Level and ecological risk of four common metals in surface water along the Qinhuangdao coastal areas, China

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Abstract: Heavy metals have been a widespread environmental contamination. Due to their associated ecological risk, the presence in water environment has attracted broad attention to public. Here 4 most common metals including copper (Cu), lead (Pb), cadmium (Cd) and zinc (Zn) were determined in surface water along the Qinhuangdao coastal areas, China. And their ecological risk was assessed using species sensitivity distribution (SSD) method. Total 12 stations were designed near the main estuary in the study area. The results showed that the concentrations of Cu, Pb, Cd and Zn of surface water were in the range of 847.81-1602.81µg/L, 0.42-1.59µg/L, 1.82-7.99µg/L and 26.9 -59.36µg/L, respectively. According to the National Seawater Quality Standard of China (GB3097-1997), Cu concentration in each station was much higher than the standard value of IV level (50 µg/L), thus Cu could not even met the lowest level of water quality. In contrast, Pb met the I or II level of water quality, Cd and Zn met the II or III level. The HC5 (hazardous concentration for 5% of species) of each metal was obtained from their corresponding SSD curve. In case of Cu and Zn, the concentration at all sites exceeded their HC5 values, suggesting both of them had adverse effect on the aquatic organism, especially Cu. While Pb concentration at all sites was much lower than its HC5 value, thus Pb had no negative effect on aquatic life. In case of Cd, the concentration at 5 sites was higher than its HC5 value, and the other 7 sites was lower than its HC5 value, suggesting that adverse effect only occur at partial region in the study area. The RQ (risk quotient) value of Cu varied between 1355.41 and 2621.28, far larger than 1, indicating that 100% of sites had a much higher risk. The RQ of Zn varied between 6.06 and 13.88 (>1) indicating that Zn had a high risk in the study area. In case of Cd, the RQ ranged from 0.94 to 4.41 and about 92% of sites were larger than 1, suggesting that Cd had a high risk in these regions, while 8% of sites (0.1<RQ<1)had a medium risk. In case of Pb, the RQ ranged from 0.04 to 0.13 and about 92% of sites (<0.1) had a low risk in these regions and about 8% of sites (0.1<RQ<1) had a medium risk. The results indicated that the ecological risk was in the following: Cu>Zn>Cd>Pb. The Cu pollution level extremely high during this investigation, and a much higher ecological risk could already occur, thus Cu should be paid more attentions. Meanwhile, both Zn and Cd also were important contaminations in the study area.

1. Introduction

Heavy metal has been one of main environmental pollutants, and aroused much attention because of their potential toxicity, persistence, bioaccumulation and biomagnifications through food chains [1-5]. It is well-known that organisms in different trophic level have been suffering from metal toxicities [6]. Accumulation of heavy metals in organisms shows different tolerant capabilities among aquatic food chains [7] and human health is under threats from exposure to heavy metals through seafood intake [8].
Coastal and estuarine areas are often the final repository of anthropogenic pollutants. Therefore heavy metal pollution in coastal and estuarine ecosystems has long been widely concerned and has been studied by many researchers worldwide [9-11]. Pan & Wang (2012) [12] reported that high metal contents can be detected across the coasts in China, which is closely associated with accelerated economic growth in the past decades.

Liaodong Bay locates in the north of Bohai Sea, and belongs to a semi-enclosed bay with a long residence time. Qinhuangdao coastal area locates at the south-western corner of Liaodong Bay, and this region is a shallow embayment. There are multiple rivers into sea including Tang River, Xin River, Dai River, Yang River, Man-made River and Sha River along Qinhuangdao city. Here the main objective is to reveal the polluted status of 4 common metals including Cu, Cd, Pb, Zn, and assess their ecological risk near estuary along the Qinhuangdao coastal area, China.

2. Materials and methods

2.1. Study area and sample collection

Twelve stations were selected in the Qinhuangdao coastal area where several rivers flowed into the Liaodong Bay (Figure 1). All the sites located near the estuary and coastal tourist resort. The field sampling was carried out on May 10-11, 2016. The sea water samples were collected in clean polyethylene sampling bottles, and then were filtered through the 0.45μm synthetic fabric membranes. The nitric acid solution (2 mol/L) was added to adjust the pH of water samples to be <2. All the samples were transported to the laboratory in an icebox, and stored in dark at 4℃ for metal analysis.

The temperature (T), pH, dissolved oxygen (DO) in surface water were measured in situ using a Multi-parameter water quality meter (HACH HQ30d, USA). Salinity was measured on-site by a Master Refractometer (ATAGO, Japan).

2.2. Sample analysis and risk assessment

Metal mixed standards of liquid state (GSB04-1767-2004) were purchased from National Standard Material Center (China). The Cu, Cd, Pb and Zn concentrations were analyzed using ELAN6100 DRC ICP-MS (Perkin-Elmer, USA). All analytical procedures were strictly monitored through quality assurance and quality control. Quantification was performed by the external standard method using metal reference material mixture, with correlation coefficients for calibration curves all higher than 0.999. The range of recovery rate was 95.5~107.61%. The sample determination results were corrected by results of blank controls and recovery rates.

The National Seawater Quality Standard of China (GB3097-1997) was used to assess the seawater quality. And the species sensitivity distribution (SSD) was used for ecological risk analysis.

The hazardous concentration for 5% of species (HC₅) is the estimated 5th percentage of the distribution, i.e., the concentration makes the 95% of the species in an ecosystem protected [13]. The HC₅ value was obtained from the corresponding SSD curve. And then the PNEC (predicted no effect concentration) is calculated by the following equation:

\[
PNEC = \frac{HC_5}{AF}
\]  

AF is an assessment factor in the range of 1 and 5, reflecting the uncertainties of data [14]. In this study, the value of AF is set as 3 according to the number of species tested, quantity and quality of toxicity data and model goodness of fit. The ‘risk quotient’ (RQ) was used to determine the ecological risk [15]:

\[
RQ = \frac{MEC}{PNEC}
\]

Here MEC means measured environmental concentration. A risk level can be ranked as low, medium and high if the RQ is <0.1, 0.1~1.0 and ≥1.0, respectively.
3. Results and discussion

3.1. The primary environmental conditions at the sampling time
The results showed that the T, pH, DO and salinity ranged from 18.8 to 21.7 °C, from 8.92 to 9.44, from 8.17 to 13.45 mg/L and from 26 to 36‰, respectively.

3.2. Pollution levels and water quality assessment
The concentrations of Cu, Pb, Cd and Zn in surface water were in the range of 847.81-1602.81 µg/L, 0.42-1.59 µg/L, 1.82-7.99 µg/L and 26.9-59.36 µg/L, respectively. The comparative levels of four metals in the different stations were showed in Figure 2. It showed the highest concentration of Cu was found at site Q12 and the second was at site Q6, while the lowest one was found at site Q10 following by Q11. The highest concentration of Pb was at Q9 and the second was at site Q12, while the lowest was at site Q4 following by Q3. The highest concentration of Cd was at Q12 and the second at site Q6, while the lowest was at site Q5 following by Q1. The highest concentration of Zn was at site Q6 and the second at site Q12, while the lowest one at site Q4 following by Q5.
3.3. Risk assessment of four heavy metals in surface water

According to the National Seawater Quality Standard of China (GB3097-1997), the quality of seawater is divided into four levels. Based on the site-specific concentration, Cu concentration at all stations were much higher than the standard value for IV level (50µg/L). The Cu levels were 16.96-32.06 times in 12 stations as high as 50µg/L, indicating that the study area suffered from heavy Cu pollution. For Pb, water quality at 11 stations attained I level (<1µg/L), while only 1 station met II level (1-5µg/L). In case of Cd, water quality at 7 stations attained II level (1-5µg/L), and the other 5 stations meet III level (5-10µg/L). In case of Zn, water quality at 8 stations attained II level (20-50µg/L), the other 4 stations meet III level (50-100µg/L). The results suggested that Cu pollution was particularly serious.

The ecotoxicological data of the representative species from the main taxa of marine aquatic organisms are used to develop the SSD curves. Durán and Beiras (2013) [16] have established the SSD curves of Cu, Pb, Cd and Zn according to the above method, and the curves were used as reference in the present study. The four heavy metals shows different toxicity to the tested organisms, and Cu is the most toxic metals for most of the species. The HC₅ value of each metal was obtained from its SSD curve, and they were 1.90µg/L for Cu, 36.90µg/L for Pb, 5.31µg/L for Cd and 12.36µg/L for Zn, respectively [16]. And then the HC₅ of these four metals was used for the following analysis. The concentration levels of both Cu and Zn in all stations (Figure 2) were much higher than their corresponding HC₅ value, suggesting that the aquatic organism had been affected adversely by Cu and Zn pollution. In contrast, the Pb levels in all stations were much lower than its HC₅ value, suggesting that Pb pollution was negligible and no adverse effect happened to the local organism. In case of Cd, there were 5 stations (Q6,Q7,Q8,Q10 and Q12) where the concentration of Cd was higher than its HC₅ value, while the one in the other 7 stations was lower than its HC₅ value, suggesting that Cd at Q6,Q7,Q8,Q10 and Q12 stations had negative effect on the aquatic life.
Based on the HC5 values, the RQ values of each metal in all the stations were calculated using Eq2 (Figure 3). The results showed that the RQ values of Cu varied between 1355.41 and 2621.28, 100% of sites have a very high ecological risk with RQ values much larger than 1.0. In contrast, the RQ values of Pb ranged from 0.04 to 0.13, about 92% of sites (11 stations) showed a low ecological risk and 8% (only 1 station) showed a medium ecological risk with a RQ value between 0.1 and 1.0. In case of Zn, the RQ values ranged from 6.06 to 13.88, 100% of sites showed a high ecological risk with RQ >1. In case of Cd, the RQ values varied between 0.94 and 4.41, about 92% of sites (11 stations) showed a high ecological risk with a RQ>1.0 and 8% (1 station) showed a medium ecological risk with a RQ value between 0.1 and 1.0. According to the RQ, the ecological risk caused by metal pollution in the study area decline in order: Cu>Zn>Cd>Pb. Comparing with the Cu concentration of the surface water in other coastal area [2,6,8,17], the pollution was extremely high along the Qinhuangdao coastal area. It should arouse much attention of relevant departments, and the pollution source of Cu needs further investigation.

4. Conclusions
The concentrations of Cu, Pb, Cd and Zn in surface water along the Qinhuangdao coastal area varied between 847.81-1602.81µg/L, 0.42-1.59µg/L, 1.82-7.99µg/L and 26.9-59.36µg/L, respectively. According to the National Seawater Quality Standard of China (GB3097-1997), Cu at all the stations did not attained IV level (>50µg/L); Pb attained I level (<1µg/L) or II level (1-5µg/L); For Cd and Zn, water quality meet II level (1-5µg/L for Cd, 20-50µg/L for Zn) or III level (5-10µg/L for Cd, 50-100µg/L for Zn). Based on SSD curves, the HC5 were 1.90µg/L for Cu, 36.90µg/L for Pb, 5.31µg/L for Cd and 12.36µg/L for Zn, respectively. The RQ values ranged from 1355.41 to 2621.28 for Cu, 0.04 to 0.13 for Pb, 0.94 to 4.41 for Cd and 6.06 to 13.88 for Zn, respectively. The results indicated that Cu and Zn at 100% sites had a high ecological risk, while Cd at 92% sites had a high ecological risk. In contrast, the ecological risk of Pb in the study area was negligible. Therefore, the ecological risk decline in order: Cu>Zn>Cd>Pb. Comparing to other coastal area, the Cu pollution was extremely high and should be paid more attention. Furthermore, the people living in this region try to eat less the seafood that is easily enriched metals such as shellfish.

Figure 3. The RQ values of each metal in different stations
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