



Attenuating toluene mobility in loess soil modified with anion–cation surfactants

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Received 22 October 2001; received in revised form 29 March 2002; accepted 29 March 2002

Abstract

Soils, subsoils, and aquifer materials can be modified with hydrophobic cationic surfactants to increase their sorption capabilities for organic contaminants. The objective of this study was to examine in detail the sorptive characteristics of the natural loess soil and the resultant organo-modified soils for aqueous-phase neutral organic compounds (NOCs) in an attempt to define the operative sorptive mechanisms. Under the laboratory conditions, a series of modified loess soils in this study were prepared by replacing the cations of loess soil with both cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) and anionic surfactant sodium dodecylbenzene sulfonate (SDBS). Toluene was selected as an indicator to study the sorption behavior of the NOCs in loess soils. The sorption isotherms of toluene in soil samples obtained using the batch equilibration method. The results indicated that natural loess had a poor sorption capability for NOCs, and sorption isotherms of toluene appeared likely nonlinear and fit the Freundlich equation very well. When the soils were coated with large alkyl surfactants such as HDTMA-Br, sorption isotherms correspondingly became linear and the sorptive capability was prominently dependent on the quantity of hexadecyltrimethylammonium (HDTMA) and SDBS added into the soils. The study could provide an essential basis on attenuation of organic contaminants in the subsurface environment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sorption; Partition; Adsorption; Surfactant; Toluene; Loess soil

1. Introduction

Loess soils topographically cover the vast land expanding from central Asia to north China where oil fields are widely exploited, and oil resulted in the severe contamination of soils

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and water resources. Because of the natural conditions of the loess soil regions at northern China, the critical concern is to utilize the available cleanup techniques that would be applied for the in situ remediation of petroleum polluted soils. Among all the possible remediation alternatives, the essential study of sorption and transformation of organic compounds in the soil matrix must be taken into full account. Low organic matter clays, soils and aquifer materials usually have very little retardation capabilities for common organic pollutants. The earlier studies have demonstrated that replacing the native inorganic exchangeable cations of clay minerals, soils and subsoils with organic cations of the form $[(\text{CH}_3)_3\text{NR}]^+$ greatly enhanced the sorptive abilities of the soils for organic contaminants [1–5]. A countermeasure to protect groundwater from hazardous leachates produced at the land surface is to restrain the mobility of pollutants or fix them within the unsaturated zone. Sorption of organic compounds by soil surfaces brings about the attenuation of contaminants in the subsurface environment. If this process occurs naturally when surfactants are introduced into the soil matrix, it may be a basis for remedial action at contaminated sites. For example, cationic surfactants could be percolated or injected into an aquifer downgradient from a source of contamination to set up a temporary barrier against migration. Alternatively, they could be used in conjunction with in situ bioremediation or by other methods to eliminate the target contaminants permanently [6,7]. If anionic and cationic surfactants coexist in water or soil matrix, they can simultaneously be adsorbed by suspended particles or soil surfaces. The sorbed surfactants affect the sorption property of soils, and the transport and transformation behavior of organic contaminants. Thus, a better understanding of the sorption properties and mechanisms of organic compounds on anion–cation and single-cation organosols can provide useful knowledge for remediation of contaminated soil and groundwater aquifer.

The critical issues in studying the sorption behavior of organic compounds on modified soils are the stability of organo-clay/soil complexes, and the sorption efficiency of modified soil materials for organic contaminants. Xu and Boyd [3] concluded that hexadecyltrimethylammonium (HDTMA) was initially adsorbed by cation exchange in the interlayer of the soil, this exchange process was accompanied by the stoichiometric release of inorganic cations (H^+ or Ca^{2+}). It was also reported that sorption of HDTMA with loadings up to 70% cation exchange capacity (CEC) was nearly quantitative and resulted in a equivalent release of Ca^{2+} from the soils, indicating ion exchange as the sole mechanism over this range. At greater loadings, HDTMA was sorbed both by ion exchange and hydrophobic bonding. In addition, the selectivity coefficient for HDTMA replacing Ca^{2+} was very high (10^7 – 10^9 between 0.1 and 0.8 CEC), indicating the higher chemical stability of HDTMA–soil complex at these loadings [8]. Sorption of organic compounds was viewed as a partitioning process involving the cationic surfactant-derived organic phase, in analogy to the function of natural soil organic matter [9,10]. The surfactant-derived organic matter was more effective than natural loess soil for sorbing hydrophobic organic contaminants from water because of the comparatively low polarity of the HDTMA phase [11,12]. Recent studies have been conducted on the sorption properties and mechanism of organic compounds to organobentonite [7]. However, from our findings, no studies have been reported on the sorption of anion–cation surfactants on the loess soils that have a low CEC and organic matter.

The objective of this study was to examine in detail the sorptive characteristics of organosols for aqueous-phase neutral organic compounds (NOCs) and define the operative

sorptive mechanisms. The research results could be used to prevent groundwater contamination from petroleum leaching through the vadose zone in the arid and semi-arid regions in Asia, where oil fields are widely distributed on the loess land.

2. Materials and methods

2.1. Materials

The loess soil sample for the experiments was collected from the subsurface, 50–60 cm depth in an uncontaminated area in Lanzhou City, China. The CEC of the soil was 3.21 cmol/kg, which was determined by Atomic Absorption Spectrometry with Ca^{2+} as an index cation and a 0.1 mol l^{-1} BaCl_2 solution as the extracting reagent. The organic carbon content (OC) was measured using $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ oxidation at 180–185 °C in an oil bath according to the methodology reported by Li, et al. [13]. The chemicals used in this study were all analytical grade. The water used was organic free, double distilled. hexadecyltrimethylammonium bromide (HDTMA-Br) and sodium dodethylbenzene sulfonate (SDBS) surfactants were used to treat the loess soils in the cationic and anionic–cationic forms, respectively. The structures of the surfactants are shown in Fig. 1. A typical soil sample was measured for three times, then the mean values were calculated, respectively, and the main properties of loess soil sample are listed in Table 1. The natural soil and a series of anion–cation and single-cation organosols were characterized by X-ray diffraction (XRD) and OC analysis. The results are displayed in Table 2.

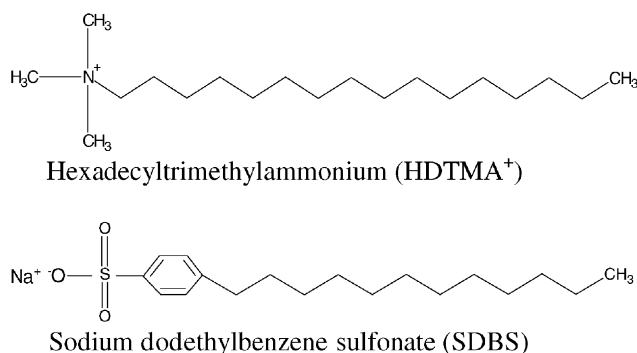


Fig. 1. Chemical structures of the surfactants used to prepare the organosols.

Table 1
Physical and chemical properties of the loess soil sample

Bulk density (g/cm ³)	OC (%)	CEC (cmol/kg)	pH (water/soil = 1)	Sand (%)	Silt (%)	Clay (%)
1.38	0.10	3.21	8.14	18.8	53.9	27.4

Table 2

Interlayer spacing and organic carbon content of the loess soil sample, single-cation or anion–cation organosoils

Soil samples	Interlayer spacing of soil samples (Å)	Experimental organic carbon contents (%)	Calculated organic carbon contents (%)
Natural soil	7.049	0.101	0.101
60HDTMA	7.052	0.532	0.529
80HDTMA	7.065	0.675	0.680
100HDTMA	7.072	0.809	0.834
120HDTMA	7.078	0.950	0.980
60HDTMA/20SDBS	7.051	0.565	0.633
80HDTMA/20SDBS	7.059	0.810	0.779
100HDTMA/20SDBS	7.068	0.916	0.926
120HDTMA/20SDBS	7.088	1.046	1.072

Calculated values were equal to the total organic carbon contents both from natural soil and added surfactants.

2.2. Properties of toluene

The aqueous solubility (S), octanol–water partition coefficient (K_{OW}), and partition coefficient normalized to soil OC (K_{OC}) of toluene are 515 mg l^{-1} , 490, and 302, respectively [14].

2.3. Preparation of organosoils

A series of anion–cation and single-cation organosoils were prepared by coating loess soil sample with aqueous solutions of either cationic surfactant or a mixture of anionic and cationic surfactants. A total of 500 g air-dried soil samples were mixed with 1 l of various surfactant solutions, then, 2 l of distilled water was added. The mixtures were subjected to mechanical stirring at room temperature for 5 h, and the modified soils were separated by centrifugation and washed repeatedly by distilled water until bromide ions derived from the cation surfactant solution were undetectable as indicated by 0.01 M AgNO_3 solution. Finally, the soil samples were air dried, passed through a 1 mm sieve, then stored in glass bottles at room temperature for later use.

Modified soils were identified by a prefix that indicated the percent of the loess soil's CEC replaced by surfactant ions followed by the abbreviation for the specific type of anionic surfactant SDBS or cationic surfactant HDTMA. For example, 100HDTMA indicated that a modified soil had 100% of loess soil CEC replaced by a hexadecyltrimethylammonium cation (HDTMA^+). In the cases where anionic–cationic mixed surfactants SDBS and HDTMA were coated onto loess soil, two abbreviations were used for the categorization of the modified soils. Thus, 100HDTMA/20SDBS identified the anion–cation surfactant modified soil that had 100% CEC replaced by HDTMA^+ plus 20% CEC coated by SDBS altogether.

2.4. Sorption procedures

Sorption isotherms were obtained by adding various toluene solutions to 50 ml amber vials capped with Teflon-faced silicon septa. To ensure the sorption amount of the

solute between 20 and 80%, a weight of 9 g of unmodified soil or 4.5 g of the modified soil mixed with about 45 ml toluene solutions with the different concentrations from 5 to 70 mg l⁻¹, minimizing the headspace by filling the vials to the top. Sodium azide was used as a biocide at a concentration of 200 mg l⁻¹. To obtain equilibrium, the soil-solution mixture was initially stirred with a vortex agitator and placed in a shaker for continuous mixing at 200 rpm for about 24 h at 25 °C in the dark. After equilibration, the vials were withdrawn and centrifuged at 3200 × *g* for 30 min. A 10.00 ml volume of the supernatants was removed, then extracted with 2.50 ml carbon disulfide, and analyzed immediately. Meanwhile, the blank experiments without adding sorbent were performed to determine the losses of solute due to adsorption on glass walls and other losses under the same conditions. The solid-phase concentration was calculated by the difference between the initial and final concentration of the organic compounds in the aqueous phase.

2.5. Analytical procedures

Analysis of toluene in the carbon disulfide extracts was made by gas chromatography (GC) with a FID detector and OV-17 column. Peak areas were recorded by external standards to determine the concentration of toluene. With the detection limits of 0.05 mg l⁻¹, a 95% recovery of toluene measured from the blanks, was used to adjust the sorption data by dividing the tested aqueous toluene. The GC conditions were as follows: column temperature 120 °C; detection temperature 200 °C; carrier gas N₂ 50 ml min⁻¹, H₂ 50 ml min⁻¹; and sample size 1 μl.

3. Results and discussion

3.1. Analysis of X-ray diffraction and organic carbon contents in the soils

The XRD analysis with 75% relative humidity in the laboratory showed that the interlayer spacing of the natural loess soil was 7.049 Å. The interlayer spacing of modified soil samples increased gradually with increasing amounts of surfactants used in synthesizing the organosols. However, on increasing, the maximum extent of the interlayer spacing changed from 7.049 Å for the natural soil to 7.088 Å for the modified soils. The increase was not significant because the loess soils in northern China are the quartzose and collapsible sediments, so the specific surfaces of the loess soils on saturation hardly exhibit the expansion, unlike natural bentonite. Consequently, the data indicate that a limited quantity of the surfactants was incorporated on the modified soil surfaces.

The experimental values of organic contents of the prepared soils agreed well with the theoretical values, which were calculated by assuming that 100% of added organic cation or anion-cation surfactant combined with the soil. Comparison of the calculative values and measured organic contents using a one-sided paired *t*-test [15] indicated that the differences between the calculative and measured values were not statistically significant ($P = 0.05$).

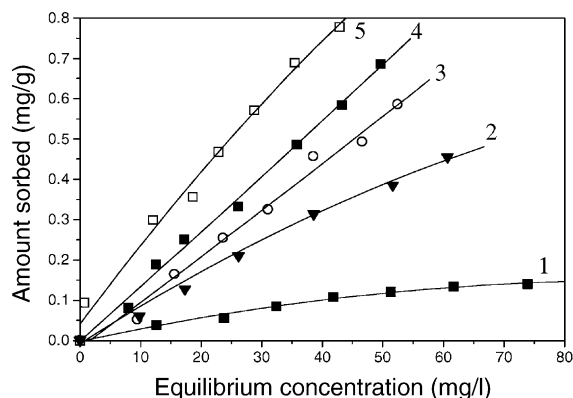


Fig. 2. Sorption isotherms of toluene on natural soil and anion–cation organosols at 25 °C. (1) Natural soil; (2) 60HDTMA/20SDBS; (3) 80HDTMA/20SDBS; (4) 100HDTMA/20SDBS; (5) 120HDTMA/20SDBS.

3.2. Sorption isotherms of toluene on anion–cation and single-cation organosols

Sorption isotherms for toluene at 25 °C on anion–cation and single-cation modified soils including natural soil isotherms are shown in Figs. 2 and 3, respectively. All the experimental batch sorption data were fit to a sorption model using nonlinear least-squares regression. From Figs. 2 and 3, it can be seen that the sorption of toluene to anion–cation organosols increased gradually when the added amount of HDTMA was increased, meanwhile the range of corresponding CEC values varied from 60 to 120%.

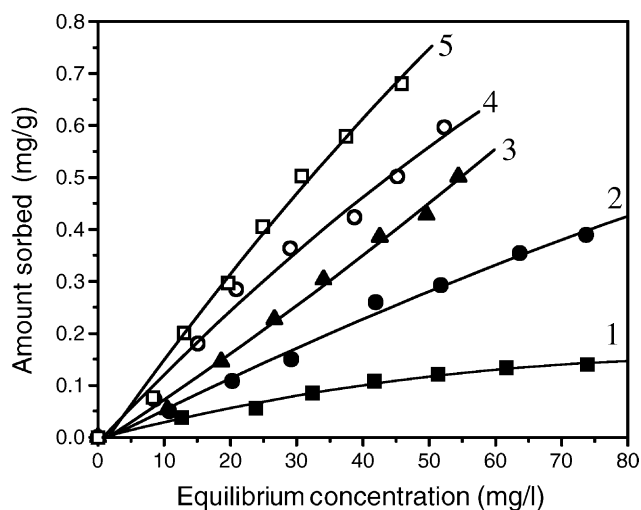


Fig. 3. Sorption isotherms of toluene on natural soil and single-cation organosols at 25 °C: (1) natural soil; (2) 60HDTMA; (3) 80HDTMA; (4) 100HDTMA; (5) 120HDTMA.

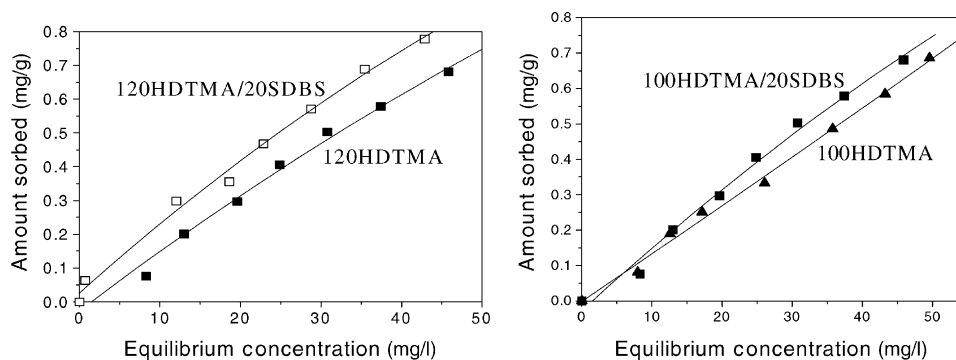


Fig. 4. Comparisons of sorption isotherms of toluene on organosols modified by anion–cation and single-cation surfactants, respectively, at 25 °C.

The comparison of sorption isotherms of toluene on anion–cation organosols and on corresponding single-cation organosols is illustrated in Fig. 4. The extent of sorption of toluene both on 120HDTMA/20SDBS and 100HDTMA/20SDBS modified soils was greater than corresponding 120HDTMA, 100HDTMA single-cation modified soils. The same trend could be found in the other modified soils, which suggested that anion–cation mixed organosols provided more effective partition media than the corresponding single-cation organosols. Therefore, the mixed anion–cation organosols have a greater sorptive capacity than the corresponding single-cation organosols for the NOCs in loess soils.

However, in the previous study on the sorption behavior of ionic organic compounds such as *p*-nitrophenol on organobentonite [7], the sorption magnitude of *p*-nitrophenol on soil modified with 100DTMA/20SDS was less than that of those modified with 100DTMA. The results might be caused by the difference in properties of organic compounds *p*-nitrophenol versus toluene or the variety of soil textures. The soil incorporated with anionic surfactants might repel the ionized *p*-nitrophenol while nonpolar compounds, such as toluene, seemed to be associated with OC of the soil. In this case, partition was considered to be the main sorption mechanism.

3.3. Sorption mechanisms of toluene in natural and modified soils

As usual [16], for a natural soil with low organic matter, it was assumed that there were two types of interactions between organic compounds and soils, i.e. adsorption and partition were related, respectively, to the mineral surfaces and the organic matter of the soil media. Therefore, the chemical–biological degradation and reactions were often neglected in this environment. The sorption amount of organic compounds to organosols can then be defined as:

$$Q_T = Q_A + Q_P \quad (1)$$

where Q_T is the total amount of the organic compounds sorbed to the modified soils; Q_A and Q_P are the amounts sorbed by adsorption and partition mechanisms, respectively. Here, we

defined K_P as the partition coefficient and K_A as the adsorption coefficient, with the equation:

$$K_P = \frac{Q_P}{C_e} \quad (2)$$

$$K_A = \frac{Q_A}{C_e} \quad (3)$$

in which C_e is the equilibrium concentration of the organic compounds in the aqueous phase. The OC-normalized partition coefficient (K_{OC}) is calculated by the following equation.

$$K_{OC} = \frac{K_P}{f_{OC}} \quad (4)$$

The values of f_{OC} obtained from the experiments, are displayed in Table 2. The values of K_P obtained from linear regression sorption data of toluene (see Table 3).

For the natural loess soil, the regression of the data can be suitably described as:

$$Q_T = aC_e^n \quad (5)$$

where a and n are constants. According to Eqs. (1), (2), (4) and (5), the sorption amount contributed by partition (Q_P) and adsorption (Q_A), respectively, can be estimated by the following equations.

$$Q_P = K_{OC} f_{OC} C_e \quad (6)$$

$$Q_A = Q_T - K_{OC} f_{OC} C_e \quad (7)$$

Based on the previous studies [4,17], adsorption appeared to be nonlinear, and was dependent on the surface areas of the mineral. In contrast, partition seemed to be linear. Fig. 5 shows the total amount of sorption of toluene and the relative contributions that adsorption and partition made to the sorption of toluene on natural loess soils. The values of Q_P were determined by Eq. (6), and Q_A values were calculated by Eq. (7) both using data from curve 1 in Figs. 2 and 3. The curve Q_P is linear, while the curve Q_A is nonlinear. Under this situation where the soils had low OC ($f_{OC} = 0.101\%$), the effects of adsorption (Q_A) seemed comparatively significant compared to partition (Q_P , see in Fig. 5).

Table 3

Linear regression data for simulated isotherms at high concentrations, and partition coefficients (K_P , K_{OC})

Soil samples	Regression equations of high concentration of toluene solution (20–70 mg l ⁻¹)	r^2	K_P	K_{OC}
60HDTMA/20SDBS	$Q_T = 0.0075C_e + 0.0078$	0.995	7.5	1327
80HDTMA/20SDBS	$Q_T = 0.0113C_e + 0.010$	0.983	11.3	1395
100HDTMA/20SDBS	$Q_T = 0.0136C_e + 0.050$	0.996	13.6	1485
120HDTMA/20SDBS	$Q_T = 0.0172C_e + 0.061$	0.992	17.2	1644
60HDTMA	$Q_T = 0.0074C_e + 0.012$	0.996	7.4	1391
80HDTMA	$Q_T = 0.0096C_e + 0.051$	0.987	9.6	1422
100HDTMA	$Q_T = 0.0119C_e + 0.077$	0.990	11.9	1471
120HDTMA	$Q_T = 0.0143C_e + 0.040$	0.992	14.3	1505

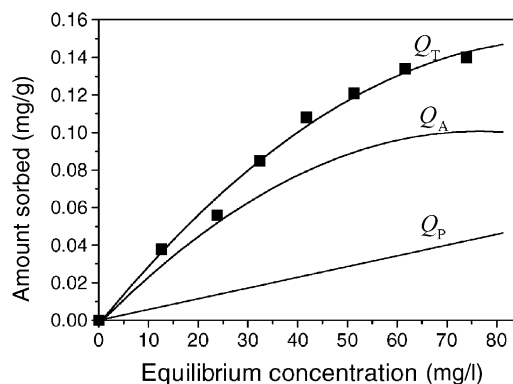


Fig. 5. Comparison of the partition and adsorption contributions to the total amount of toluene sorbed onto natural loess soil.

For the modified soils, however, the sorptive affinity was greatly enhanced, and the shapes of the sorption isotherms were different from that of the natural soil (see Figs. 2 and 3). The results of linear regression analysis of the sorption data suggested that solute partition in the soils modified by single-cation or anion-cation organosols, appeared to be the main mechanism for the sorption of toluene in water-soil system. The sorption isotherm at the high concentration ranged from 20 to 70 mg l⁻¹ in aqueous phase, appears to approach linearity. A series of linear regression equations and the calculated values of K_p and the associated experimental data are listed in Table 3. It can be seen that both the partition coefficient (K_p) and K_{OC} increased with an increase of surfactant amount, and the values of K_{OC} in the modified soils increased significantly compared with the measured value of K_{OC} 302 in the natural soils. It proved that the surfactant-derived organic matter had greater sorption capabilities than natural soil organic matter.

It is evident that multiple mechanisms must have been involved in the sorption of toluene by the organosols. Aromatic molecules, because of their planar shape and delocalized π electrons, can interact strongly with $[(CH_3)_3NR]^+$, causing a reorientation of the alkyl chains. The solute molecules solvated by the cationic ammonium centers and alkyl chains of $[(CH_3)_3NR]^+$ [18], can be realized from a parallel to more vertical position relative to the mineral sheets. Furthermore, they can be concomitantly adsorbed onto the vacated mineral surfaces by the hydrophobic sorptive process of nature [6]. Solute partitioning into the HDTMA or SDBS phase is also an important concurrent mechanism, therefore, it might be the combination effect of solvation and partitioning altered the shape of the sorption isotherms.

4. Conclusion

Loess soil with a low OC has little sorptive capabilities for organic contaminants in the soil environment, and, thus, they do nothing to diminish the potential for organic pollutants with high solubility to leach through the unsaturated zone to potentially threaten the groundwater.

This study provided several characteristics of the natural loess soils: low organic content, low CEC, and poor adsorption capacity. The related sorption isotherms fit the Freundlich equation very well. Incorporation of loess soil with surfactants could be improved for the retardation of organic pollutants in the soil matrix. The experiments proved that the surfactant-modified soils were much more effective sorbent of toluene, a NOC, than natural soil. In addition, the loess soils coated with anion–cation surfactants had a higher sorptive capacity than corresponding single-cation organosols. Sorption isotherms were dependent on the specific solute and sorbent, however, for natural loess soils, sorption isotherms of NOC appeared likely nonlinear. When the soils were coated with large alkyl surfactants such as HDTMA, sorption isotherms correspondingly became linear, providing evidence that the sorption occurred by multiple mechanisms, including surface-sorption, partition, and solvation, and others. For the remediation of organic contaminated land, an available and economical approach is to hold up the hazardous materials within topsoils by enhancing the soil sorption capacity prior to phytoremediation and biodegradation.

Acknowledgements

We would like to express our sincere gratitude to the reviewers for their valuable suggestions and kind help. The research fund was supported by National Natural Science Foundation of China with Project No. 29977015.

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