Heavy metal concentrations and ecological risk assessment for surface sediment of Da Qaidam Salt Lake in Qaidam Basin, northern Tibetan Plateau

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Abstract. The paper focused on heavy metal (Cr, Cu, Pb, Zn, As, Co, Ni and Mn) concentrations from surface sediment in the southeastern Da Qaidam Salt Lake. Based on the pressed powder pellet method and X-ray fluorescence spectrometry analysis, as well as the enrichment factor, geoaccumulation index and potential ecological risk index, the possible sources and pollution level of heavy metals were studied. The results showed that spatial distributions of heavy metal concentration were indicative of nonuniform characteristics in different zones of Da Qaidam Salt Lake, the average enrichment level of heavy metals followed the decreasing order: $EF(As) > EF(Mn) > EF(Cu) > EF(Zn) > EF(Pb) > EF(Cr) > EF(Ni) > EF(Co)$, and arsenic was the main heavy metal contaminant. In a word, the level of heavy metal pollution in the southeastern Da Qaidam Salt Lake was not strong, but anthropogenic emissions would become the main source of heavy metals along with the frequent and strong human activities in the surrounding region.

1. Introduction
Heavy metals accumulated in lake sediment for a long time are very difficult to be degraded by organisms, and the toxicological effects will emerge when heavy metal concentrations reach a certain level [1]. In addition, as the typical potential ecological risk pollutants, heavy metals accumulated in lake sediment will be re-released into the overlying water body when the external conditions are appropriate, causing the secondary pollution to water body consequently [2-3]. Da Qaidam Salt Lake is known for its liquid and solid boron resource in the northern Qaidam Basin, earlier studies focused on the distribution characteristics, sources and ore-forming mechanism of borate deposits [4-5]. However, little attention has been paid to the heavy metal concentrations and ecological risk assessment correlated with human activities. Here we report the results of heavy metal concentrations from surface sediment in the southeastern Da Qaidam Salt Lake, aiming to illuminate the distribution characteristics and possible sources of heavy metal pollutants, and distinguish the anthropogenic pollution components. Finally, based on the enrichment factor (EF), geoaccumulation index (Igeo) and potential ecological risk index (PERI), the heavy metal pollution level of surface sediment from Da Qaidam Salt Lake was quantified and evaluated.
2. Materials and methods

2.1. Sample descriptions
The surface sediment samples were collected by HY. ETC-200 sludge sampler from the southeastern Da Qaidam Salt Lake, and all the sampling sites far away from pollution sources (Fig. 1). The sampling resolution varied from 1 cm to 3 cm according to the sediment characteristics. All the sediment samples were stored in cool rooms at 4 °C, which were prepared for X-ray fluorescence spectrometry (XRF) analysis.

Fig. 1. The sampling sites of surface sediment in the southeastern Da Qaidam Salt Lake.

2.2. Analytical methods
The samples for XRF analysis were prepared by the pressed powder pellet method. Samples were weighed at 4.00 g and dried in an oven at 105 °C for 2 hours. Firstly, grinded in a mortar and pestle, and passed through a 63-μm sieve. Then, loaded the mold and flattened the sample, edged it with boric acid backing, and hold pressure 1 minute under 30 tons pressure. Finally, pressed into the round sample with edge diameter of 40 mm. The same preparation method was also used for the standard sample. The experiment was conducted at Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China.

2.3. Assessment methods

2.3.1. Enrichment factor
According to Ergin et al [6], the metal enrichment factor (EF) is defined as follows:

\[
EF = \frac{\left( \frac{Me}{Al} \right)_{sample}}{\left( \frac{Me}{Al} \right)_{background}}
\]

(1)

where \(\left( \frac{Me}{Al} \right)_{sample}\) is the measured concentration of the examined metal to Al ratio in the sediment, and \(\left( \frac{Me}{Al} \right)_{background}\) is the geochemical background value of metal to Al ratio.

2.3.2. Geoaccumulation index
The geoaccumulation index \(I_{geo}\) was originally defined by Müller for metal concentrations in the < 2 μm fraction [7], and developed for the global standard shale values, which is expressed as follows:

\[
I_{geo} = \log_{2} \left( \frac{C_n}{1.5B_n} \right)
\]

(2)
where $C_n$ is the measured concentration of the examined metal ($n$) in the sediment, $B_n$ is the geochemical background value of the metal ($n$), and factor 1.5 is the background matrix correction factor due to lithologic effects.

2.3.3. Potential ecological risk index

The potential ecological risk index ($PERI$) was originally defined by Håkanson for aquatic pollution control [8], which is expressed as follows:

$$PERI = \sum E_i = \sum T_i \times C_i = \sum T_i C_i / C_i$$  \hspace{1cm} (3)

where $E_i$ is the potential ecological risk index of heavy metal ($i$), $T_i$ is the toxic-response index of heavy metal ($i$), and the toxic-response index of Cr, Cu, Pb, Zn and As is 2, 5, 5, 1 and 10, respectively [9], $C_i$ is the pollution factor, $C_i'$ is the measured value of heavy metal ($i$) in the surface sediment, $C_i'$ is the background value of corresponding heavy metal ($i$). In this study, the $E_i'$ value of Cr, Cu, Pb, Zn, As and $PERI$ value were redefined as shown in Table 1.

Table 1. The critical range and grades of $E_i$ and $PERI$ value.

| $E_i'$ | ecological risk of metal ($i$) | $PERI$ | potential ecological risk |
|--------|-------------------------------|--------|---------------------------|
| <30    | low risk                      | >40    | no risk                   |
| 30–60  | moderate risk                 | 40–120 | low risk                  |
| 60–120 | high risk                     | 120–240| moderate risk             |
| 120–240| very high risk                | 240–400| high risk                 |
| ≥240   | extremely high risk           | ≥400   | very high risk            |

3. Results and discussion

3.1. Distribution of heavy metals

As shown in Fig. 2, the Cr, Cu, Pb and Zn concentrations varied similarly, with a gradually decreasing variation trend from the shore to lake center in general. It should be pointed out that the Cr, Cu, Pb and Zn concentrations peaked synchronously at sample site 11, which can be considered as a sedimentation enrichment center. The arsenic concentration was characterized by decreasing–increasing–decreasing variation trend. The Mn, Ni and Co concentrations varied similarly, with a gradually increasing variation trend from the shore to lake center as a whole. Here, the geochemical data from subbottom profile DCD03 in Da Qaidam Salt Lake were selected as the background values of heavy metal. As shown in Table 2, except Co concentration, the Cr, Cu, Pb, Zn, As, Ni and Mn concentrations were higher than the background values. In addition, the average concentration of Mn reached 675.12 mg·kg$^{-1}$, with the enrichment coefficient of 1.38. The average concentration of heavy metals followed the decreasing order: Mn > Zn > Cr > Ni > Cu > Pb > As > Co. Consequently, the quality of surface sediment in the southeastern Da Qaidam Salt Lake had begun to deteriorate. However, the Cr, Cu, Pb, Zn, As, Mn, Ni and Co concentrations in surface sediment did not exceed the national environmental soil quality standard (GB15618–2009).
Fig. 2. The distribution of Cr, Cu, Pb, Zn, As, Mn, Ni and Co concentrations from surface sediment in the southeastern Da Qaidam Salt Lake.

Table 2. The average concentrations and enrichment coefficients of heavy metal from surface sediment in the southeastern Da Qaidam Salt Lake versus the background values from sediment profile DCD03 and national environmental soil quality standard (GB15618–2009).

| Metals | Average | Enrichment Coefficients | Background Values | GB15618–2009 |
|--------|---------|--------------------------|-------------------|---------------|
| Cr     | 56.22   | 1.19                     | 47.17             | 250~350       |
| Cu     | 25.29   | 1.27                     | 19.87             | 100~200       |
| Pb     | 24.13   | 1.19                     | 20.36             | 600           |
| Zn     | 63.09   | 1.26                     | 50.15             | 300           |
| As     | 14.01   | 2.06                     | 6.79              | 20            |
| Co     | 10.27   | 0.80                     | 12.87             | 40            |
| Ni     | 27.64   | 1.11                     | 24.99             | 90            |
| Mn     | 675.12  | 1.38                     | 490.80            | —             |

3.2. Enrichment factors and possible sources of heavy metal
In this study, the enrichment factor (EF) was used to evaluate anthropogenic impacts on heavy metals from surface sediment based on element aluminum (Al). Here, the background value of element Al is 66970.59 mg·kg$^{-1}$. It should be noted that, the assessment criteria referenced to the EF values. If the EF value ranged from 0.5 to 1.5, suggesting that the trace metals may be entirely from crustal materials or natural weathering processes [10]. However, if the EF value is greater than 1.5, suggesting that the trace metal are provided by point pollution sources, non-point pollution sources and biota [10-11].
As shown in Table 3, the EF(Cr) value ranged from 0.96 to 1.17 with an average value of 1.07, the EF(Cu) value ranged from 0.97 to 1.33 with an average value of 1.13, the EF(Pb) value ranged from 0.83 to 1.45 with an average value of 1.08, the EF(Zn) value ranged from 1.02 to 1.25 with an average value of 1.12, the EF(As) value ranged from 1.23 to 2.43 with an average value of 1.87, the EF(Mn) value ranged from 0.63 to 2.16 with an average value of 1.31, the EF(Ni) value ranged from 0.54 to 1.63 with an average value of 1.04, and the EF(Co) value ranged from 0.29 to 1.29 with an average value of 0.76. Therefore, the average enrichment level of heavy metals from surface sediment in the southeastern Da Qaidam Salt Lake followed the decreasing order: EF(As) > EF(Mn) > EF(Cu) > EF(Zn) > EF(Pb) > EF(Cr) > EF(Ni) > EF(Co). Obviously, the average value of EF(As) was greater than 1.5, suggesting that the arsenic was delivered from the point pollution sources, non-point pollution sources and biota. However, the average values of EF(Cr), EF(Cu), EF(Pb), EF(Zn) and EF(Co) ranged from 0.5 to 1.5, indicating that these heavy metals may be entirely from crustal materials or natural weathering processes.

The previous studies found that the arsenic was mainly derived from the metallurgy, power generation and industrial boilers, then contaminated the surrounding soils and rivers by dust [12]. The use of pesticides and fertilizers contained As also contributed less to As pollution [12]. Our recent study found that the thermal spring from Wenquangou in the northern Da Qaidam Town contained a certain amount of element As, which finally flowed into the lake basin and contributed less to As accumulation. In addition, the matrix bedrock, decay of plant and animal residues, combustion of coal and petroleum products, Ni-bearing sedimentation of atmospheric particles, discharge of waste water from mining and metallurgy were the main sources of element Ni [13]. From the above, it is concluded that, before the emergence of human activities, natural erosion of rock-forming minerals was the main factor of heavy metal accumulation in lake sediments. After that, anthropogenic emissions became the main source of heavy metal along with the frequent and strong human activities in the surrounding region.

3.3. Geoaccumulation index and potential ecological risk index

As shown in Fig. 3, the Igeo(Cr) value ranged from -0.88 to 0.02 with an average value of -0.36, the Igeo(Cu) value ranged from -0.96 to 0.26 with an average value of -0.28, the Igeo(Pb) value ranged from -0.71 to -0.01 with an average value of -0.36, the Igeo(Zn) value ranged from -0.87 to 0.17 with an average value of -0.28, the Igeo(As) value ranged from -0.46 to 0.88 with an average value of 0.42, the Igeo(Mn) value ranged from -0.81 to 0.18 with an average value of -0.17, the Igeo(Ni) value ranged from -1.04 to -0.15 with an average value of -0.46, and the Igeo(Co) value ranged from -1.94 to -0.49 with an average value of -0.95. Except sampling site 12', the Igeo(As) values were above zero, indicating that the heavy metal As from surface sediment in the southeastern Da Qaidam Salt Lake was in slightly polluted status. In addition, the heavy metals such as Mn, Zn, Cu and Cr from individual sampling sites of surface sediment were in slightly polluted status, and the heavy metals such as Pb, Co and Ni were in pollution-free status.

Furthermore, as shown in Table 4, the Ei values of heavy metal such as Cr, Cu, Pb, Zn and As were below 30, which belonged to the low ecological risk elements. Especially, the Ei value of As was the highest, which was the main factor for the increase of potential ecological risk index. Consequently, it can be concluded that the contaminant As from surface sediment in the southeastern Da Qaidam Salt Lake was the main cause of pollution. The PERI results also showed that the surface sediment in the southeastern Da Qaidam Salt Lake was in slightly polluted status, which corresponded with the results obtained from the geoaccumulation index method.
Fig. 3. The $I_{geo}$ values of Cr, Cu, Pb, Zn, As, Mn, Ni and Co concentrations from surface sediment in the southeastern Da Qaidam Salt Lake.

Table 3. The enrichment factors of Cr, Cu, Pb, Zn, As, Mn, Ni and Co from surface sediment in the southeastern Da Qaidam Salt Lake.

| Site | $EF$(Cr) | $EF$(Cu) | $EF$(Pb) | $EF$(Zn) | $EF$(As) | $EF$(Mn) | $EF$(Ni) | $EF$(Co) |
|------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1    | 1.08     | 1.12     | 0.91     | 1.02     | 2.35     | 0.79     | 0.77     | 0.55     |
| 2    | 1.13     | 1.33     | 1.08     | 1.25     | 1.74     | 0.63     | 0.54     | 0.29     |
| 3    | 1.09     | 1.25     | 1.10     | 1.16     | 1.40     | 0.94     | 0.88     | 0.63     |
| 4    | 1.02     | 1.14     | 0.93     | 1.11     | 1.79     | 0.73     | 0.68     | 0.54     |
| 5    | 1.02     | 1.05     | 0.87     | 1.09     | 2.03     | 0.89     | 0.85     | 0.51     |
| 6    | 1.07     | 0.97     | 0.83     | 1.04     | 2.43     | 1.12     | 1.13     | 0.78     |
| 7    | 0.96     | 1.17     | 1.02     | 1.10     | 1.90     | 1.26     | 0.90     | 0.70     |
| 8    | 1.11     | 1.07     | 1.04     | 1.13     | 1.40     | 1.36     | 0.86     | 0.63     |
| 9    | 1.05     | 1.13     | 1.17     | 1.16     | 2.07     | 1.83     | 1.31     | 0.96     |
| 10   | 1.07     | 1.17     | 1.45     | 1.21     | 2.17     | 2.10     | 1.58     | 1.22     |
| 11   | 1.02     | 1.13     | 1.18     | 1.11     | 1.23     | 1.37     | 1.02     | 0.72     |
| 12   | 1.08     | 1.03     | 1.22     | 1.10     | 1.45     | 2.16     | 1.43     | 1.07     |
| 13   | 1.17     | 1.13     | 1.21     | 1.11     | 2.29     | 1.88     | 1.63     | 1.29     |

Table 4. The potential ecological risk index of Cr, Cu, Pb, Zn and As from surface sediment in the southeastern Da Qaidam Salt Lake.

| Site | $E'_i$(Cr) | $E'_i$(Cu) | $E'_i$(Pb) | $E'_i$(Zn) | $E'_i$(As) | PERI | potential ecological risk |
|------|-------------|-------------|-------------|-------------|-------------|------|--------------------------|
| 1    | 2.47        | 6.43        | 5.20        | 1.17        | 26.85       | 42.12| low risk                 |
| 2    | 3.05        | 8.98        | 7.27        | 1.69        | 23.48       | 44.47| low risk                 |
| 3    | 2.84        | 8.16        | 7.18        | 1.52        | 18.25       | 37.95| no risk                  |
| 4    | 2.62        | 7.34        | 5.97        | 1.44        | 23.17       | 40.54| low risk                 |
| 5    | 2.56        | 6.55        | 5.47        | 1.36        | 25.43       | 41.37| low risk                 |
| 6    | 2.44        | 5.54        | 4.70        | 1.19        | 27.64       | 41.51| low risk                 |
| 7    | 2.52        | 7.68        | 6.68        | 1.45        | 24.92       | 43.25| low risk                 |
| 8    | 2.78        | 6.69        | 6.51        | 1.41        | 17.44       | 34.83| no risk                  |
| 9    | 1.89        | 5.08        | 5.27        | 1.05        | 18.72       | 32.01| no risk                  |
| 10   | 1.67        | 4.60        | 5.70        | 0.95        | 17.05       | 29.97| no risk                  |
| 11   | 2.56        | 7.12        | 7.45        | 1.40        | 15.46       | 33.99| no risk                  |
| 12   | 1.63        | 3.86        | 4.59        | 0.82        | 10.87       | 21.77| no risk                  |
| 13   | 1.94        | 4.70        | 5.03        | 0.93        | 19.03       | 31.63| no risk                  |
4. Conclusions
The spatial distributions of heavy metal concentration were indicative of nonuniform characteristics in the southeastern Da Qaidam Salt Lake, and the lake sediment quality had begun to deteriorate. The PERI(As) was much higher than other heavy metals, which was the main heavy metal contaminant in surface sediment. In summary, the level of heavy metal pollution in the southeastern Da Qaidam Salt Lake was not strong, but anthropogenic emissions would become the main source of heavy metals along with the frequent and strong human activities in the surrounding region.

Acknowledgement
We thank Derong Wang for laboratory assistance, and Rongchang Hong for assistance with fieldwork. This work was supported by the National Natural Science Foundation of China (41501052, U1407206), Qinghai Natural Science Foundation of China (2017-ZJ-928Q), the Second Tibetan Plateau Scientific Expedition and Research Program (2019QZKK0805) and Thousand Talents Plan of Qinghai Province (Grant to XY Min).

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