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Decennary Variations of Dissolved Heavy Metals in Seawater of Bohai Bay, North China

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Abstract Characteristics of the spatial and temporal distributions of selected dissolved heavy metals (Cu, Zn, Pb, Hg and Cd) in Bohai Bay, north China was investigated. Water samples from 22 sites were collected and analyzed for the selected metals with atomic absorption spectrometry from the year of 1996 to 2005. Relatively high concentrations of Cu, Zn, Pb and Hg were detected, with maximum concentrations in the 10-year period of 16.30, 422.00, 40.40, 0.23 μg/L respectively. The concentrations of Cd in all samples were quite low, with maximum level of 0.89 μg/L. The spatial distribution of dissolved Cu, Zn and Pb was analogous, where their average concentrations generally descended from the coastline to the central areas of the bay. Differently, for Hg and Cd, relatively high concentrations occurred not only in inshore but also in offshore areas. Measured data of heavy metals were compared with sea water quality standard of China (SWQSC). Cd concentrations in all samples were below SWQSC Grade-I. The percentages of Cu, Zn, Pb, and Hg at Grade-III levels in Bohai Bay were 2.67%, 30.00%, 30.43% and 0.36%, respectively, suggesting the severe contamination of Zn and Pb in this area. Terrestrial inputs via different rivers and sewages may be the important source for the heavy metals contamination.

Keywords Dissolved heavy metals · Bohai Bay · Sea water quality · Assessment

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Heavy metals in the sea water are among the most serious pollutants due to their toxicity, persistence and bioaccumulation characteristics (Pekey 2006; Osher et al. 2006; Lafabrie et al. 2007). Unlike organic contaminants which may be decomposed in the environment naturally, heavy metals in the aquatic environments may be enriched by organisms, converted to organic complexes, or deposited into sediments (Liu et al. 2009). The occurrence and distribution of heavy metals in the estuaries, coastal, bay and sea environments have been extensively investigated around the world (Pempkowiak et al. 2000; Tang et al. 2002; Sweeney and Sañudo-Wilhelmy 2004; Gavriil and Angelidis 2005). Most of these researches were focused on the heavy metals in the sediments, only a few on dissolved heavy metals in sea water, due to the smaller variations in sediments than in the water phase.

In China, most estuaries, bays, and seas adjacent to big cities have high contamination of heavy metals (Wang et al. 2005). This problem is especially severe in Bohai Bay, northern China, due to the fact that this bay is surrounded by highly industrialized areas, and the bay is semi-enclosed, making the exchange of bay water with the open sea difficult. The pollution in Bohai Bay therefore has attracted many concerns, and existing information indicates that this area had been severely contaminated in recent 20 years. Some publications have reported the heavy metals contamination of Bohai Bay in the past few years (Zhang et al. 2002; Hua et al. 2005; Wang et al. 2005;

Wang and Li 2006; Wang and Wang 2007; Liu et al. 2007), however, no comparison was available to show the spatial and temporal distribution of heavy metals in the sea water in a 10-year duration. This study is to address this concern. Heavy metals including Cu, Zn, Pb, Cd and Hg were measured in sea water samples from 22 sites in the Bohai Bay from the year of 1996 to 2005, to investigate the spatial and temporal variations of heavy metals in this area.

Materials and Methods

Sampling sites were located along the shoreline of Tianjin, China, as shown in Fig. 1. Sea water samples were collected three times (May, August and October) a year from 1996 to 2005. Site 2, 4, 5, 6, 10, 12, 15 were selected considering the input of contaminants from different rivers, and others were located in the adjacent coastal area. Sea water samples were collected in pre-cleaned and acid washed polypropylene bottles. A sample of 500 mL of water was taken by immersing the bottles beneath the water and lifting up. Two pipette drops of concentrated nitric acid was added, and the water sample was filtered through 0.45 μm Millipore filters and stored in a cooler while in the field, and transferred to a cold room (4°C) once in the laboratory. For the dissolved phase, samples were acidified to pH less than two by adding nitric acid into the water. The preservation and analysis of sea water was strictly carried out according to the Specification for Marine

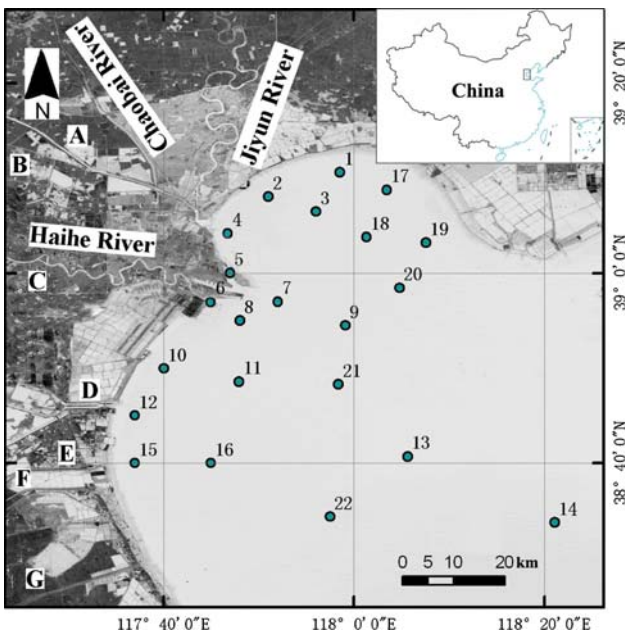

Fig. 1 The sampling sites in Bohai Bay. *A*: Yongdingxin River; *B*: Jinzhong River; *C*: Dagupaiwu River; *D*: Duliujian River; *E*: Ziyaxin River; *F*: Beipai River; *G*: Nanpaiwu River

Table 1 Sea water quality standard of China for selected heavy metals, μg/L

Element	Grade-I	Grade-II	Grade-III
Cu	5	10	50
Zn	20	50	100
Pb	1	5	10
Cd	1	5	10
Hg	0.05	0.20	0.50

Monitoring (GB 17378.4-1998, China) (SBQTS 1998). Cu, Pb, Cd and Zn were determined with Flame Atomic Absorption Spectrometry, and Hg was determined with Cold Vapor Atomic Absorption Spectrometry. The limits of detection (LODs) of Cu, Zn, Pb, Cd and Hg were 0.20, 3.10, 0.03, 0.01 and 0.001 μg/L, respectively. The sea water quality was assessed by comparing detected metal concentrations to the sea water quality standard of China (GB 3097-1997, China; SWQSC), which was shown in Table 1 (SEPA 1998).

Results and Discussion

Average concentrations (mean values of May, August and October) of Cu, Zn, Pb, Cd and Hg at 22 sites in Bohai Bay during 1996–2005 were shown in Fig. 2. Different metals undertook their own temporal variations. Take Cu for example, the average concentrations of Cu at site 1 and 11 were relatively high, which were 5.30 and 5.00 μg/L, respectively, in 1996, while most average concentrations were lower than 5.00 μg/L (SWQSC-I) during 1997–1999, with the exception of 6.30 μg/L at site 15 in 1998 and 5.60 μg/L at site 8 in 1999. The average concentrations in 2000 became higher, with the average concentrations exceeding 6.00 μg/L. During 2001–2003 the average concentrations became lower with the maximum level of 4.10 μg/L. The highest average concentration in 2004 was found at site 6 at 8.60 μg/L. Although this value was still lower than that of SWQSC-II (10 μg/L), it was notable that the maximum value was 16.30 μg/L, which was much higher than SWQSC-II. In 2005, only at sites 1 and 6 the average concentrations were higher than 5.00 μg/L.

From Fig. 2 it also can be seen that total Cu levels in 10 years at all sites except for site 17 and 18 were high, and this trend at sites near the estuarine areas seemed more evident, indicating the terrestrial inputs of metals to the bay are important. Similar results could be made on other metals.

Mean concentrations of heavy metals at different sites during 1996–2005 were shown in Fig. 3. It clearly indicates relatively small fluctuations in the mean values of selected heavy metals. Mean concentrations of the five

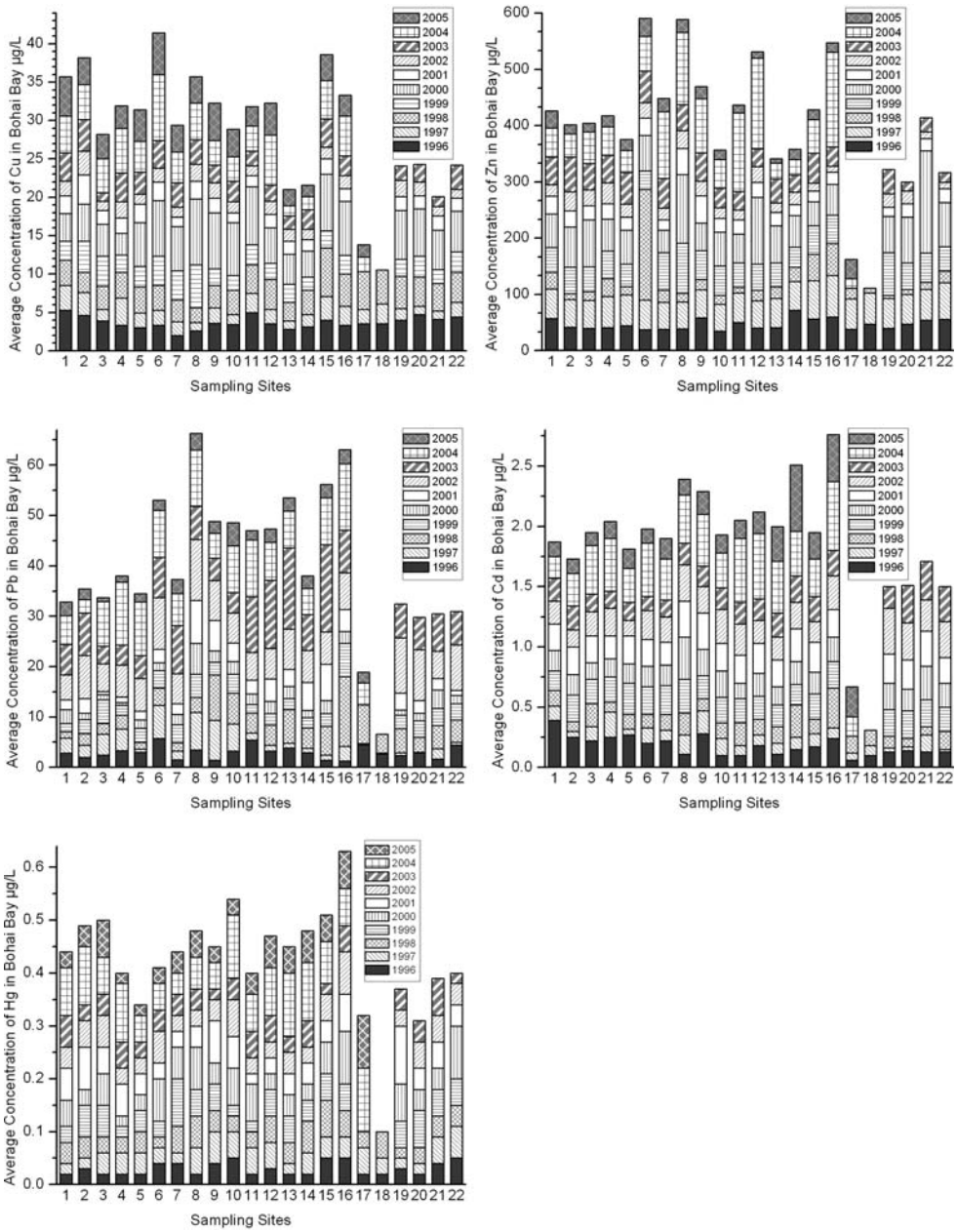

Fig. 2 The average concentrations of selected heavy metals in different sites of Bohai Bay in 1996–2005

metals were relatively stable from 1996 to 2003, and elevated in 2004, then decreased in 2005 to stay at relatively stable levels. Specifically for instance, the mean levels of Cu, Zn and Hg in 2000 were up to 5.69 ± 3.98, 73.01 ± 61.30, and 0.06 ± 0.04 μg/L respectively, which were higher than those in 1999 and 2001. The variations of dissolved heavy metals found in the present study are consistent with previous result reported by Wang and Wang (2007). They compared different heavy metals data from earlier researches in this area and found that average concentrations of dissolved heavy metals tended to increase from the beginning of 1980s to the middle of 1990s, then declined and became stable in recent years. Present study confirms this trend.

The 10-year average concentrations of dissolved heavy metals at 22 sites were shown in Fig. 4. The relatively high levels of Cu, Zn and Pb occurred at site 6, 8, 15 and 16, indicating a general descending trend from the coastline to the central area. For Cd, relatively high mean values occurred at site 2, 8, 9, 14 and 16. This distribution showed that the contamination of Cd did not restrict to one area, and relatively high concentrations occurred not only inshore but offshore. The same trend was found for Hg. Mean values of Hg at site 2, 8, 10, 16, 17 and 19 were relatively high. In general, heavy metals concentrations in the coastal areas were higher than in the central areas, indicating the pollutants inputs from land. Inputs from rivers accounted for a big proportion (Zhao and Kong

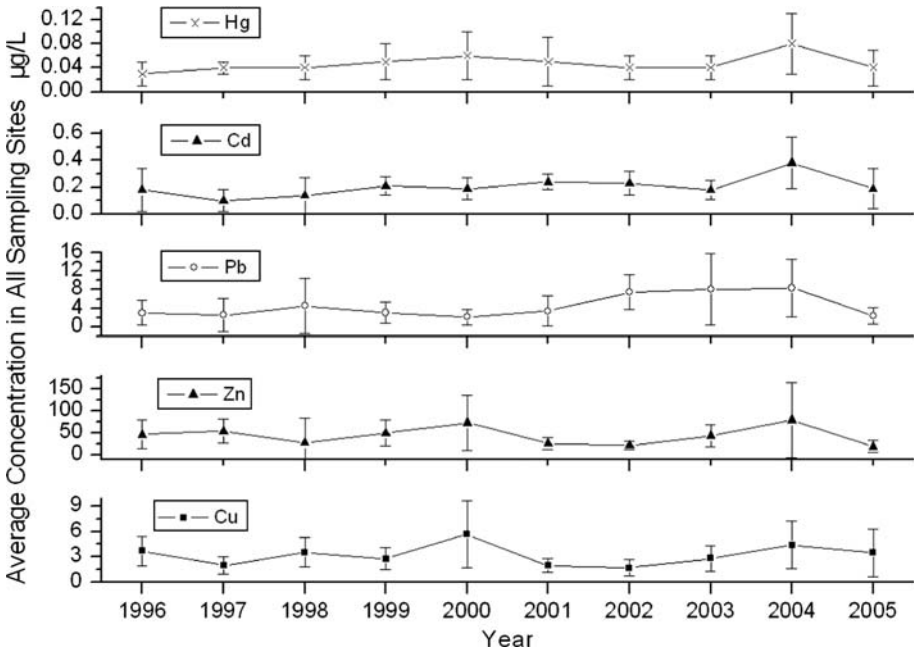

Fig. 3 The average concentrations of heavy metals in all sites in different year

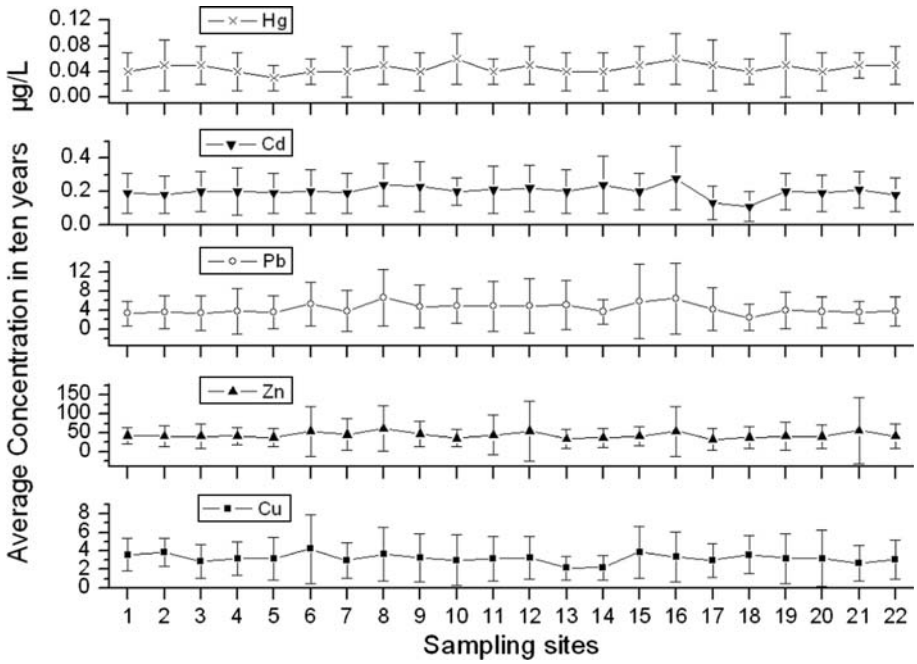

Fig. 4 The decennary average concentrations of heavy metals at different sites

2000; Wang and Li 2006; Zhang et al. 2007; Wang and Wang 2007). For example, in 2004, Yongdingxin River discharged 8 ton of heavy metals into Bohai sea (SOA 2004). In 2005, Dagupaiwu River, Yongdingxin River discharge 36 and 2 ton of heavy metals into Bohai Sea, respectively (SOA 2005). The direct discharge of sewage from industrial zones was also an important source for heavy metals in the coastline of Bohai Bay (Zhang 2001). A large amount of industrial wastewater was discharged into sea water, resulting in the increase of heavy metals at the coastal sites.

To assess the quality of the sea water in Bohai Bay, measured heavy metals data were compared with Sea Water Quality Standard of China (SWQSC). The statistic results were shown in Table 2. From the Table we can see that Cd contamination in this area was slight, with all Cd concentrations lower than SWQSC Grade-I. However, Zn and Pb contamination were serious, with large proportions of concentrations at SWQSC Grade-II and III levels. The contamination of Cu was not serious and concentrations at most sites (70% sea water samples) were lower than SWQSC Grade-I. Contamination levels of Hg in this area

Table 2 The percentage (%) of heavy metals in corresponding grade of SWQSC in different site/year

Site/year	Cu			Zn			Pb			Cd			Hg		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
S1	86.2	13.8	0.0	10.7	57.1	32.1	24.1	58.6	17.2	100.0	0.0	0.0	62.1	37.9	0.0
S2	72.4	27.6	0.0	21.4	53.6	25.0	20.7	58.6	20.7	100.0	0.0	0.0	69.0	31.0	0.0
S3	86.2	13.8	0.0	35.7	35.7	28.6	37.9	37.9	24.1	100.0	0.0	0.0	72.4	27.6	0.0
S4	96.6	0.0	3.5	14.3	50.0	35.7	31.0	37.9	27.6	100.0	0.0	0.0	82.8	17.2	0.0
S5	86.2	10.3	3.5	21.4	53.6	25.0	20.7	51.7	27.6	100.0	0.0	0.0	86.2	13.8	0.0
S6	82.8	6.9	10.3	21.4	42.9	35.7	6.9	55.2	37.9	100.0	0.0	0.0	75.9	24.1	0.0
S7	82.8	17.2	0.0	32.1	35.7	32.1	20.7	62.1	17.2	100.0	0.0	0.0	82.8	17.2	0.0
S8	79.3	17.2	3.5	25.0	35.7	39.3	13.8	34.5	48.3	100.0	0.0	0.0	75.9	24.1	0.0
S9	82.8	13.8	3.5	17.9	46.4	32.1	3.5	62.1	34.5	100.0	0.0	0.0	72.4	27.6	0.0
S10	86.2	10.3	3.5	35.7	39.3	25.0	13.8	51.7	31.0	100.0	0.0	0.0	62.1	34.5	3.5
S11	86.2	10.3	3.5	25.0	50.0	25.0	13.8	44.8	37.9	100.0	0.0	0.0	79.3	20.7	0.0
S12	79.3	17.2	3.5	28.6	42.9	28.6	17.2	51.7	27.6	100.0	0.0	0.0	69.0	31.0	0.0
S13	96.3	3.7	0.0	34.6	42.3	23.1	14.8	51.9	29.6	100.0	0.0	0.0	77.8	22.2	0.0
S14	96.0	4.0	0.0	33.3	41.7	20.8	20.0	48.0	32.0	100.0	0.0	0.0	80.0	20.0	0.0
S15	69.0	24.1	6.9	28.6	46.4	25.0	13.8	51.7	34.5	100.0	0.0	0.0	55.2	44.8	0.0
S16	86.2	10.3	3.5	28.6	28.6	42.9	13.8	44.8	41.4	100.0	0.0	0.0	44.8	55.2	0.0
S17	91.7	8.3	0.0	36.4	36.4	27.3	33.3	33.3	33.3	100.0	0.0	0.0	75.0	25.0	0.0
S18	75.0	25.0	0.0	28.6	42.9	28.6	50.0	25.0	12.5	100.0	0.0	0.0	87.5	12.5	0.0
S19	90.5	4.8	4.8	35.0	35.0	30.0	19.1	52.4	28.6	100.0	0.0	0.0	76.2	19.1	4.8
S20	90.5	4.8	4.8	25.0	50.0	25.0	14.3	66.7	19.0	100.0	0.0	0.0	76.2	23.8	0.0
S21	90.5	9.5	0.0	35.0	30.0	35.0	9.5	71.4	19.1	100.0	0.0	0.0	66.7	33.3	0.0
S22	81.0	19.1	0.0	40.0	35.0	25.0	23.8	47.6	28.6	100.0	0.0	0.0	47.6	52.4	0.0
1996	78.8	21.2	0.0	30.3	30.3	39.4	22.7	59.1	18.2	100.0	0.0	0.0	83.3	16.7	0.0
1997	100.0	0.0	0.0	6.8	40.9	52.3	54.6	25.0	20.5	100.0	0.0	0.0	90.9	9.1	0.0
1998	84.9	13.6	1.5	59.1	34.1	6.8	22.7	48.5	28.8	100.0	0.0	0.0	75.8	24.2	0.0
1999	91.7	8.3	0.0	11.7	48.3	40.0	8.3	81.7	10.0	100.0	0.0	0.0	68.3	31.7	0.0
2000	58.3	26.7	15.0	0.0	38.3	61.7	26.7	70.0	3.3	100.0	0.0	0.0	63.3	36.7	0.0
2001	98.3	1.7	0.0	35.0	61.7	3.3	23.3	53.3	23.3	100.0	0.0	0.0	68.3	30.0	1.7
2002	98.3	1.7	0.0	45.0	53.3	1.7	3.3	21.7	75.0	100.0	0.0	0.0	73.3	26.7	0.0
2003	91.8	8.2	0.0	14.3	49.0	36.7	2.0	38.8	59.2	100.0	0.0	0.0	83.7	16.3	0.0
2004	72.9	20.8	6.3	16.7	27.1	56.3	8.3	20.8	70.8	100.0	0.0	0.0	27.1	70.8	2.1
2005	77.6	18.4	4.1	57.1	40.8	2.0	16.3	79.6	4.1	100.0	0.0	0.0	75.5	24.5	0.0
Total	85.1	12.3	2.7	27.2	42.8	30.0	18.5	50.9	30.4	100.0	0.0	0.0	71.2	28.5	0.4

I, II and III represent the SWQSC grade-I, II and III, respectively

were at different degrees. Of all sample locations site 16 was the most contaminated one.

From Table 2 we can also see the sea water quality in different years. For example, contamination of Cu and Zn was severe in 2000, with 42% and 100% of the total sea water concentrations higher than SWQSC Grade-II. The slightest contamination of them occurred in 1997 and 1998, respectively. For Pb, the worst scenario occurred in 2003, with the percentage at Grade-I, II, and III of 2.03%, 38.78%, and 59.19%, respectively. For Hg, the worst and slightest contamination occurred in 2004 and 1997, respectively. According to sea water quality assessment (SOA 2004, 2005), the percentages of Cu, Zn, Pb, Cd and Hg at SWQSC Grade-III in Bohai Bay were 2.67%, 30.00%, 30.43%, 0.00%, and 0.36%, respectively, suggesting the severe contamination of Zn and Pb in this area.

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