



Organic diagenesis in sediment and its impact on the adsorption of bisphenol A and nonylphenol onto marine sediment

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ABSTRACT

Hydrophobic organic contaminants in marine water are mostly adsorbed onto (partitioned into) sediment organic matter (SOM). To study the impact of SOM diagenesis on sediment adsorption properties, artificial sediment with rich SOM content was incubated for more than 120 days. The sediment was sampled every week, and batch sediment adsorption tests were conducted with bisphenol A (BPA) and nonylphenol (NP) as the model pollutants. The results show that the amount of organic matter loaded in the sediment decreased by nearly 80% during incubation. For the incubated sediment, the BPA partition coefficient, K_d , decreased whereas the organic normalized partition coefficient, K_{oc} , more than doubled. The experiments with NP show an even greater increase in K_{oc} . Organic matter diagenesis shows a profound effect on the adsorption behavior of sediment, as the SOM residue has an increasing affinity and partition capacity for organic contaminants.

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1. Introduction

Adsorption and partition at the water–sediment interface is an important mechanism for the removal of organic pollutants from the water column. The fate, stability and transport of pollutants in a marine environment also largely depend on their adsorption onto sediment (Brandt et al., 1999; Cornelissen et al., 2005). Research has shown that hydrophobic organic contaminants are mostly distributed on suspended solids and in the bottom sediment rather than in the aqueous phase (Voice and Weber, 1983; Cornelissen et al., 2005). The overwhelming importance of organic matter in sediment to the adsorption of chemical pollutants has been widely recognized. According to the partition theory (Chiou et al., 1979; Maund et al., 2002), the adsorption of organic contaminants onto sediment strongly depends on the organic fraction of the sediment. It has been reported that the adsorption of selected endocrine disruptors and antibiotics may be proportionally related to the fraction of organic matter in natural sediment (Xu et al., 2008; Xu and Li, 2009).

The adsorption of chemical pollutants onto sediment with rich organic content is complex and dynamic because of sediment organic matter (SOM) diagenesis. Solid organic matter enters natural water as particulate organic matter from various origins, including algal bloom, storm water runoff, sewage discharge and sometimes

feed and waste from mariculture activities. In the coastal waters of Hong Kong, sediment often has a high organic content because of inputs from the Pearl River and other flows from the Pearl River Delta region (Xu et al., 2008; Xu and Li, 2009). Under natural conditions, the labile fraction of SOM mineralizes biologically within a few months or years, whereas the refractory portion undergoes a series of alterations in properties (Boudreau, 1997). Bacterial growth and decay play an important role in the biodegradation and biotransformation of SOM in sediment (Grathwohl, 1990; deBruyn and Gobas, 2004). Hence, SOM degradation and diagenesis affect the adsorption behavior and capacity of sediment (Liu and Lee, 2007). However, the dynamics of SOM transformation and its impact on the adsorption of environmental pollutants by the sediment have not been well addressed.

Endocrine disrupting chemicals (EDCs) constitute a group of organic pollutants currently of great concern due to their potential adverse effects on human health and biological fecundity (Collins, 2008). They can be highly stable and remain in the environment for years, incurring long-lasting ecological harm (Cohn et al., 2007). Among the large group of EDCs, bisphenol A (BPA) and nonylphenol (NP) are two representative contaminants in Hong Kong and the Pearl River Delta region (Kueh and Lam, 2008; Peng et al., 2008). The fate and transport of BPA and NP in marine water are closely related to the adsorption properties and especially the organic content of sediment (John et al., 2000; Xu et al., 2008). However, there is little research on the influence of organic degradation and transformation in marine sediment on the adsorption and partition capabilities of such sediment. In the study described here,

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experiments were carried out to investigate the dynamic process of SOM diagenesis and its effect on the adsorption behavior of sediment, using BPA and NP as the model EDCs. The results are of great importance to the modeling and impact assessment of environmental contaminants in the marine water–sediment system.

2. Materials and methods

2.1. Artificial sediment

Artificial sediment with a high organic load was prepared for the experiments according to guideline 218 of the Organization for Economic Co-operation and Development (OECD, 2004), with minor modifications. Briefly, the sediment consisted of 50% (w/w) quartz sand, 20% (w/w) kaolin clay, 20% (w/w) flour powder and 10% (w/w) natural sediment collected from Victoria Harbour, Hong Kong. The flour powder was used as the SOM input, and the natural sediment was added to bring microbial inoculums in the artificial sediment. The sediment was mixed thoroughly before incubation.

2.2. Model chemicals

Two typical EDCs, BPA and NP, were chosen as the model pollutants for the sediment adsorption tests. Both BPA and NP in powder form with greater than 99% analytical purity were supplied by Sigma–Aldrich. The water solubility of BPA is 381 mg/L (Li et al., 2007) and that of NP 5 mg/L (Brix et al., 2001), while the octanol–water partition coefficient ($\log K_{ow}$) of BPA is 3.4 (Zeng et al., 2006) and that of NP 4.48 (Ahel and Giger, 1993). The stock solutions were made in 25% and 100% (v/v) acetonitrile for BPA and NP, respectively, and the stocks were kept in a refrigerator at 4 °C before use.

2.3. Sediment incubation

The sediment was placed into each of more than 30 glass dishes for incubation. Each circular dish was 6 cm in diameter and 1 cm in depth. The sediment dishes were placed on the bottom of a large water tank filled with 10 L of saline marine water, which was made with reef salt to have a salinity of 10‰. Circulation and aeration were conducted for the overlaying water in the sediment incubation tank, and the water was changed daily. Throughout sediment incubation, one dish of sediment was retrieved from the water tank every week (two weeks in the late stage of incubation) for analysis and the adsorption tests.

2.4. Sediment characterization: organic and biomass contents

The total organic carbon (TOC) content in a sediment sample was measured using a TOC analyzer (TOC-5000, Shimadzu) with a solid sample module (SSM-5000A, Shimadzu). Each measurement was made three times to ensure accuracy. In addition, the fraction of volatile solids (VS) in the sediment was measured in accordance with the Standard Methods (APHA, 1999).

The growth in biomass during sediment incubation was observed directly with a fluorescence microscope (Eclipse E600, Nikon). The sediment was homogenized into a suspension and filtered onto a membrane filter. The sample was then stained with SYTO9 for 5 min to target microbial cells in the sediment. The filtered sample was observed under the microscope with light excitation and emission wavelengths of 488 nm and 543 nm, respectively. In addition, the biomass dynamics in the sediment was evaluated based on the change in lipid phosphorus (lipid-P) content. Lipid-P was obtained from the sediment suspension by

chloroform–methanol extraction and potassium persulfate digestion and the quantity determined using the ammonium molybdate spectrophotometric method (Findlay et al., 1989). The lipid-P content determined was used as an indication of active cells in the sediment during incubation.

2.5. Batch adsorption experiments

Batch adsorption testing was conducted on each incubated sediment sample following a procedure that has been used previously (Gao et al., 1998; Xu and Li, 2009). In brief, the sediment was placed as an adsorbent in a series of conical flasks, each with 0.8 g dry mass of the sediment. For BPA adsorption, solutions of different concentration, from 5 to 50 mg/L, were poured into the flasks to 50 mL each in volume. Sodium azide was added into the solutions at a concentration of 0.2% (w/v) to prevent biodegradation (Gao et al., 1998). The flasks were sealed with parafilm and placed in a temperature-controlled shaking incubator (Polyscience, USA) at a shaking rate of 100 rpm for the adsorption test at 25 °C for 12 h to reach equilibrium. Upon completion, the sediment mixture from each flask was centrifuged to remove the solids, and the BPA concentration in the aqueous phase was measured by a high-performance liquid chromatograph (HPLC). From the difference between the initial and final BPA concentrations, the amount of BPA adsorbed onto the sediment in each flask was determined. Batch experiments were conducted in a similar fashion on the incubated sediment to assess NP adsorption. The initial NP concentration was fixed at around 2 mg/L, and the amount of sediment placed in a series of flasks varied from 0.1 to 0.8 g in dry mass. After adsorption, the sediment was removed by centrifugation, and NP

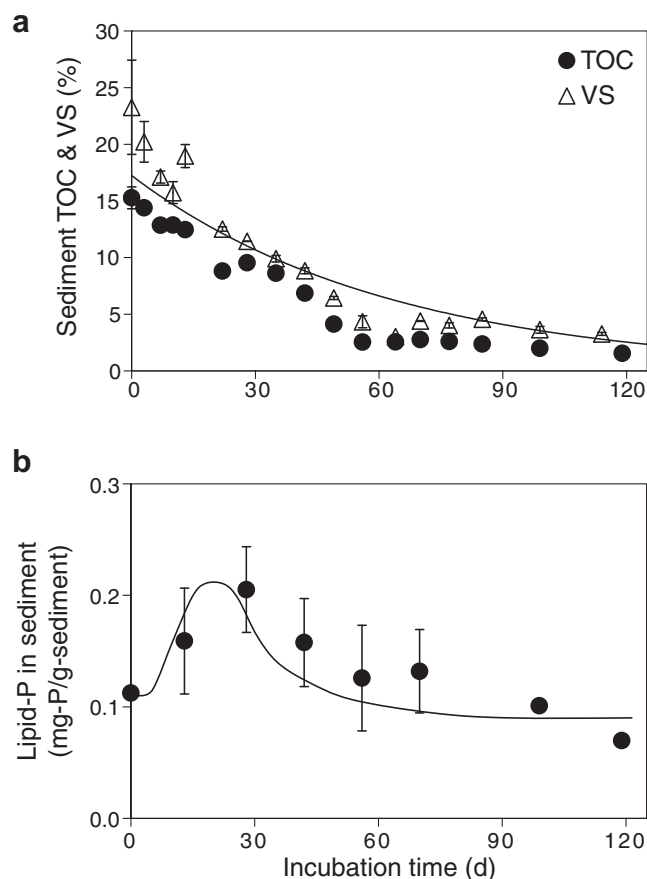


Fig. 1. Changes in (a) TOC and VS and (b) lipid-P content in the artificial sediment during laboratory incubation.

in the water was extracted and detected by a gas chromatograph (GC).

2.6. Chemical analysis

The BPA concentration in water was measured using the HPLC system (Waters 2695) with a C18 column (5 μ m, 2.1 \times 150 mm) for separation and a photodiode array detector (Waters 2996) for detection and quantification. The mobile phase was a mixture of acetonitrile and water (50:50, v/v), and the flow rate was 1.0 ml/min. Under these chromatographic conditions, baseline separation could be obtained within 8 min. The peak area at the wavelength of 205 nm was used for BPA quantification. The limits of detection and quantification were about 0.03 and 0.1 mg/L, respectively.

As NP is a semi-volatile substance, it was measured using a GC (Agilent 6890) with a flame ionization detector (FID). Prior to GC measurement, NP was extracted from the water solutions using hexane. Four ml of hexane was used to extract NP from a 30 ml water sample. The extraction was repeated three times, and the organic phases were combined. The extract was evaporated first by a nitrogen gas flow and then re-dissolved into 1 ml of hexane. The NP extract was measured by the GC-FID with an HP-5 column (30.0 m \times 250 μ m \times 0.25 μ m). The GC temperature program was initialized at 70 $^{\circ}$ C for 4 min and then increased to 280 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min. The retention time of NP under these program conditions was 23.7 min. The recovery of NP extraction and measurement procedure was in a range of 88.5–99.9%. The limits of detection and quantification were around 0.3 and 1 mg/L, respectively.

3. Results and discussion

3.1. Organic matter transformation and biomass dynamics during sediment incubation

SOM degradation was well demonstrated by the reduction in sediment organic matter during incubation. As flour is readily biodegradable, its degradation was rapid in the first two months of sediment incubation (Fig. 1a). The TOC fraction of the sediment decreased continuously from around 15% to less than 3% after two months. SOM degradation and diagenesis were confirmed by

the significant decrease in the VS content in the sediment. Bacterial growth and decay are believed to play an important role in the degradation and transformation of SOM during sediment incubation. After two months of incubation, the rate of SOM reduction became much slower, and the organic residue in the sediment appeared to be more refractory in nature.

Observation of the sediment samples stained by SYTO9 under the fluorescence microscope revealed significant bacterial growth during incubation. Microbial cells became more abundant in the sediment, which correlates well with SOM degradation. Growth was faster in the early stage, especially the first month, of sediment incubation. Biomass growth and decay dynamics were assessed by measuring the lipid-P content in the sediment. Based on the lipid-P content, the biomass grew rapidly in the first month and reached its peak after about 30 days. Thereafter, biomass decay appeared to be more dominant, resulting in a decrease in lipid-P content in the incubated sediment (Fig. 1b). The changes in the organic matter and lipid-P content in the sediment suggest that microbial growth converted a large portion of the flour SOM into biomass during the first month of sediment incubation, after which biomass decay apparently dominated SOM transformation in the sediment.

3.2. Change in the adsorption behavior of the sediment for BPA

The adsorption behavior of BPA onto the sediment after various periods of incubation can be well described by a linear correlation for the concentration range tested (Fig. 2). Hence, the partition model in the following form is adopted for the adsorption isotherm of BPA onto the sediment.

$$Q_e = K_d C_e \quad (1)$$

where Q_e and C_e are the equilibrium concentrations of BPA in the sediment and bulk solution, respectively, and K_d is the partition coefficient. The organic normalized partition coefficient, K_{oc} , was obtained as follows:

$$K_{oc} = K_d / f_{oc} \quad (2)$$

where f_{oc} is the fraction of organic carbon in the sediment.

The change in SOM quantity and properties during sediment incubation was found to have a great influence on the adsorption behavior and capacity of the sediment. The partition coefficient of BPA in the sediment decreased during the incubation process (Fig. 3a). The decrease in K_d was more rapid in the first two months or so, compared to the later phase of incubation. Following the partition theory, the K_d decrease was likely brought about by the reduction in the organic content of the sediment. However, the organic carbon normalized BPA partition coefficient increased considerably with time (Fig. 3b). The K_{oc} value was initially around 100 L/kg-sediment TOC, which is close to the K_{oc} of 85.7 L/kg-sediment TOC determined for pure flour, and increased to a level of around 225 L/kg-sediment TOC. The increase in K_{oc} indicates the greater adsorption capacity of the organic matter of the sediment. The SOM residue after incubation would become increasingly humic-like with the increase in adsorption capacity. The rate of K_{oc} increase was more rapid in the second month of sediment incubation (Fig. 3b), concurrent with the SOM degradation and biomass decay shown in Fig. 1. In general, the great reduction in SOM due to diagenesis decreased the overall partition capacity of the sediment solids for BPA. However, the organic normalized partition coefficient more than doubled after sediment incubation.

3.3. Change in the adsorption behavior of the sediment for NP

The adsorption of NP onto the sediment can also be well described by the partition model (Eq. (1)) for the concentration range tested (Fig. 4), while the partition capacity is specified by partition

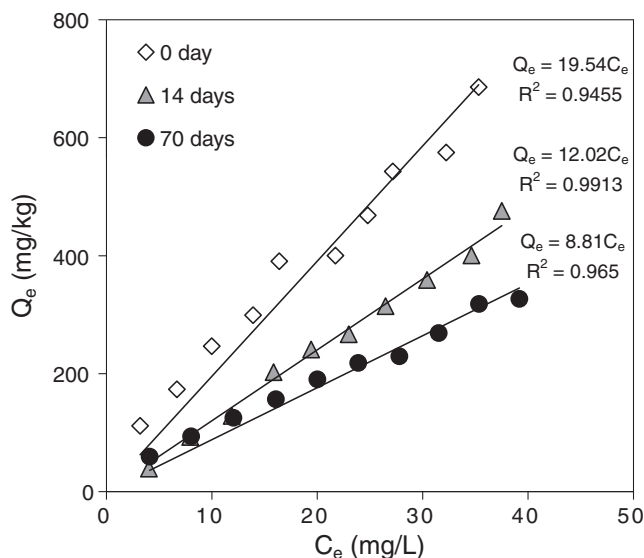


Fig. 2. The isotherms of BPA adsorbed onto the sediment after various periods of incubation.

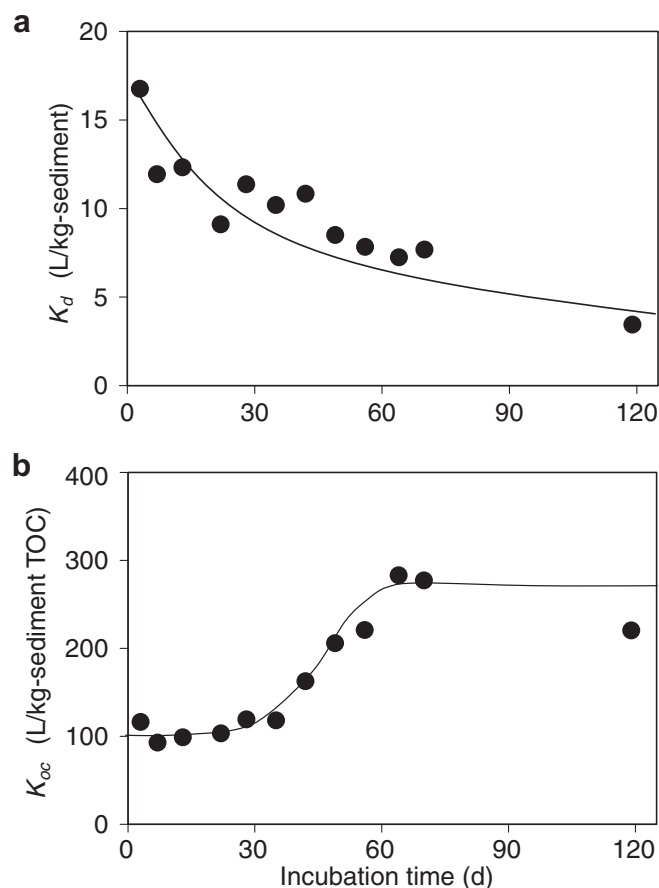


Fig. 3. (a) K_d and (b) K_{oc} for the partition of BPA in the sediment as a function of the incubation time.

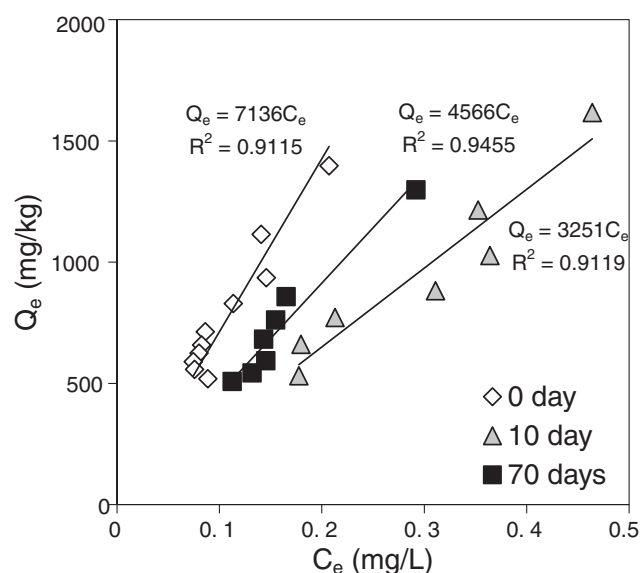


Fig. 4. The isotherms of NP adsorbed onto the sediment during incubation.

coefficients K_d and K_{oc} . The results show that SOM degradation during incubation had an even greater influence on NP adsorption onto the sediment. The K_d of NP decreased for the first 10 days or so and then increased continuously afterward (Fig. 5a). The incubated sediment eventually had a greater mass-based K_d value

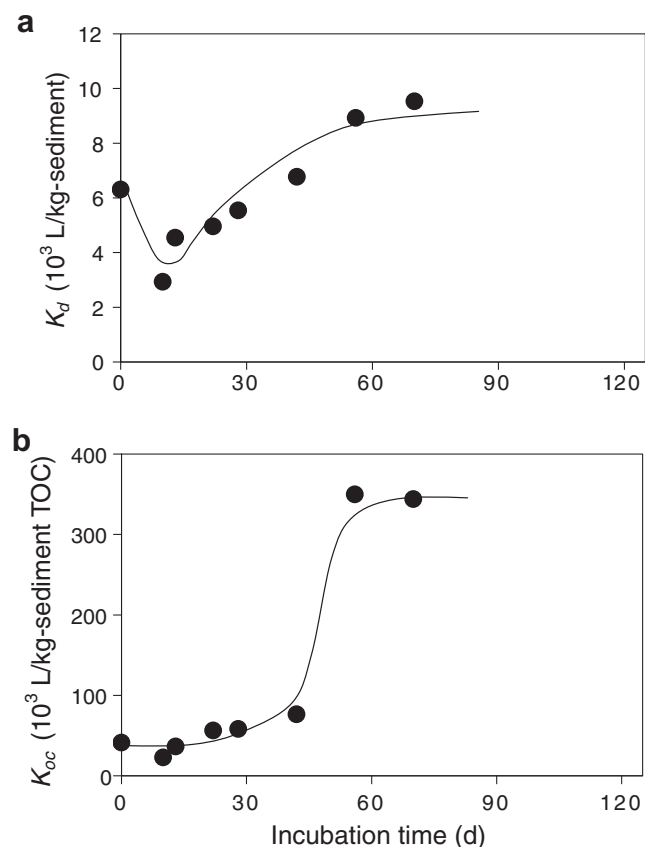


Fig. 5. (a) K_d and (b) K_{oc} for the partition of NP in the sediment as a function of the incubation time.

(9500 L/kg-sediment) compared to the original sediment. Meanwhile, the organic-based K_{oc} increased more than seven times from less than 5×10^3 L/kg-sediment TOC to around 3.5×10^4 L/kg-sediment TOC (Fig. 5b). Similar to the case with BPA, most of the K_{oc} increase took place in the second month of sediment incubation. This remarkable change again correlated well with the observed degradation and transformation of organic matter in the sediment (Fig. 1). The SOM residue after diagenesis became more humic-like with the much greater partition capacity for NP.

3.4. The influence of SOM degradation and diagenesis on EDC adsorption onto sediment

The results of the sediment incubation and adsorption experiments indicate a profound impact of sediment diagenesis on the adsorption behavior of environmental pollutants onto sediment with rich organic content. The readily biodegradable organic solids in the artificial sediment were transformed in three ways. The first was the mineralization of organic to carbon dioxide via biodegradation, which resulted in the direct reduction of SOM. A related process was microbial growth through organic utilization, which transformed the organic molecules into biomass. The third process was biomass decay and mineralization, which led to the formation and accumulation of humic materials in the sediment. With the increase in humic content, the SOM residue would have a greater chemical adsorption and partition capacity (Murphy et al., 1990; Hiller et al., 2009). The present experimental study revealed that most of the change in K_{oc} occurred in the later phase of SOM degradation, which corresponds well with the endogenous decay of biomass in the sediment (Fig. 1).

Previous research has suggested that fresh organic solids entering the water–sediment system mainly consist of biopolymers with limited sorptive capacity, and that SOM is transformed by diagenesis into humic-like substances in sediment (Grathwohl, 1990). Humic matter has been found to have great adsorption and partition capacity for organic pollutants in aquatic environments (Chiou et al., 1979; Xu et al., 2008). During sediment diagenesis, SOM undergoes biotransformation and biodegradation, which alters both the chemical and physical properties of the sediment. As a result, the SOM residue has an increasing affinity and adsorption capacity for organic contaminants, especially the more hydrophobic organics, such as NP, compared to the more hydrophilic organics, such as BPA. Thus, SOM dynamics and its influence on the adsorption and transport of EDCs and other emerging environmental pollutants in sediment should not be overlooked. This is particularly important to the marine system with rich organic load into the sediment.

4. Conclusions

- Diagenesis of organic matter in sediment was well demonstrated with artificial sediment under laboratory conditions. During sediment incubation, over 80% of the initial SOM biologically degraded along with biomass growth, and the biomass was eventually transformed into humic-like matter in the sediment.
- The change in SOM quantity and properties greatly affects the adsorption behavior and capacity of sediment for environmental pollutants. The partition coefficient, K_d , of the sediment for BPA decreased from 15 L/kg-sediment at the beginning to about 5 L/kg-sediment by the end of 4 months of incubation. However, the organic normalized partition coefficient, K_{oc} , increased more than twofold from 90 L/kg-sediment TOC to around 225 L/kg-sediment TOC. For the adsorption of NP onto the incubated sediment, the experiments showed a general increase in K_d and an increase of more than seven times in K_{oc} . It is argued that the sediment diagenesis process results in SOM residue with an increasing affinity and partition capacity for organic contaminants.

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