Elution of bisphenol A and its chlorination by-products from lined pipes in water supply process


ABSTRACT

Elution of bisphenol A (BPA), chlorinated BPAs (i.e., 3-chlorobisphenol A, sum of 3,5-dichlorobisphenol A and 3,3'-dichlorobisphenol A, 3,3',5-trichlorobisphenol A, and 3,3',5,5'-tetrachlorobisphenol A) and 2,4,6-trichlorophenol (TCP) from lined pipes coated with two epoxy resins were investigated in a 24-month continuous test passing tap water. BPA, chlorinated BPAs, and TCP were not detected in the tap water at the outlet of lined pipes in most cases. However, all of these chemicals were detected in the tap water after 16 h of retention. The sums of BPA and chlorinated BPAs in the retained tap water were usually high when the residual chlorine levels were low. The residual chlorine was related to temperature, residual chlorine in the tap water at the inlet of lined pipes, and the elapsed time. From the results of leach tests, it was indicated that no marked changes in BPA concentration over the 24 months of the continuous test. Chlorinated BPAs and TCP were accumulated on the surface of lined pipes during the continuous test.

INTRODUCTION

Bisphenol A (BPA) is widely used in many products, such as raw materials of polycarbonate and epoxy resins, phenol resin, and plastic polyester (Water Supply Division (WSD), Health Service Bureau (HSB), Ministry of Health, Labour, and Welfare (MHLW) 2003). BPA is selected as an item for further study in drinking water regulation in Japan and its provisional target value is 100 μg/L.

There have been many previous studies regarding the occurrence and treatability of BPA in water supply systems, particularly as it was reported to show estrogenic activity (Kunikane 1999b; Vanderford & Snyder 2006; Stiles et al. 2008). It is known that some materials used for water supply system such as epoxy resin contain BPA (United States Environmental Protection Agency (USEPA) 2010) and therefore it is considered that elution from such materials is one of the contamination sources of BPA in drinking water. It was reported that BPA was detected in seven of 39 leaching water after leach test for materials and equipment which are currently used or used in the past to supply water (Kunikane 1999a). It was also reported that BPA was detected in leaching water after leach test for three epoxy resins (Bae et al. 2002). Moreover, continuous tests involving passing tap water into several pipes were conducted over a period of 20 or 24 months (Kunikane 2002, 2005). Leach tests for some compounds including BPA were conducted at several time intervals during the continuous tests, and BPA was detected in some leaching water samples.

BPA with two phenolic groups rapidly reacts with chlorine (Deborde & von Gunten 2008). Hu et al. (2002) reported that 13 products (e.g., chlorinated BPAs and 2,4,6-trichlorophenol (TCP)) were identified as chlorination by-products of BPA. BPA and five types of chlorinated BPAs were also detected in final effluents from wastewater recycling plants (Fukazawa et al. 2001). With regard to chlorination by-products of BPA, it was reported that the estrogen receptor binding affinity after 60 min of chlorination of BPA was 24 times higher than that before chlorination (Hu et al. 2002). It was also reported that some halogenated BPAs acted as agonists in a yeast two-hybrid thyroid hormone activity assay with and without rat liver S9 mix (Terasaki et al. 2011). From these results, it was considered that it was important to evaluate the elution of both BPA and its chlorination by-products in the presence of chlorine. However, in the previous studies (Kunikane 1999a, 2002, 2005; Bae et al. 2002), the waters without chlorine such as mineral water were used as leaching water and only BPA elution was evaluated.

In the present study, elution of BPA and its chlorination by-products from lined pipes coated with epoxy resins was investigated by continuous tests passing tap water into lined pipes over a period of 24 months to evaluate profiles of their elution in the presence of chlorine. Leach tests using leaching water without chlorine were also performed to support the results of continuous test. Moreover, the occurrence of BPA and its chlorination by-products in tap water was examined to evaluate concentrations of chlorination by-products of BPAs in tap water and effects of renovation work of water pipes on the concentrations of BPA and its chlorination by-products in tap water.

MATERIALS

Reagents and solutions

All reagents used were for analytical grade or higher. Standards of BPA, TCP, and BPA-d16 and purified water were purchased from Wako Pure Chemicals (Osaka, Japan). Chlorinated BPAs (i.e., 3-chlorobisphenol A (CIBPA), 3,5-dichlorobisphenol A (3,5-diClBPA), 3′,3′-dichlorobisphenol A (3,3′-diClBPA), 3,3′,5-trichlorobisphenol A (triClBPA), and 3,3′,5,5′-tetrachlorobisphenol A (tetraClBPA)) were synthesized by the previously reported procedure (Fukazawa et al. 2001). The chlorinated BPAs were confirmed by nuclear magnetic resonance (NMR) and gas chromatography coupled with mass spectrometry (GC–MS) (Terasaki et al. 2011). These chlorinated BPAs and TCP were reported to be chlorination by-products of BPA (Fukazawa et al. 2001; Hu et al. 2002).

Preparation of lined pipes

Several non-lined steel pipes (Steel Gas Pipe (SGP), 20 mm × 1.2 m) were lined using two types of liquid epoxy resin (epoxy resins A and B). The epoxy resins A and B are major types used for renovation work of water pipes among the epoxy resins using BPA as raw base resin material. The water pipes lined with epoxy resin A and B were designated as lined pipes A and B, respectively. These lined pipes were used for the continuous test and leach test after washing for 1 h by passing tap water through the pipes. The flow rates of tap water were 1 L/min for lined pipe A and 5 L/min for lined pipe B based on their usual washing conditions after water pipe renovation work using epoxy resins A and B.

METHODS

Continuous test of lined pipes

To simulate elution of BPA and its chlorination by-products from water pipe in households, continuous test passing tap water into lined pipes A and B was performed at 23 °C in our laboratory over a period of 24 months (i.e., from December 2008 to December 2010). Tap water was passed continuously into the six lined pipes A or B connected in series (inner volume, 2.3 L). The flow rate was set to 600 L/day considering average domestic water use (The Society of Heating, Air-conditioning and Sanitary Engineers of Japan 2001). Tap water was regularly sampled at the inlet and outlet of the lined pipes. Also, tap water was regularly retained for 16 h in lined pipes with reference to the leaching time in the leach test (notification No. 111; the Ministry of Health and Welfare (MHW, now MHLW) 1997) by turning off the valves at both inlet and outlet of lined pipes, except for 90 min of retention after 3 days. In
sampling, residual chlorine in the samples was quenched with sodium ascorbate (Kanto Chemical Co., Tokyo, Japan). After sampling, continuous test with passing of tap water into lined pipes was started again.

**Leach test of lined pipes and glass sheets**

Leach tests of new lined pipes A and B and those after 24 months of the continuous test were performed using the method of notification No. 111 (MHW 1997). Leaching water was prepared using purified water with the following water quality data: pH 7.0 ± 0.1; hardness 45 ± 5 mg/L; alkalinity 35 ± 5 mg/L; temperature 23 °C. Chlorine was not added to leaching water. The lined pipes were washed with purified water three times and were filled with leaching water at 23 °C and stored for 16 h. Contact surface area of epoxy resins per sample volume was 0.2 m²/L.

Glass sheets (200 mm × 70 mm × 2 mm) were coated with epoxy resins A or B and leach tests were performed. Water quality of leaching water was the same as those for lined pipes. The three glass sheets were initially washed with tap water and then with purified water. The procedures were repeated three times. Another three glass sheets were washed three times only with purified water. Leaching water was passed over the glass sheets three times. The glass sheets were leached with leaching water at 23 °C for 16 h. Contact surface area of epoxy resins per sample volume was 0.0546 m²/L.

For both leach tests for lined pipes and glass sheets, the leaching water after leach test was collected in glass containers. Blank tests were performed in parallel. That is, leaching water was stored in a glass container for 16 h. BPA and its chlorination by-products were not detected in the blank samples.

**Sampling of tap water**

From January to March 2009, tap water samples were collected from 11 faucets at houses in Kanto region, Japan. The tap water from one of 11 faucets was also sampled in June, October, and December 2011 because renovation work of water pipes using epoxy resin was conducted in the building. Sampling was performed in accordance with the procedures described for analysis of lead in drinking water (WSD, HSB, MHLW 2002). That is, tap water was initially flowed at 5 L/min for 5 min, and the tap was turned off and the tap water was retained for 15 min. Then, the tap was turned on and 5 L of tap water was collected at 5 L/min. In sampling, residual chlorine in tap water was quenched with sodium ascorbate.

**Analytical methods**

Concentrations of BPA and its chlorination by-products in the samples were determined by liquid–liquid extraction followed by liquid chromatography–tandem mass spectrometry (LC–MS/MS) (Asahi et al. 2010). 3,5-DiClBPA and 3,3'-diClBPA could not be separated chromatographically, and therefore the concentrations of their sum (diClBPA) were determined. BPA-d16 was used as a surrogate for BPA and chlorinated BPAs. Separation and detection were performed using an HP1100 high-performance liquid chromatography system (Agilent Technologies, Santa Clara, CA), and an API 3000 or API 4000 tandem mass spectrometers (AB SCIEX, Foster City, CA), respectively. The quantification limits were 1.0 ng/L for BPA, 0.9 ng/L for ClBPA, 1.5 ng/L for diClBPA, 0.7 ng/L for triClBPA, 0.6 ng/L for tetraClBPA, and 10 ng/L for TCP.

**RESULTS AND DISCUSSION**

**Elution of BPA and its chlorination by-products from lined pipes during continuous test**

After 1 h of passing tap water into the lined pipes, BPA and its chlorination by-products were not detected in tap water at the outlets of the lined pipes A and B. After 3 days, BPA was detected at 1.1 ng/L in tap water at the outlet of lined pipe A, and TCP was detected at 13 and 12 ng/L in tap water samples at the outlets of lined pipes A and B, respectively. Neither BPA nor its chlorination by-products were detected in tap water at either sampling time point at the inlets of the lined pipes. It was reported that BPA was detected in all of 10 drinking water samples at concentrations from 0.5 to 2.0 ng/L when an analytical method with a lower detection limit of 0.02 ng/L was developed (Kuch & Ballschmiter 2001). Thus, it was considered that
BPA might be frequently detected at the outlets if its quantification limit was less than one-tenth. After 3 days, BPA and its chlorination by-products were also investigated in tap water after 90 min of retention, and were detected in both lined pipes A and B (data not shown). BPA concentration in the retained tap water reflected elution from the lining resin and its decomposition by residual chlorine. Those of chlorination by-products reflected elution from the lining resin, its decomposition by residual chlorine, and formation by the reaction between chlorine and the parent compound. Thus, the concentrations of BPA and its chlorination by-products in retained tap water were considered to increase during retention in lined pipes although they were decomposed by the residual chlorine. From these results, after 3 days, tap water samples were sampled after retention in lined pipes.

Figure 1 shows the profiles of the concentrations of BPA and chlorinated BPAs in tap water after 16 h of retention in lined pipes A and B during the continuous test. BPA and its chlorinated BPAs were not detected in tap water at the inlet, except for diCIPBPA in lined pipe A after 12 months (i.e., 2.3 ng BPA/L). After 24 months, BPA and its chlorinated BPA in tap water at the outlet were investigated, but were not detected. BPA was always detected in the retained tap water at concentrations from 3.9 to 150 ng/L for lined pipe A and from 2.6 to 12 ng/L for lined pipe B. They were from 20 to 650 ng/m² and from 15 to 60 ng/m², respectively, when BPA elution was expressed as the amounts of BPA elution per contact surface area of lined pipe. BPA concentrations in the retained tap water did not decrease during 24 months although fluctuations over time were observed. Also, it was shown that BPA concentrations in the retained tap water of the lined pipes A and B were not so different. One reason for this result was considered to be that the types of epoxy resin were not so different although their manufactures were different. With regard to chlorinated BPAs, the concentrations of CIIPBPA, diCIIPBPA, triCIIPBPA, and tetraCIIPBPA in the retained tap water of lined pipe A were 2.6–40, 6.9–77, <0.7–21, and <0.6–4.0 ng BPA/L, respectively. Those of lined pipe B were 6.1–75, 6.1–100, 2.1–21, and <0.6–3.1 ng BPA/L, respectively. Thus, all chlorinated BPAs investigated were detected and their concentrations in the retained tap water of the two lined pipes were similar ranges. CIPBPA and diCIPBPA were always detected, and their concentrations were relatively high.

The sums of the concentrations of BPA and chlorinated BPAs in the retained tap water of lined pipe A were 34–270 ng BPA/L (170–1,400 ng BPA/m²) and those of lined pipe B were in 22–220 ng BPA/L (110–1,100 ng BPA/m²) (Figure 2(a)). In the case of lined pipe A, the high concentrations of the sums were the retained tap waters after 24 and 6 months. Those of lined pipe B were the retained tap waters after 6 months and 3 weeks. The residual chlorines in tap water at inlet ranged in concentration from 0.38 to 0.66 mg/L, and always decreased during 16 h of retention (Figure 2(b)). In particular, the residual chlorines in the retained tap water after 6, 18, and 24 months were very low or undetectable for lined pipe A. Those after 3 and 6 weeks, 6, 18, and 24 months were very low or undetectable for lined pipe B. As described above, the concentrations of BPA and its chlorination by-products reflected elution, decomposition, and formation. Thus, it was shown that the sums of the concentrations of BPA and chlorinated BPAs...
in the retained tap water were occasionally high when the residual chlorines were very low.

Figure 2(c) shows the profiles of temperature in tap water samples at the inlet and retained tap water in lined pipes during the continuous test. The temperature in the tap water after 16 h of retention was from 20 to 24°C because room temperature was controlled at 23°C. On the other hand, the temperature in the tap water at the inlet fluctuated widely; the temperatures were high at 6, 9, and 18 months ranging from 23 to 24°C but low at 3 and 6 weeks, 3, 12, and 24 months ranging from 9.7 to 15°C. Among the time points with high temperature in the tap water at the inlet, residual chlorine levels at 6 and 18 months were low or undetectable. In these cases, the residual chlorine levels decreased at a relatively high rate due to the high temperature of the tap water at the inlet. On the other hand, residual chlorine levels at 3 and 6 weeks and 24 months were low, although the temperature was low. In the case of 3 and 6 weeks, this was assumed to be because elapsed times were relatively early, and thus chlorine consumption rate at the surface of lined pipe was relatively high. The low residual chlorine levels at 24 months, however, were assumed to be because of the low residual chlorine level in tap water at the inlet.

Figure 3 shows the profiles of TCP concentration in the retained tap water during the continuous test. TCP was always detected in the retained water at concentrations from 28 to 12,000 ng/L for lined pipe A and from 33 to 12,000 ng/L for lined pipe B. Like the case of BPA and chlorinated BPAs, the TCP concentrations in the retained tap water of lined pipes A and B were similar. The concentration of TCP was higher than that of BPA by one order of magnitude. Thus, it was assumed that the precursor of TCP in the retained water was not only BPA but also other compounds in epoxy resins, and the contribution of BPA might be low. For example, it was reported that phenol concentration in leaching water was higher than that of BPA after the leach test of epoxy resins by using mineral water as leaching water (Kunikane 1999a). Phenol is also known to be a precursor of TCP by chlorination. Also, the TCP concentrations were fluctuated and were extremely high after 24 months, the longest elapsed time. One possible reason for this result was that high molecular weight compounds in the epoxy resin were gradually decomposed and transformed TCP during the continuous test.

Leach test of BPA and its chlorination by-products

In the previous section, elution of BPA and its chlorination by-products in tap water were investigated. To support the results in the results, leach tests for new lined pipes and those after 24 months of continuous test were performed.
using leaching water without chlorine (Table 1). In the case of new lined pipes, BPA concentration in leaching water of lined pipe A was 170 ng/L (850 ng/m²) and that of line pipe B was 120 ng/L (600 ng/m²). With regard to chlorination by-products of BPA, CI\textsubscript{BPA} and diCI\textsubscript{BPA} were detected.

To investigate the reason of the detections of chlorinated BPAs in leaching water of new lined pipes, the effects of washing epoxy resins with tap water on leach tests were evaluated using glass sheets coated with epoxy resins. In case of epoxy resin A, CI\textsubscript{BPA}, and TCP were detected when the glass sheets were washed with tap water. On the other hand, in case of epoxy resin B, CI\textsubscript{BPA} and diCI\textsubscript{BPA} were detected when the glass sheets were washed with purified water, and CI\textsubscript{BPA}, diCI\textsubscript{BPA} and TCP were detected when the glass sheets were washed with tap water. From these results, it was considered that chlorination by-products of BPA were formed on the surface of epoxy resins during 1 h of passing tap water before the continuous test of line pipes. Also, it was presumed that chlorinated BPAs may be contained in epoxy resin B although their contents were lower than that of BPA (Table 1).

The leach tests of BPA from epoxy resins have been investigated using leaching water without chlorine (Kunikane 1999a; Bae et al. 2002; Romero et al. 2002). It was reported that BPA was detected in four of seven leaching water after 16 h of the leach tests of epoxy resins at 23 °C, and the amounts of BPA elution were from 400 to 5,600 ng/m² (Kunikane 1999a). In particular, that of epoxy resins for pipe renovation was 4,000 ng/m², which was not so different from the present study. It was also reported that the amounts of BPA elution were from 10,700 to 1,730,000 ng/m² after 24 h of the leach test of three epoxy resins were increased at higher temperature (20–100 °C) (Bae et al. 2002). Moreover, it was reported that the amounts of BPA elution were from 20,000 to 30,000 ng/m² after 5 days of the leach test of three epoxy paints at 40–45 °C (Romero et al. 2002). The results of the present study were lower than those by Bae et al. (2002) and Romero et al. (2002). It was presumed that the reasons for different results were the difference of the types of epoxy resins and conditions of leaching test, such as temperature and leaching time.

### Table 1 | Concentrations of BPA and its chlorination by-products in leaching water after leach test

<table>
<thead>
<tr>
<th>Sample</th>
<th>BPA\textsuperscript{a} (ng/L)</th>
<th>CI\textsubscript{BPA}\textsuperscript{a} (ng BPA/L)</th>
<th>diCI\textsubscript{BPA}\textsuperscript{a} (ng BPA/L)</th>
<th>triCI\textsubscript{BPA}\textsuperscript{a} (ng BPA/L)</th>
<th>tetraCI\textsubscript{BPA}\textsuperscript{a} (ng BPA/L)</th>
<th>TCP\textsuperscript{a} (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lined pipe A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New lined pipe</td>
<td>170 (850)</td>
<td>83 (420)</td>
<td>15 (75)</td>
<td>&lt;0.7 (&lt;3.5)</td>
<td>&lt;0.6 (&lt;3.0)</td>
<td>&lt;10 (&lt;50)</td>
</tr>
<tr>
<td>After 24 months of continuous test</td>
<td>250 (1,300)</td>
<td>96 (480)</td>
<td>70 (350)</td>
<td>41 (210)</td>
<td>15 (65)</td>
<td>16,000 (80,000)</td>
</tr>
<tr>
<td>Lined pipe B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New lined pipe</td>
<td>120 (600)</td>
<td>8.7 (44)</td>
<td>2.3 (11)</td>
<td>&lt;0.7 (&lt;3.5)</td>
<td>&lt;0.6 (&lt;3.0)</td>
<td>&lt;10 (&lt;50)</td>
</tr>
<tr>
<td>After 24 months of continuous test</td>
<td>71 (360)</td>
<td>56 (280)</td>
<td>92 (460)</td>
<td>35 (180)</td>
<td>8.1 (41)</td>
<td>15,000 (75,000)</td>
</tr>
<tr>
<td>Glass sheet coated by epoxy resin A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After washing with tap water</td>
<td>140 (2,600)</td>
<td>5.2 (96)</td>
<td>&lt;1.5 (&lt;27)</td>
<td>&lt;0.7 (&lt;13)</td>
<td>&lt;0.6 (&lt;11)</td>
<td>13 (240)</td>
</tr>
<tr>
<td>After washing with purified water</td>
<td>420 (7,700)</td>
<td>&lt;0.9 (&lt;16)</td>
<td>&lt;1.5 (&lt;27)</td>
<td>&lt;0.7 (&lt;13)</td>
<td>&lt;0.6 (&lt;11)</td>
<td>&lt;10 (&lt;180)</td>
</tr>
<tr>
<td>Glass sheet coated by epoxy resin B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After washing with tap water</td>
<td>52 (950)</td>
<td>6.9 (130)</td>
<td>2.3 (42)</td>
<td>&lt;0.7 (&lt;13)</td>
<td>&lt;0.6 (&lt;11)</td>
<td>17 (310)</td>
</tr>
<tr>
<td>After washing with purified water</td>
<td>54 (990)</td>
<td>4.3 (79)</td>
<td>1.5 (27)</td>
<td>&lt;0.7 (&lt;13)</td>
<td>&lt;0.6 (&lt;11)</td>
<td>&lt;10 (&lt;180)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Units of values in parentheses are ng/m² for BPA and TCP, and ng BPA/m² for CI\textsubscript{BPA}, diCI\textsubscript{BPA}, triCI\textsubscript{BPA} and tetraCI\textsubscript{BPA}.
For both lined pipes A and B, the sums of BPA and chlorinated BPAs in leaching water after leach tests for new lined pipes were not so different from those after 24 months of continuous test. Concentrations of chlorinated BPAs and TCP in leaching water of new lined pipes were higher than those after 24 months of continuous test. These results agreed with those in the previous section. It was also confirmed that chlorinated BPAs and TCP were formed during continuous test of lined pipes, and were accumulated on the surface of the lined pipe. It was reported that BPA was not detected in leaching water after the 16 h of leach tests for 20 or 24 months of continuous tests of lined and non-lined pipes of several materials at 23 °C, although BPA was detected in some leaching waters at the beginning of the continuous test (Kunikane 2002, 2005). In the reports, the leaching water was mineral water. The results in the previous studies were different from those in the present study. The reasons for the difference were assumed that in the previous studies (Kunikane 2002, 2005), the resins used for lined pipes were not only epoxy resins but also other materials. In addition, in case of the epoxy resins, BPA was used for raw base resin material in both the present and previous studies, but liquid epoxy resins were used in the present study and epoxy resins for powder coating were used in the previous studies.

**BPA and its chlorination by-products in tap water**

BPA concentration in tap water was determined after 15 min of retention because BPA was not detected in tap water at the outlet of lined pipes. BPA was not detected in 11 retained tap water samples in January and March 2009. One tap water was resampled in June 2009 because renovation work of water pipes using epoxy resin was conducted in the building. Sampling was conducted 2 days after renovation work. BPA and TCP were detected in the retained tap water at concentrations of 2.0 and 46 ng/L, respectively. In this building, tap water samples both before and after 15 min of retention were further sampled in October and December 2011 and no BPA, chlorinated BPA, or TCP was detected. Thus, BPA was only detected in the retained tap water at a low concentration just after the water pipe renovation work. As in the case of lead water pipes, it is better to use tap water from these pipes for purposes other than drinking and cooking.

**CONCLUSIONS**

1. The results of 24 months of continuous tests indicated that BPA, chlorinated BPAs, and TCP were not present in tap water at the outlets of lined pipes, except for BPA after 3 days (1.1 ng/L).
2. In the continuous test, BPA, chlorinated BPAs, and TCP were detected in the tap water after 16 h of retention. The sums of the concentrations of BPA and chlorinated BPA in the retained tap water of lined pipes A and B water were 34–270 and 22–220 ng BPA/L, respectively. The sums in the retained tap water were usually high when the residual chlorine levels were low.
3. Leaching tests of lined pipes indicated that BPA concentration in leaching water did not change markedly during 24 months of the continuous test. Chlorinated BPAs were also shown to accumulate on the surface of lined pipes during the continuous test.
4. BPA and TCP were detected in tap water after 15 min of retention 2 days after water pipe renovation work using epoxy resin in the building, and their concentrations were 2.0 and 46 ng/L, respectively. In other cases, BPA, chlorinated BPAs, and TCP were not detected in either tap water or retained tap water.

**ACKNOWLEDGEMENTS**

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MHW 1997 Test for criteria of structure and material of feed water device (Notification No. 111) (in Japanese).


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