overestimation on the jet-fuel contamination of subsurface in partitioning tracer method.

Table 5
Average saturations of residual jet-fuel estimated by the volume measurement and the partitioning tracer method, and the modified average saturation considering the sorption fraction of tracers.

Test soils	Tracers	S_n^{mea} [a]	S_n^{est} [b]	S_n^{modi} [c]
Jumunjin sand	4-Methyl-2-pentanol	0.16	0.11	
	2-Ethyl-1-butanol	0.16	0.15	
	Hexanol	0.16	0.12	
Weathered granite soil	4-Methyl-2-pentanol	0.10	0.06	
	2-Ethyl-1-butanol	0.10	0.09	
	Hexanol	0.10	0.06	
MIX A	4-Methyl-2-pentanol	0.16	0.15	0.11
	2-Ethyl-1-butanol	0.16	0.20	0.15
	Hexanol	0.16	0.19	0.14
MIX B	4-Methyl-2-pentanol	0.19	0.19	0.15
	2-Ethyl-1-butanol	0.19	0.24	0.17
	Hexanol	0.19	0.23	0.18
MIX C	4-Methyl-2-pentanol	0.15	0.20	0.08
	2-Ethyl-1-butanol	0.15	0.28	0.15
	Hexanol	0.15	0.26	0.14

[a] The average saturation of residual jet-fuel by the method of volume measurement.

[b] The average saturation of residual jet-fuel estimated by the partitioning tracer method.

[c] The average saturation of residual jet-fuel modified by considering the effect of sorption.

The average saturation of residual jet-fuel estimated by the partitioning tracer method (Eq. (3), S_n^{est}) is summarized in Table 5 and compared with that by the volume measurement. For the Jumunjin sand and the weathered granite soil having negligible amount of organic carbon contents, S_n^{est} was little lower than S_n^{mea}. Among three tracers used in this study, 2-ethyl-1-butanol showed the most accurate estimation on the residual saturation possibly due to the least sorption by the soils in the concentration range tested (Fig. 3). However, the average saturations of residual jet-fuel in MIX A to C were generally overestimated up to 87.4% in MIX C when using 2-ethyl-1-butanol, which should be attributed to the organic carbon contents in the soils. To exclude the effect of tracer sorption to the soil organic carbon from the S_n^{est}, S_n^{est} was modified by considering the sorption fraction of tracers to the soil, which could be calculated as follows:

$$S_n^{modi} = \frac{R_{ct} - R_{uct}}{R_{ct} - R_{uct} + K_{nw}} \qquad (5)$$

where S_n^{modi} is for the average saturation of residual jet-fuel considering the jet-fuel contamination and soil organic matter, R_{uct} is for the retardation factor of alcohols without the jet-fuel contamination, and R_{ct} is for the retardation factor of alcohols with the jet-fuel contamination. In this system, R_{uct} implies the retardation caused by the tracer sorption to the soil, while R_{ct} is the retardation by both of the tracer sorption to soil and the tracer partitioning into jet-fuel. The S_n^{modi} values for MIX A, MIX B and MIX C are summarized in Table 5, which showed that the accuracy of estimation on the residual saturation could be enhanced when excluding the sorption fraction of tracer to the soil organic carbon. The highest accuracy of estimation was found with 2-ethyl-1-butanol and the lowest with 4-methyl-2-pentanol after the effect of tracer sorption onto the soil matrix was removed. Therefore, the highest accuracy of estimation could be found with using 2-ethyl-1-buanol as a partitioning tracer and chloride as a nonpartitioning tracer, since the S_n^{modi} values showed the strongest correlation with the S_n^{mea} values. In the case of 4-methyl-2-pentanol, since the estimation accuracy also increased with S_n^{mea} after the sorption effect was removed, it was likely to be expected that 4-methyl-2-pentanol could estimate the S_n^{modi} value above 78.9% accuracy if the S_n^{mea} value is higher than 0.19, even though the accuracy within this study was low.

4. Summary and conclusion

The purpose of this study is to investigate the effect of soil organic matter on the partitioning tracer method to quantify the jet-fuel contamination. The results from the partitioning experiments indicated that the alcohols used in this study showed the different partitioning behaviors depending on their partition coefficients. The sorption results showed that considerable amounts of 4-methyl-2-pentanol and hexanol were sorbed to the soils and the sorption amounts of 2-ethyl-1-butanol were relatively smaller than those of the other alcohol tracers. The column experiments demonstrated that the accuracy for the jet-fuel quantification in partitioning tracer method was reduced with increasing the soil organic carbon contents, however, these accuracies could be enhanced by considering the sorption fraction of tracer to the soils, especially for the tracer of 2-ethyl-1-butanol.

Acknowledgment

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