



## Evolution of submicron organic aerosol in polluted air exported from Tokyo

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[1] Ground-based measurements of aerosols and trace gases were conducted at an urban site in Tokyo (Komaba) and a site 50 km to the north (Kisai) during July–August 2004. An Aerodyne aerosol mass spectrometer (AMS) was deployed at each measurement site to investigate the chemical evolution of submicron organic aerosol (OA) in polluted air. The mass concentrations of OA at the Kisai site were systematically higher than those at the Komaba site and were correlated with ozone under southerly conditions. The rate of increase of OA at the Kisai site is investigated using the photochemical age derived from the ratio of alkyl nitrates to their parent hydrocarbons. The OA concentrations in processed air (age of 8–16 h) were 4–5 times larger than those in fresh emissions (age  $\sim$  0), suggesting that the OA concentrations can be significantly enhanced within  $\sim$ 0.5 days under conditions of high photochemical activity. **Citation:** Takegawa, N., et al. (2006), Evolution of submicron organic aerosol in polluted air exported from Tokyo, *Geophys. Res. Lett.*, 33, L15814, doi:10.1029/2006GL025815.

### 1. Introduction

[2] Organic compounds often constitute a major fraction of total fine particle mass in urban air [e.g., *Takegawa et al.*, 2006; *Turpin et al.*, 2000]. Export of anthropogenic emissions from urban areas, combined with emissions of volatile organic compounds (VOCs) from biogenic sources, can significantly affect the distributions of organic aerosol (OA) in surrounding regions [e.g., *Russell and Allen*, 2005]. *de Gouw et al.* [2005] have suggested that the formation of secondary organic aerosol (SOA) in anthropogenic plumes is more efficient than previously assumed, based on an extensive data set obtained during the New England Air Quality Study (NEAQS). A recent model simulation has shown that there is a large missing source of SOA in the free troposphere over East Asia [*Heald et al.*, 2005]. Current understanding of the emission of primary organic aerosol (POA) and the formation of SOA is in-

creasing but is still limited [*Turpin et al.*, 2000], causing significant uncertainty in estimating the effects of OA on regional/global climate change [*Kanakidou et al.*, 2005]. The major purpose of this study is to investigate the photochemical evolution of OA in polluted air exported from Tokyo using the data obtained at urban and suburban sites during the summer of 2004.

### 2. Measurements

[3] Ground-based measurements of aerosols and trace gases were conducted at an urban site in Tokyo (Komaba: 35°39'N, 139°40'E) and a suburban site (Kisai: 36°05'N, 139°33'E) from July 25 to August 14, 2004. The Komaba site is at the Research Center for Advanced Science and Technology, University of Tokyo. The Kisai site is at the Center for Environmental Science in Saitama, which is located about 50 km north of the Komaba site. The Kisai site is therefore downwind of the Komaba site under southerly conditions.

[4] At the Komaba site, the sample air was aspirated from the rooftop of the observatory building (18 m above ground level (AGL)). At the Kisai site, a temporary observatory house (two-level) was constructed prior to the measurement period. The sample air was aspirated from the rooftop of the house (6.5 m AGL) through a 1/2-inch outer diameter stainless steel tube and a 3/4-inch outer diameter Teflon tube for the aerosol and gas inlets, respectively.

[5] Size-resolved chemical composition of submicron aerosol was measured using an Aerodyne aerosol mass spectrometer (AMS) both at the Komaba and Kisai sites. The performance and data process of the AMS deployed at the Komaba site (Komaba AMS) are described by *Takegawa et al.* [2005]. The AMS deployed at the Kisai site (Kisai AMS) was operated in the same configuration as the Komaba AMS. The performance of the Kisai AMS was basically the same as the Komaba AMS, except for a higher sample flow rate. The mass concentrations of submicron OA measured by the AMS were compared with those of PM<sub>1</sub> organic carbon (OC) measured using a thermal-optical carbon analyzer (Sunset Laboratory, Inc., USA). The sampling of OC was made using a semi-continuous instrument (every 1 h) at the Komaba site and using a low-volume sampler (every 3 h) at the Kisai site. The regression slope of OA versus OC was  $1.8 \pm 0.1$  ( $r^2 = 0.89$ ) and  $1.8 \pm 0.3$  ( $r^2 = 0.64$ ) at the Komaba and Kisai sites, respectively. These values are consistent with the OA/OC ratios of 1.6–2.1 reported by *Turpin and Lim* [2001]. The accuracy of the OA measurements, including the uncertainties in the relative ionization efficiency, particle collection efficiency, and AMS size-cut, is difficult to

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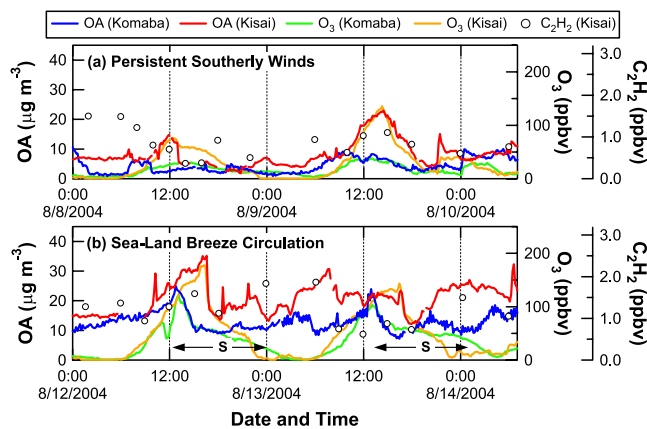
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**Figure 1.** (a) Example of time series of OA,  $\text{O}_3$ , and  $\text{C}_2\text{H}_2$  observed at the Komaba and Kisai sites during phase 1 (persistent southerly winds). (b) Same as Figure 1a but for phase 2 (sea-land breeze circulation). The periods of southerly winds at the Komaba site are indicated by arrows.

evaluate because some of these uncertainties depend on the physical and chemical properties of aerosols in ambient air. A more detailed evaluation of the AMS data during this period will be presented elsewhere (T. Miyakawa et al., manuscript in preparation, 2006). The 10-min averages of these data are used for the present analysis.

[6] Ozone ( $\text{O}_3$ ) was measured using an ultraviolet (UV) absorption technique and reactive nitrogen ( $\text{NO}_x$  and  $\text{NO}_y$ ) was measured using a  $\text{NO}-\text{O}_3$  chemiluminescence technique [Takegawa et al., 2006] both at the Komaba and Kisai sites. Hydroxyl radical (OH) was measured only at the Komaba site using a laser-induced fluorescence technique [Kanaya et al., 2001]. On-line measurements of  $\text{C}_2-\text{C}_7$  hydrocarbons (every 1 h) were conducted at the Komaba site using a GC-FID system [Takegawa et al., 2006]. Measurements of hydrocarbons and alkyl nitrates were conducted at the Kisai site using a whole air sampling technique [Simpson et al., 2003]. Although the sampling interval was 2–6 h, the actual integration time was 5–10 s for each sample. The whole air sample data were merged with the 10-min average data without averaging/smoothing.

### 3. Results and Discussion

#### 3.1. Temporal Variations

[7] The meteorological conditions from July 31 to August 14, 2004 are classified into two phases. The data obtained during July 25–30 are not used for the classification because northerly or easterly winds were dominant during this period. Phase 1 is from July 31 to August 9 (10 days total), when a stable anticyclone was located east of Tokyo and persistent southerly winds were dominant over the Komaba and Kisai sites. This means that relatively clean maritime air passed over Komaba and was transported to Kisai. Figure 1a shows an example of the time series of OA,  $\text{O}_3$ , and ethyne ( $\text{C}_2\text{H}_2$ ) during phase 1.  $\text{C}_2\text{H}_2$  is used to normalize the OA concentration in section 3.3. The concentrations of  $\text{O}_3$  and OA at the Kisai site were higher by a factor of 2–3 than the Komaba site. There is a time lag of

2–3 h in the peak levels of  $\text{O}_3$  and OA at the downwind Kisai site, as compared to the Komaba site. These features suggest that significant formation of  $\text{O}_3$  and SOA took place in polluted air exported from Tokyo. For comparison, the transport time of air masses between the two sites is estimated to be 4–5 h, based on a wind speed of  $\sim 3 \text{ m s}^{-1}$  at around noon. However, we note that the timing of the peaks of  $\text{O}_3$  and OA at the Kisai site depends not only on the transport time of the air masses but also on the diurnal variation of solar radiation and the additional injections of precursors during transport.

[8] Table 1 summarizes the median mixing ratios of  $\text{NO}_x$ ,  $\text{C}_2\text{H}_2$ , toluene, and isoprene during phase 1. Most of the anthropogenic trace gases (including  $\text{NO}_x$  and  $\text{C}_2\text{H}_2$ ) observed at the Kisai site were lower than or comparable to those at the Komaba site, while toluene was significantly higher at the Kisai site. According to an emission inventory developed by Kannari et al. [2004], large emission sources of  $\text{NO}_x$ ,  $\text{C}_2\text{H}_2$ , and toluene are mostly located in the vicinity of the Komaba site (within  $\sim 10 \text{ km}$  distance). However, our measurements suggest that the additional injection of toluene during transport may be more important than  $\text{NO}_x$  and  $\text{C}_2\text{H}_2$ . As for isoprene, large emission sources are located at  $\sim 30 \text{ km}$  west of the two sites (forests and mountains). The interpretation of isoprene is rather complicated because of its high reactivity (lifetime  $< 1 \text{ h}$ ).

[9] Phase 2 is from August 10 to August 14 (5 days total), when a stable anticyclone was located over Tokyo and the sea-land breeze circulation was dominant. This means that air masses were stagnant over this region. Figure 1b shows an example of the time series of OA,  $\text{O}_3$ , and  $\text{C}_2\text{H}_2$  during phase 2. The minimum concentration of OA increased compared to Figure 1a, indicating an accumulation of pollutants during this period. This led to high concentrations of  $\text{O}_3$  and OA ( $> 100$  parts per billion by volume (ppbv) and  $> 20 \mu\text{g m}^{-3}$ , respectively) even at the Komaba site.

#### 3.2. Photochemical Age

[10] We estimate the photochemical age of the observed air masses using the ratio of alkyl nitrates to their parent hydrocarbons. Based on the results from previous studies [Simpson et al., 2003, and references therein], we chose 2-pentyl nitrate (2-PeONO<sub>2</sub>) and *n*-pentane (*n*-C<sub>5</sub>H<sub>12</sub>) for the present analysis. The relationship between the 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratio and the photochemical age (*t*) is given by:

$$\frac{[2-\text{PeONO}_2]}{[n-\text{C}_5\text{H}_{12}]} = \frac{\beta k_A}{(k_B - k_A)} \left(1 - e^{(k_A - k_B)t}\right) \quad (1)$$

where  $\beta$  is the fractional yield, and  $k_A$  and  $k_B$  are the pseudo-first order rate coefficients for the formation and destruc-

**Table 1.** Median Mixing Ratios of  $\text{NO}_x$  and Selected VOCs<sup>a</sup>

Species	Komaba	Kisai
$\text{NO}_x$ , ppbv	14.3 (10.2–19.2)	9.5 (5.9–12.7)
Ethyne, ppbv	0.52 (0.37–0.69)	0.53 (0.36–0.81)
Toluene, ppbv	0.81 (0.63–1.45)	2.2 (1.1–6.7)
Isoprene, ppbv	0.15 (0.06–0.52)	0.09 (0.06–0.13)

<sup>a</sup>Values in parentheses are the 25th and 75th percentiles.

tion, respectively, of 2-PeONO<sub>2</sub>. The reader is referred to *Simpson et al.* [2003] for details about these parameters. Considering that *n*-C<sub>5</sub>H<sub>12</sub> is emitted predominantly from anthropogenic sources, equation (1) can be used to estimate the photochemical age of anthropogenic emissions.

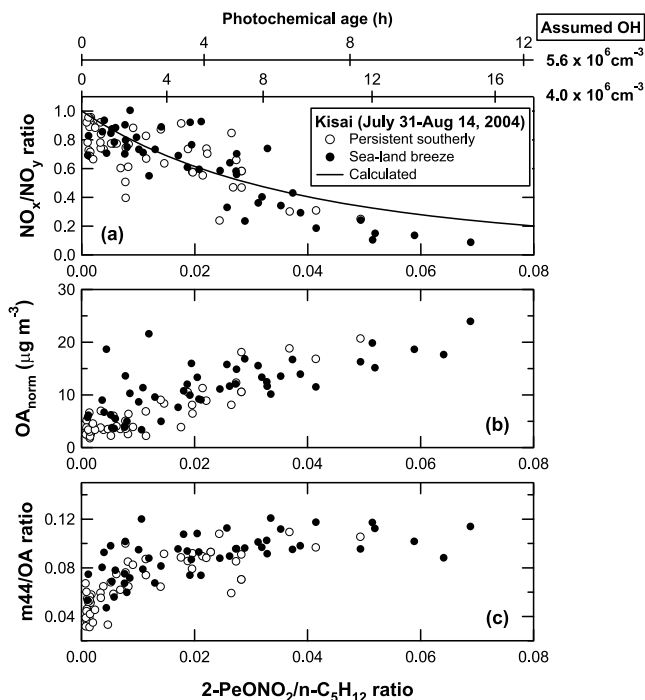
[11] It should be noted that there are several assumptions in equation (1): (a) the effects of dilution/mixing on the 2-PeONO<sub>2</sub> and *n*-C<sub>5</sub>H<sub>12</sub> concentrations are distinguishable from those of photochemical reactions, (b) the reaction of *n*-C<sub>5</sub>H<sub>12</sub> with OH is the rate-limiting step in the formation of 2-PeONO<sub>2</sub>, (c) the initial concentration of 2-PeONO<sub>2</sub> is zero, and (d) the OH concentration is constant over the time period considered. The validity of assumptions (a)–(c) is examined as follows. *McKeen et al.* [1990] showed that the effect of mixing on the ratios of NMHCs significantly depends on the reactivity of NMHCs under conditions of continuous emissions. Here we consider 2-butyl nitrate (2-BuONO<sub>2</sub>) and *n*-butane (*n*-C<sub>4</sub>H<sub>10</sub>), which are less reactive than 2-PeONO<sub>2</sub> and *n*-C<sub>5</sub>H<sub>12</sub>, respectively. The linear regression slope of the observed 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> versus 2-BuONO<sub>2</sub>/*n*-C<sub>4</sub>H<sub>10</sub> ratios agrees well (~9%) with that predicted based on equation (1) and the similar equation for 2-BuONO<sub>2</sub> (not shown). This result suggests that the photochemical evolution of 2-PeONO<sub>2</sub> can be well described by equation (1).

[12] The assumption (d) is tested by considering two cases. The first case assumes the average OH concentration of  $4.0 \times 10^6 \text{ cm}^{-3}$  during the daytime (6:00–18:00LT), while the second case assumes the average OH of  $5.6 \times 10^6 \text{ cm}^{-3}$  around the daytime peak (10:00–14:00LT). The average temperature of 303 K (6:00–18:00LT) is used for both cases. The photochemical age calculated by the second case is shorter by 40% than the first case. This number can be interpreted as the possible uncertainty due to assumption (d).

### 3.3. Evolution of Submicron Organic Aerosol With Air Mass Aging

[13] Figure 2 shows the NO<sub>x</sub>/NO<sub>y</sub> ratio, OA<sub>norm</sub>, and *m*44/OA ratio as functions of the 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratio observed at the Kisai site during phases 1 and 2. *m*44 represents the equivalent concentration of organic fragments represented by the *m/z* 44 peak and is a good marker of oxygenated organic compounds [*Zhang et al.*, 2005]. OA<sub>norm</sub> represents the normalized OA concentration, which is defined as  $\text{OA}_{\text{norm}} = \text{OA} \times \overline{\text{C}_2\text{H}_2}/\text{C}_2\text{H}_2$ .  $\overline{\text{C}_2\text{H}_2}$  (= 0.804 ppbv) represents the average C<sub>2</sub>H<sub>2</sub> mixing ratio at the Kisai site during the whole period (July 25–August 14, 2004). This means that the OA concentrations are normalized by C<sub>2</sub>H<sub>2</sub> to account for the heterogeneity of the source strength of POA and VOCs and for the atmospheric dilution effect. If the POA/C<sub>2</sub>H<sub>2</sub> ratios are constant with aging and there is no production of SOA, OA<sub>norm</sub> remains constant. This is basically the same data processing as done by *de Gouw et al.* [2005]. The photochemical lifetime of C<sub>2</sub>H<sub>2</sub> is estimated to be 90 h (OH =  $4.0 \times 10^6 \text{ cm}^{-3}$ ). Although we need a small correction to account for the photochemical loss of C<sub>2</sub>H<sub>2</sub> in aged air, we use C<sub>2</sub>H<sub>2</sub> because of its low background level (~0.13 ppbv).

[14] Figure 2 represents an ensemble of many events rather than a Lagrangian history for a particular event because the data were obtained at various local times on



**Figure 2.** (a) NO<sub>x</sub>/NO<sub>y</sub> ratio as a function of the 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratio observed at the Kisai site during phase 1 (open) and phase 2 (solid). The top axis indicates the photochemical age calculated using equation (1). The curve indicates the decay of NO<sub>x</sub> against OH reaction. (b) Same as Figure 2a but for OA<sub>norm</sub>, where OA<sub>norm</sub> is the normalized OA concentration. It is defined as  $\text{OA}_{\text{norm}} = \text{OA} \times \overline{\text{C}_2\text{H}_2}/\text{C}_2\text{H}_2$ , where  $\overline{\text{C}_2\text{H}_2} = 0.804 \text{ ppbv}$  is the average C<sub>2</sub>H<sub>2</sub> at the Kisai site. (c) Same as Figure 2a but for the *m*44/OA ratio.

various days at the Kisai site. In spite of this variability, the NO<sub>x</sub>/NO<sub>y</sub> ratio exhibits a systematic decrease with the 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratio. There is no significant difference in the dependence of the NO<sub>x</sub>/NO<sub>y</sub> ratio on the 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratio between phases 1 and 2. The phase 2 air masses tend to be older than phase 1, which is consistent with the fact that air masses were stagnant over this region during phase 2. The decrease rate of the NO<sub>x</sub>/NO<sub>y</sub> ratio based on OH =  $4.0 \times 10^6 \text{ cm}^{-3}$  (~0.10 h<sup>-1</sup>) agrees well with the loss rate of NO<sub>x</sub> against OH reaction (~0.09 h<sup>-1</sup>). We also estimated the rate of decrease of the ethene (C<sub>2</sub>H<sub>4</sub>)-to-C<sub>2</sub>H<sub>2</sub> ratio (~0.10 h<sup>-1</sup>) and found good agreement with the loss rate of C<sub>2</sub>H<sub>4</sub> against OH reaction (~0.12 h<sup>-1</sup>) (not shown). These agreements support the validity of using equation (1) as a quantitative measure of the photochemical age of anthropogenic emissions.

[15] In Figures 2b–2c, both OA<sub>norm</sub> and the *m*44/OA ratio show a systematic increase with air mass aging. The *m*44/OA ratio rapidly increased at the early processing stage but only slowly increased after that. This is due to the similar changes in OA and *m*44 with aging, suggesting that the observed increase in OA was mainly due to the increase in oxygenated organic compounds through processing of anthropogenic emissions. This process includes (a) formation of SOA from anthropogenic VOCs, (b) formation of SOA from biogenic VOCs by oxidants produced from anthropo-

genic precursors, (c) oxidation of POA, and (d) deposition of OA. The effects of (a) and (b) are not distinguishable in the present analysis, although the observed VOC mixing ratios (e.g., Table 1) may provide some information on these effects. The effect of (c) is difficult to evaluate because this process is not well understood. *Robinson et al.* [2006] showed that the oxidation of some POA compounds could be important on a time scale of a few days. As for the effect of (d), the removal lifetime of fine particles due to dry deposition is estimated to be 2–5 days, assuming a deposition velocity of  $0.5 \text{ cm s}^{-1}$  [Lovett, 1994] and a typical mixing height of 1–2 km. Therefore, it is likely that the effects of (c) and (d) were small on the time scale considered in this analysis (<16 h).

[16] At 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratios of 0–0.002 (fresh emissions), the average  $\pm 1\sigma$  of OA<sub>norm</sub> is found to be  $3.6 \pm 1.4 \mu\text{g m}^{-3}$ . The average OA/C<sub>2</sub>H<sub>2</sub> ratio in the fresh emissions is calculated to be  $\sim 4.5 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$ . This value is much higher than the POA/C<sub>2</sub>H<sub>2</sub> emission ratio estimated from the inventory ( $\sim 0.08 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$ ) [Kannari et al., 2004], although there could be large uncertainties in the emission inventory. At 2-PeONO<sub>2</sub>/*n*-C<sub>5</sub>H<sub>12</sub> ratios of 0.05–0.07 (processed air), the average  $\pm 1\sigma$  of OA<sub>norm</sub> is found to be  $19.1 \pm 3.2 \mu\text{g m}^{-3}$ . The processed air corresponds to photochemical ages of 11–16 h and 8–11 h at OH =  $4.0 \times 10^6$  and  $5.6 \times 10^6 \text{ cm}^{-3}$ , respectively. Based on these results, it is estimated that OA (normalized by C<sub>2</sub>H<sub>2</sub>) increased from 3.6 to 16.4  $\mu\text{g m}^{-3}$  after 8–16-h photochemical processing, which gives an increase rate of  $0.8\text{--}1.6 \mu\text{g m}^{-3} \text{ h}^{-1}$ . Note that we made a correction (from 19.1 to 16.4  $\mu\text{g m}^{-3}$ ) to account for the photochemical loss of C<sub>2</sub>H<sub>2</sub> in the processed air ( $\sim 14\%$ ).

[17] Turpin and Huntzicker [1995] first identified high SOA episodes during the Southern California Air Quality Study (June–August 1987). *de Gouw et al.* [2005] have found a factor of  $\sim 4$  increase in submicron OC after 10 h of processing during NEAQS (July–August 2002), corresponding to an increase rate of  $\sim 0.5 \mu\text{g m}^{-3} \text{ h}^{-1}$  (OA/OC ratio = 1.78). A common feature found in previous studies and this study is that the mass concentrations of OA can be significantly enhanced within  $\sim 0.5$  days under conditions of high photochemical activity.

[18] We should note that the above discussion has focused on the evolution of OA in the processed air. The average OA<sub>norm</sub> during phases 1 and 2 are found to be  $8.8 \mu\text{g m}^{-3}$ , suggesting that enhancement of OA by aging ( $8.8\text{--}3.6 = 5.2 \mu\text{g m}^{-3}$ ) can account for  $\sim 60\%$  of the total OA observed at the Kisai site on average during this period. It is likely that most of this enhancement can be attributed to SOA, as discussed earlier. *Schauer et al.* [1996] estimated that only  $\sim 30\%$  of OA (<2  $\mu\text{m}$ ) was attributed to SOA at  $\sim 90$  km east of downtown L.A. (Rubidoux) on 1982 annual average. Further investigations are needed to estimate the contribution of SOA to total OA in surrounding regions of Tokyo on an annual average basis.

#### 4. Conclusions

[19] The evolution of submicron OA in polluted air exported from Tokyo was investigated using AMS data obtained during July–August 2004. A large increase in OA was found at a site downwind of Tokyo, suggesting a significant formation of SOA with air mass aging. We

estimated that OA (normalized by C<sub>2</sub>H<sub>2</sub>) increased from  $\sim 4$  to  $\sim 16 \mu\text{g m}^{-3}$  in processed air (photochemical age of 8–16 h), corresponding to an increase rate of  $0.8\text{--}1.6 \mu\text{g m}^{-3} \text{ h}^{-1}$ . These results could be useful for the validation of chemical transport models in future studies.

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