Adsorption and desorption of 2,4,6-trichlorophenol onto and from ash as affected by Ag^+ , Zn^{2+} , and Al^{3+}

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Abstract Metal cations and organic pollutants mostly co-exist in the natural environment. However, their interactions in adsorption processes have yet to be adequately addressed. In the current study, the effect of inorganic cations with different charges (Ag^+ , Zn^{2+} , and Al^{3+}) on the adsorption and desorption of 2,4,6-trichlorophenol (TCP) onto and from processed ash derived from wheat (*Triticum aestivum* L.) straw was investigated. The adsorption and desorption of TCP were both nonlinear; the isotherm and kinetics curves fitted well using the Freundlich equation and a pseudo-second-order model, respectively. The presence of Ag^+ promoted TCP adsorption, while Zn^{2+} and Al^{3+} reduced TCP adsorption onto ash. The desorption of TCP from ash showed obvious hysteresis, and the presence of Ag^+ , Zn^{2+} , and Al^{3+} caused the desorption to be less hysteretic. The suppression of TCP adsorption by Zn^{2+} and Al^{3+} was ascribed to the partial overlapping of adsorption groups between TCP and metal ions. Al^{3+} had a stronger inhibition effect than that of Zn^{2+} due to its higher binding capacity and larger hydrated ionic radius than those of Zn^{2+} . Enhanced adsorption of TCP onto ash by Ag^+ was ascribed to its ability to reduce the competitive adsorption of water molecules on ash surface by replacing the original ions, such as Na^+ and Ca^{2+} , and compressing the hydrated ionic radius of these metal ions. In addition, Ag^+ was able to bind with the aromatic organic compounds containing π -electrons, which resulted in a further increase of TCP adsorption by ash.

Keywords Adsorption · Ash · 2,4,6-Trichlorophenol · Ag^+ · Zn^{2+} · Al^{3+}

Introduction

Plant stalks and other residues left after crops have been harvested are burned in situ in many countries and areas of the world. Ash resulting from such burning may greatly increase the black carbon (BC) content in agricultural soil (Naidu et al. 1998). BC in soils and sediments plays important roles in the adsorption of neutral organic contaminants through the well-known mechanism of contaminant partitioning with soil/sediment organic matter (Wang et al. 2009). Ash has a porous rigid structure and large surface area, meaning it is an effective adsorbent for hydrophobic organic compounds and can seriously affect their fate in the environment (Yang and Sheng 2003; Dilip et al. 2006; Srivastava et al. 2005). For example, Toth et al. (1999) found that soil that has experienced kangaroo grass burning exhibits significantly reduced diuron plant toxicity. Meanwhile, research on crop-residue-derived chars suggests that pyrolysis-derived charcoal adsorption of neutral organic contaminants takes place almost exclusively as surface adsorption, while low-temperature decomposition-derived charcoal adsorption is characterized mainly by surface adsorption, but also accompanied by distribution (Chun et al. 2004).

2,4,6-TCP (TCP) is a pollutant whose control is considered a high priority by the US Environmental Protection Agency (USEPA), as well as in China (Keith and Telliard 1979; Zhou et al. 1991), as it can result in lymphoma, leukemia, and liver cancer through oral exposure in animals (Wang et al. 2005). It is often found in emissions from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenol or certain aromatic acids with hypochlorite, or during the disinfection of water (Chaliha and Bhattacharyya 2008). TCP has also been widely used as a preservative, pesticide, and antibacterial agent, which can then be released into the water system from soil, thus causing poisoning of the ecosystem.

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Therefore, the adsorption and desorption of TCP onto and from soil and soil components are important to understand its migration behavior in the environment. Cea et al. (2005), through a study based on soil from southern Chile, suggested that the formation of inner- and outer-sphere complexes between deprotonated molecules and active sites in soil are the main sorption mechanisms for chlorophenols, and that chlorophenol sorption in neutral form could be induced by hydrogen bond formation between the phenolic hydroxyl group and the neutral surface, followed by ligand exchange with consequent deprotonation. Kung and McBride (1991) reported that TCP adsorption by Fe and Al oxides is realized through inner complex formation, while Wang et al. (2005) found that TCP adsorption by humic acid-modified montmorillonite and illite is greater than by either mineral its pure form. More recently, Wang et al. (2009) suggested that TCP adsorption on wheat ash can be ascribed to surface adsorption and concurrent partitioning into the residual organic matter phase.

Carbonaceous materials, including ash, are also effective adsorbents in removing heavy metals (e.g., As^{5+} , Cd^{2+} , Cr^{6+} , Cu^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+}) from the aqueous phase (Chen et al. 2009; Seco-Reigosa et al. 2013; Shah et al. 2013; Wang et al. 2009, 2011). It is common in many contaminated sites to find a complex suite of organic chemicals and inorganic elements in existence together (Sprovieri et al. 2007), and the coexistence of metal ions affects the adsorption of organic contaminants to charcoal, ash, and carbon nanotubes (Chen et al. 2007, 2009; Wang et al. 2009, 2011). Chen et al. (2007) found that Cu^{2+} decreases the adsorption of 2,4-dichlorophenol, 1,2-dichlorobenzene, and naphthalene by 30–60 %, while Ag^+ increases adsorption of these solutes by wood charcoal. Wang et al. (2011) suggested that Cu^{2+} , Pb^{2+} , and Zn^{2+} diminish *p*-nitrophenol adsorption on ash, while increasing its desorption remarkably.

To our knowledge, the effect of metal cations with different charges on the adsorption of organic chemicals by ash or BC has not been adequately investigated. It should be realized that metal cations and TCP may occur together in the field, especially in soil irrigated by wastewater in countries with high levels of water shortage (Daughney and Fein 1997; Mueller et al. 1989). In the current reported study, metal cations with different charges, such as Ag^+ , Zn^{2+} , and Al^{3+} , were selected because they are abundant in the environment and occur widely in soil and water. The specific aim of the study was to examine how Ag^+ , Zn^{2+} , and Al^{3+} affect the adsorption of TCP onto ash, and the desorption from it.

Materials and methods

Materials

TCP with purity >98 % was purchased from Aldrich Chemical Co. Inc. It had a $\log K_{\text{ow}}$ of 3.67, $\text{p}K_{\text{a}}$ of 6.1, and a water

solubility Cs of 300 mg L^{-1} ($\text{pH} < 5$; Wightman and Fein 1999). AgNO_3 , $\text{Zn}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$ were of guaranteed reagent grade, while other chemicals were of analytical reagent grade or better.

Raw ash was obtained by burning air-dried wheat (*Triticum aestivum* L.) straw on a stainless steel plate ($1 \times 1 \text{ m}$) in an open field under uncontrolled natural conditions (Yang and Sheng 2003). The ash was then ground into powder and sieved (1 mm). One gram of raw ash was treated with 40 mL 1-M hydrochloric acid for 4 h and then centrifuged at $2,000 \times g$ for 20 min and the supernatant discarded. The process was repeated four times, and then treated with a mixture of hydrochloric acid and hydrofluoric acid (0.1:0.3 mol/L) four times, followed by thorough washing with distilled water to remove soluble salts and silicon. Processed ash was dried overnight at 80°C and sealed for storage.

Characteristics of the processed ash were determined as follows. The total content of C, H, and N were determined using a CHN Elemental Analyzer (Vario EL III Elementar, Germany), and the ash content was determined by combustion of the processed ash at 750°C for 4 h. Oxygen content was calculated by mass difference [Oxygen content = $100 \% - (\text{C content} + \text{H content} + \text{N content} + \text{ash content})$]. Specific surface area was measured with nitrogen at 77 K with an ASAP2020 instrument (Micromeritics Instrument Corporation, USA) and calculated using the Brunauer–Emmett–Teller equation. The group distribution was measured using a 300-MHz NMR spectrometer (Varian INOVA 300) CPMAS ^{13}C NMR. A summary of the characteristics of the processed ash is provided in Table 1.

Batch adsorption and desorption

The processed ash was applied in all the following batch adsorption and desorption experiments. Ten milligrams of processed ash were used for the adsorption of TCP. Ash was combined with the test solute(s) dissolved in 25-mL deionized water containing $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ and $100 \text{ mg L}^{-1} \text{ NaN}_3$ as a biocide in 40-mL screw-cap glass vials sealed with Teflon screw caps. All adsorption experiments were performed in triplicate. To evaluate the effect of pH on adsorption of TCP, solution pH was adjusted to 2.0–9.0 with 0.1-M HNO_3 or NaOH . In adsorption isotherms experiments, the concentrations of TCP ranged from 20 % to 80 % of its solubility, and the concentrations of the three metal cations were 0, 0.01, 0.05, and 0.1 mM. The pH was adjusted to 4.5 ± 0.1 in adsorption kinetics and isotherm experiments, where dissolved TCP was predominantly (>99.3 %) neutral, and where hydrolysis and precipitation of Ag^+ , Zn^{2+} , and Al^{3+} were negligible. This pH value is also typical of the pH of red soil in southern China. The vials were shaken at 100 rpm in a shaker (HZQ–F160, China) at $20 \pm 0.5^\circ\text{C}$, and an equilibration time of 7 days was used routinely. After centrifugation ($2,000 \times g$ for 20 min),

Table 1 Physical and chemical properties of processed ash

Ash content (%)	1.66
C content (%)	77.0
N content (%)	0.56
H content (%)	2.58
O content (%) ^a	18.2
BET surface area (m ² g ⁻¹)	410
Alkyl C (0–50 ppm) (%)	8.9
O-alkyl C (50–110 ppm) (%)	6.9
Aromatic C (110–145 ppm) (%)	73
O-aryl C (145–163 ppm) (%)	9.0
Carboxyl C (163–190 ppm) (%)	2.6
Aliphatic C (%)	7.2
Aromatic C (%)	90
Aromaticity	12.5
Aliphaticity	0.08
POC	0.182

^a Oxygen content = 100 % - (C content + H content + N content + ash content)

POC percentage of polar organic carbon, which was calculated from the peak areas listed above using the equation $POC = (O\text{-alkyl C} + O\text{-aryl C} + \text{carboxyl C}) / (\text{alkyl C} + O\text{-alkyl C} + \text{aromatic C} + O\text{-aryl C} + \text{carboxyl C}) \times 100$

TCP in the liquid phase was determined by HPLC (HP 1100, Agilent Technologies).

Desorption experiments using a sequential decant–refill technique immediately followed the completion of the adsorption experiments. The desorption solution contained 0.01 M NaNO₃ and 0.1 g L⁻¹ NaN₃. The vials were also shaken at 100 rpm in a shaker (HZQ–F160, China) at 20 ± 0.5 °C, and a desorption time of 7 days was used routinely. After centrifugation (2,000 × g for 20 min), 10 mL supernatant was removed and refilled with the same volume of fresh desorption solution. After the first desorption, TCP in solution after each desorption was determined, and the amounts of adsorption and desorption were calculated by measured concentrations. Desorption was conducted for three consecutive times, and the reaction pH was maintained at 4.5 ± 0.1 during the whole process. In the desorption process, the adsorbate loss during the operation of supernatant removal and background solution addition was <1 % and negligible.

Blank experiments indicated that recoveries of adsorbates without ash were greater than 98 % of their initial concentrations, suggesting no significant losses, degradation, or adsorption by the glass vials in the timeframe of the batch adsorption study. Therefore, the adsorbed mass was calculated by the difference between initial and final equilibrium concentrations.

Analysis of TCP

TCP in solution was determined by HPLC, which was equipped with a diode array detector at 220 nm, with an extended polar

Fig. 1 Effect of pH on the adsorption of 2,4,6-TCP (0.25 mg L⁻¹) by ash

selectivity reversed phase column of C₁₈ (15 cm × 4.6 mm). Isocratic elution was performed at a flow rate of 1.0 mL min⁻¹ with a mobile phase of methanol/water (80:20 %).

Data analysis

Adsorption kinetics of TCP onto ash was analyzed with pseudo-first-order (Eq. 1) and pseudo-second-order kinetic models (Eq. 2; Ho and McKay 1998; Benguella and Benaissa 2002):

$$\ln(q_e - q_t) = \ln q_e - k_1 t; \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (2)$$

where q_e and q_t represent the TCP adsorption amount by ash at a balanced time or a certain time t in units of milligrams per gram, and k_1 and k_2 are the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic models (h⁻¹, g mg⁻¹ h⁻¹). In the pseudo-first-order model, values of q_e and k_1 could be obtained by the intercept and slope of the linear graph for $\ln(q_e - q_t)$ versus t . In the pseudo-second-order model, $1/q_e$ and $1/k_2 q_e^2$ could be obtained by the intercept and slope of the linear graph for t/q versus t .

Fig. 2 Adsorption kinetics of 2,4,6-TCP (0.25 mg L⁻¹) onto ash

Fig. 3 Linear regressions of kinetics: (a) pseudo-first-order model; (b) pseudo-second-order model

Adsorption isotherms of TCP were fitted with the Freundlich model (Eq. 3):

$$Q = K_f C^N, \quad (3)$$

where Q and C represent the adsorbed amount (milligrams per gram) and liquid phase equilibrium concentration (milligrams per liter), respectively. K_f ($\text{mg}^{1-N} \text{g}^{-1} \text{L}^N$) is the adsorption parameter, showing the adsorption capacity, and N (dimensionless) is the Freundlich index, suggesting the degree of deviation of the isotherm from linearity.

The amount of TCP adsorbed (q_e) was calculated using the following equation:

$$q_e = \frac{(c_i - c_e)\nu}{m}, \quad (4)$$

where c_i and c_e are the initial and equilibrium concentrations of TCP in milligrams per liter, q_e is the amount adsorbed on the processed ash in milligrams per gram, ν is the volume of solution in liter, and m is the total adsorbent mass in grams. Statistical analyses were performed using Origin 7.0 and SPSS 11.5.

Results and discussion

Effect of pH on adsorption of TCP

Solution pH can cause dissociation of surface groups of ash, thus affecting its surface charge density. In addition, pH is closely related to TCP protonation level. Therefore, the impact of pH on TCP adsorption was studied (Fig. 1). As shown in Fig. 1, TCP adsorption capacity remained stable at pH 2.0–5.0 and decreased sharply at pH > 5.0. Considering the pK_a value of 6.1 for TCP, the greater sorption at low pHs (3–5) may be ascribed to the predominant species of neutral TCP. An increase of solution pH of 5–8 increased the fraction of negatively charged TCP species and the dissociation of functional groups including hydroxyl, carboxyl, and other groups exposed on the

adsorbent surface (Chen et al. 2009). Therefore, the repulsion of anionic TCP with the negatively charged surfaces of ash makes TCP sorption unfavorable. Furthermore, solubility of TCP increases rapidly when pH is above 6 (Wightman and Fein 1999). The increase in solubility decreases the driving force for sorption of TCP on ash.

Effect of time on adsorption of TCP

TCP adsorption by ash could be divided into two phases: the initial rapid adsorption stage and the subsequent slow adsorption stage (Fig. 2). TCP adsorption at the first stage could be ascribed to surface adsorption, while the second stage could be regarded as the diffusion process of TCP in ash pores. The diffusion may spread to a nearby region or micro-pore area, and the adsorption was very subtle at this stage. The adsorption of TCP reached apparent equilibrium in 3 days (Fig. 2). To achieve full adsorption, the balance time was set to 7 days in this study.

In order to better understand the adsorption kinetics of TCP on ash, pseudo-first-order and pseudo-second-order kinetic models were applied to fit and evaluate the experimental results (Ho and McKay 1998; Benguella and Benaissa 2002). The linear regression graph and fitting parameters are shown in Fig. 3 and Table 2. The pseudo-second-order kinetics model fitted the data very well ($R^2=1$), with the standard deviation being significantly smaller than the pseudo-first-

Table 2 Pseudo-first-order and second-order constants

	q_e , measured (mg g^{-1})	k	q_e , calculated (mg g^{-1})	R^2	SD%
Pseudo-first-order model	200.19	0.013	20.88	0.924	73.41
Pseudo-second-order model	200.19	0.005	200	1	0.24

$$SD = \sqrt{\frac{\sum (q_{\text{measured}} - q_{\text{calculated}})^2}{n-1}} \times 100$$

SD standard deviation

Fig. 4 Adsorption of 2,4,6-TCP by ash in the absence and presence of Ag^+ (a), Zn^{2+} (b), and Al^{3+} (c)

order kinetics model. In addition, the calculated q value (q_e , calculated) obtained through the pseudo-second-order kinetic model was closer to the measured data (q_e , measured). Therefore, the adsorption kinetics of TCP on ash could be described by the pseudo-second-order kinetics model.

Effect of Ag^+ , Zn^{2+} , and Al^{3+} on adsorption of TCP

The adsorption isotherm of TCP was nonlinear and could be fitted using the Freundlich equation (Fig. 4 and Table 3). The addition of metal cations showed different effects on the adsorption of TCP onto ash. The presence of Ag^+ enhanced TCP adsorption onto ash, and the promotion effect became more pronounced with the increase of Ag^+ initial concentrations. The presence of Zn^{2+} and Al^{3+} was able to inhibit TCP adsorption onto ash, and the suppression effects enhanced as the equilibrium concentration of Zn^{2+} and Al^{3+} in solution increased. With the same equilibrium concentration of metal ions, Al^{3+} showed stronger inhibition of TCP adsorption than Zn^{2+} .

Metal cations and TCP may react with carboxyl, hydroxyl, and phenolic groups on ash, leading to competitive effects. Previous studies with X-ray absorption spectroscopy verified that Zn^{2+} could interact with the hydroxyl and carboxyl groups on the surface of ash, and Fourier-transformed spectroscopy suggests these groups on the adsorbent could form hydrogen bonds with TCP, thus leading to a partial overlapping of adsorption sites on ash (Wang et al. 2009, 2011). However, the binding of Zn^{2+} and these groups is stronger than the hydrogen bonding of TCP with them, and Zn^{2+} inhibits TCP adsorption through competing for the adsorption sites on the ash surface.

The competitive adsorption of Al^{3+} and TCP may also be related to their adsorption sites on ash, which should be confirmed by X-ray absorption spectroscopy. As a metal ion with higher charges than Zn^{2+} , Al^{3+} had a stronger binding capacity to surface negative charges of ash than that of Zn^{2+} . Furthermore, the hydrated radius of Al^{3+} (0.45 nm) is also larger than that of Zn^{2+} (0.3 nm); hence, Al^{3+} exhibits stronger inhibition of TCP adsorption.

According to the concept of “soft and hard acids and bases,” the hardness of Ag^+ , Zn^{2+} , and Al^{3+} gradually increases, which suggests that Ag^+ was the strongest in terms of polarization ability. Ag^+ is highly polarizable and can bind with aromatic organic compounds containing π -electrons (Chen et al. 2007), resulting in further elevated TCP adsorption by ash. In addition, Ag^+ has one positive charge and a larger ionic radius than Zn^{2+} and Al^{3+} ; hence, it is relatively easier for Ag^+ to replace the metal ions (mainly solonetz metal ions such as Na^+ and Ca^{2+}) originally on ash through outer layer complexation reactions (Chen et al. 2007). This will lead to further reduction in the solubility of functional groups on the ash surface and also compress the hydrated ionic radius of these metal ions, thereby reducing the competitive adsorption of water molecules on the ash surface and increasing the adsorption of TCP.

Effect of Ag^+ , Zn^{2+} , and Al^{3+} on desorption of TCP

Obvious desorption hysteresis of TCP from ash was observed with the absence of Ag^+ , Zn^{2+} , and Al^{3+} in solution (Fig. 5). Hysteresis probably resulted due to an entrapped fraction of sorbate that was unable to re-equilibrate when decreased solute

Table 3 Freundlich constants of 2,4,6-TCP adsorbed by ash

Adsorbate	C_M^{2+} (mM)	K_f	n	R^2
TCP	0	21.99±1.70	0.408±0.027	0.994
TCP + Ag^+	0.01	27.01±2.53	0.424±0.029	0.979
	0.05	25.34±2.35	0.443±0.035	0.985
	0.10	24.25±2.24	0.455±0.034	0.975
	0.01	20.42±2.09	0.406±0.032	0.969
TCP + Zn^{2+}	0.05	19.01±2.65	0.395±0.030	0.976
	0.10	17.35±2.03	0.390±0.032	0.973
	0.01	15.46±2.00	0.394±0.023	0.959
	0.05	14.11±2.44	0.390±0.028	0.966
TCP + Al^{3+}	0.10	13.98±2.56	0.385±0.023	0.972

Fig. 5 Desorption of 2,4,6-TCP from ash: (a) in the absence of metal ions, (b) in the presence of 0.1 mM Ag^+ , (c) in the presence of 0.1 mM Zn^{2+} , and (d) in the presence of 0.1 mM Al^{3+}

concentrations were achieved during desorption. These unrecoverable and recoverable fractions could potentially be kinetically tracked to final equilibrium or irreversible conditions and the chemical stoichiometry for kinetics and equilibrium could then be established based on the measured functional groups on ash to calculate the reaction sites for TCP. The desorption hysteresis suggested that TCP was adsorbed to a large amount of irreversible adsorption sites related to the relatively more rigid structure of ash (aromatic carbon content was very high; Table 1). This was similar to previous studies on matured organic matter and kerogen, which had more obvious desorption hysteresis (Barriuso et al. 1994).

The desorption hysteresis index (HI), which was defined as the ratio of N_d to N_s ($\text{HI} = N_d/N_s$), was used to evaluate the degree of desorption hysteresis (Table 4). When both N_d and N_s values were less than 1, the smaller the HI value was, the more obvious desorption hysteresis would be. As shown in Fig. 5, the desorption coefficient N_d and HI changed from

small to large as TCP concentration increased, i.e., desorption became relatively easier. This implied that TCP adsorbed mainly on these high-energy adsorption sites, and desorption was difficult at a low concentration of TCP. As TCP concentration further increased, parts of TCP could only be adsorbed on the low-energy adsorption sites, which was relatively easy for desorption.

Desorption hysteresis of TCP from ash was also observed quite clearly with the presence of Ag^+ , Zn^{2+} , and Al^{3+} in solution (Fig. 5). In addition, the HI values increased with the presence of Ag^+ , Zn^{2+} , and Al^{3+} in solution, which suggested that the addition of Ag^+ , Zn^{2+} , and Al^{3+} could promote TCP desorption from ash. It implied that metal cations occupied part of the high-energy sites of previously adsorbed TCP, demonstrating desorption hysteresis for TCP.

Conclusions

Adsorption studies revealed the underlying mechanisms responsible for the effects of metal cations (Ag^+ , Zn^{2+} , and Al^{3+}) on TCP adsorption onto, and desorption from, wheat ash, implying that the environmental fate of metal cations and TCP in the metal–TCP system is quite different from that of either metals or TCP alone. TCP showed obvious desorption hysteresis, and the presence of Ag^+ , Zn^{2+} , and Al^{3+} promoted desorption of TCP from ash. The presence of Ag^+ increased TCP adsorption and was ascribed to its ability to reduce the competitive adsorption of water molecules on the ash surface by replacing the original metal ions, such as Na^+ and Ca^{2+} ,

Table 4 Hysteresis indexes of 2,4,6-TCP desorption from ash

TCP		TCP+ Ag^+		TCP + Zn^{2+}		TCP+ Al^{3+}	
N_d	HI	N_d	HI	N_d	HI	N_d	HI
0.019	0.047	0.059	0.129	0.032	0.082	0.045	0.116
0.059	0.146	0.103	0.226	0.076	0.194	0.086	0.223
0.064	0.158	0.113	0.248	0.082	0.210	0.093	0.241
0.075	0.185	0.120	0.263	0.095	0.243	0.101	0.262
0.081	0.200	0.124	0.272	0.098	0.251	0.105	0.272
0.078	0.193	0.119	0.261	0.095	0.243	0.099	0.257

and compressing the hydrated ionic radius of these metal ions. In addition, Ag^+ could bind with aromatic organic compounds containing π -electrons, resulting in a further increase of TCP adsorption by ash. The presence of Zn^{2+} and Al^{3+} reduced TCP adsorption onto ash and was ascribed to a partial overlapping of adsorption groups for TCP and Zn^{2+} and Al^{3+} . Such information helps our understanding of real environmental processes relating to metals and aromatics in the soil–water environment.

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