

Assessment of As, Cd, Ni and Cr Contamination in Water, Sediments and Fish of Shahid Rajaie Dam, North Iran

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Extended Abstract

Introduction

The pollution of the aquatic environment with heavy metals and trace elements has become a worldwide problem during the recent years, because they are indestructible and most of them have toxic effects on organisms. Potentially toxic elements (PTEs) added to an aquatic system by anthropogenic and natural sources are distributed during their transport between different compartments of aquatic ecosystems, such as water, sediment and biota. The main goals of present study are: 1. to determine concentrations of As, Cd, Ni and Cr in water and sediment as well as their accumulation in fishes, 2. to evaluate contamination and toxicological factor in the river and lake dam sediments and 3. to calculate monthly fish consumption limits for carcinogenic and noncarcinogenic health.

Materials and Methods

Study area

Shahid Rajaie dam is located in 40 Km south Sari City, in the north part of Iran with 160 million cubic meters capacity and approximate catchment of 1244 Km². It is constructed on Tajan River and its reservoir is fed by Shirinrood and Sefidrood rivers (in the confluence of these rivers, Tajan River is arisen). It was designed to provide irrigation, drinking, and industrial water for the region. The main activities in this area are agriculture, crop irrigation, and dairy activities. The main human settlements are upstream including Ferim, Afrachal, Ali-Abad, Sekuya villages with more than 10000 habitants as a total. Geological formations in the region in terms of lithology are mainly limestone, dolomitic limestone, sandstone, marl and shale (Fig. 1).

Sampling and analysis

For water quality assessment, 16 water samples were collected from the surface waters including 9 sites along the Shirinrood (Sh-1 to Sh-9) and 4 sites along Sefidrood (S-1 to S-4) rivers and 3 samples from Lake Dam (M-1 to M-3) during two periods (November 2012 and September 2013). The location of the sampling points is shown in Figure 1. The samples were kept at 4°C prior to analysis. Quantities of As, Cd, Ni and Cr were analyzed by ICP-MS in Westlab, Australia. Up to 26 Sediment samples were collected from Sefidrood and Shirinrood rivers and dam lake, using a pre-cleaned stainless steel grab sampler for Lake samples (SR-7 to SR-15) and using a plastic scoop for river samples (SR-1 to SR-6 and SR-16 to SR-26) in October 2012. Figure 2 shows the location of the sampling points. The collected samples were immediately stored in polyethylene bags and air-dried in the laboratory at room temperature. Then, gravel and plant root were removed. The samples were passed through a 63 micron steel sieve. The concentrations of the constituent potentially toxic elements (PTEs) were measured at Zar Azma Laboratory (Iran) using ICP-MS methods. Fish samples, including two species Barbel and *L. cephalus* of Cyprinidae family, were collected from the Lake Dam. The fish samples were washed with deionized water, packed in polyethylene bags and kept at -20°C, then, transported on ice to the laboratory. Properties of As, Cd, Cr and Ni were analyzed by atomic absorption spectrometry.

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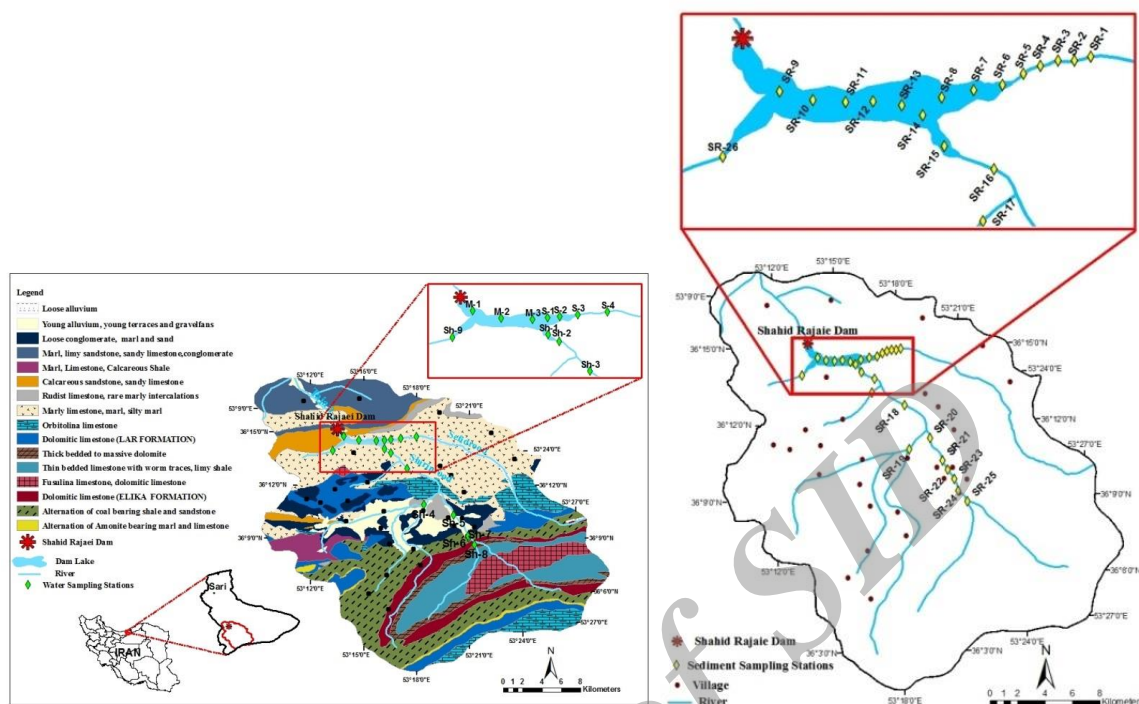


Fig. 1. Geological map of the study area and location of water sampling stations. Fig. 2: Location of sediment sampling stations

Results and Discussion

All water samples are $\text{Ca-HCO}_3\text{-SO}_4$ type. The average abundance order of PTEs for water samples in two periods are: $\text{Ni} > \text{Cr} > \text{As} > \text{Cd}$ (Table 1). Concentrations of As, Cd, Cr and Ni in all the samples are less than WHO and EPA standard. The average abundance order of PTEs for sediment samples are: $\text{Cr} > \text{Ni} > \text{As} > \text{Cd}$ (Table 2).

Table 1. Concentration of PTEs ($\mu\text{g/l}$) and Major ions (mg/l) in water

| | Na^+ | Mg^{++} | Ca^{++} | HCO_3^- | Cl^- | SO_4^- | As | Cr | Cd | Ni |
|----------------|---------------|------------------|------------------|------------------|---------------|-----------------|------|-----|------|------|
| Average | 19.0 | 5.3 | 66.4 | 200.2 | 20.9 | 65.7 | 0.39 | 2.2 | 0.11 | 7.73 |
| Max | 61.5 | 11.0 | 123.0 | 283.7 | 30.2 | 177.6 | 0.81 | 4.0 | 0.18 | 9.85 |
| Min | 11.3 | 3.3 | 55.0 | 161.7 | 12.9 | 33.2 | 0.01 | 1.0 | 0.07 | 2.80 |
| WHO | 30-60 | - | - | - | 250 | 250 | 10 | 50 | 3 | 20 |
| EPA | 50 | 150 | 200 | - | 250 | 250 | 10 | 100 | 3 | - |

Table 2. The comparison of As, Cd, Cr and Ni concentration in sediment samples with sediment quality guidelines

| PETS (mg/kg) | Cr | Ni | As | Cd |
|---------------------|-----------|-----------|-----------|-----------|
| Max | 81.05 | 57.31 | 10.80 | 0.80 |
| Min | 46.55 | 27 | 2.30 | 0.20 |
| Average | 68.13 | 37.85 | 7.40 | 0.41 |
| PEL | 90.00 | 36 | 17 | 3.53 |
| Average/PEL | 0.76 | 1.05 | 0.44 | 0.12 |
| TEL | 37.30 | 18 | 5.90 | 0.60 |
| Average/TEL | 1.83 | 2.10 | 1.25 | 0.69 |
| ERM | 370 | 51.60 | 70 | 9.60 |
| Average/ERM | 0.18 | 0.73 | 0.11 | 0.04 |
| ERL | 81 | 20.90 | 8.20 | 1.20 |
| Average/ERL | 0.84 | 1.81 | 0.90 | 0.34 |

The enrichment factor (EF), base of average shale was calculated with Equation 1.

$$EF = \frac{[M]/[Sc]_{\text{Sediment}}}{[M]/[Sc]_{\text{Background}}} \quad (1)$$

where [M]= total trace element concentration measured in sediment sample (mg/kg) and [Sc]= total concentration of scandium as the reference element (mg/kg). Enrichment factor value for As, Ni and Cr is <2 in the sediment samples (except in SR-20 station) while, the EF value for Cd in 54% of sediment samples were >2 that reveals moderate contamination (Fig. 3).

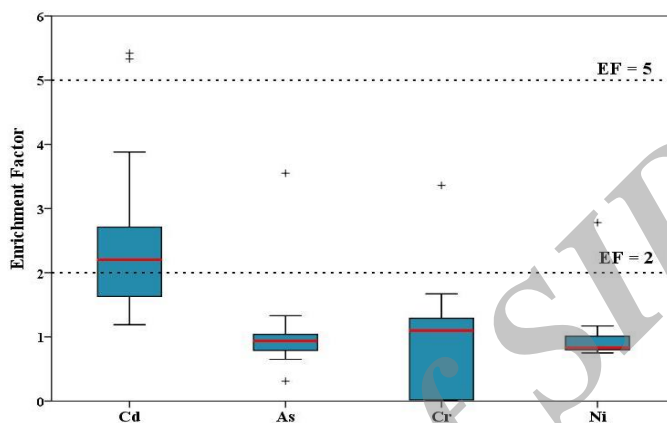


Fig. 3. Box diagram of enrichment factor for PTEs in Sediment samples

The comparison of selected elements concentration in sediment samples with sediment quality guidelines indicate that the average concentration of As, Cr and Ni in the present sediments is higher than threshold effect level (TEL). Nickel shows higher concentration than probable effect level (PEL) and effect range low (ERL) values (Table 2). These sediments based on PELQ (Equation 2) and ERMQ (Equation 3) calculations, for Cr, As, Ni and Cd indicate slightly toxic.

$$PELQ = \frac{\sum_{i=1}^n M_i / PEL_i}{n} \quad (2) \quad ERMQ = \frac{\sum_{i=1}^n M_i / ERM_i}{n} \quad (3)$$

where M_i is the concentration of element i in sediments, ERM_i and PEL_i the guideline values for the element i and n the number of metals.

The average abundance order of PTEs contents in Barbel fish is similar to water samples, while for *L. cephalus* fish it is as $Cr > Ni > Cd > As$. Chromium reveals higher concentration than WHO standard (0.15 mg/kg) in both fish species, while Ni content in Barbel fish is higher than WHO standard (0.4 mg/kg).

To estimate the public health risk of exposure to PTEs through fish consumption, the CR_{lim} for either carcinogenic (Equation 4) or non-carcinogenic (Equation 5) health effects, were calculated.

$$CR_{lim} = \frac{RfD \cdot BW}{C_m} \quad (4) \quad CR_{lim} = \frac{ARL \cdot BW}{C_m \cdot CSF} \quad (5)$$

where CR_{lim} = maximum allowable fish consumption rate (kg/d); ARL = maximum acceptable individual lifetime risk level (unit-less); BW = consumer body weight (70kg); C_m = measured concentration of chemical contaminant m in fish (mg/kg); CSF = cancer slope factor (mg/kg-d);

RfD = oral reference dose (mg/kg-d).

Equation 6 was used to convert daily consumption limits, in kilograms, to meals consumption limits over a given time period (month) as a function of meals size

$$CR_{mm} = \frac{CR_{lim} \cdot T_{ap}}{MS} \quad (6)$$

where CR_{mm} = maximum allowable fish consumption rate (meals/mo); T_{ap} = time averaging period (365.25 d/12 mo = 30.44 (d/mo)); MS = meals size (0.227 kg fish/meals).

The RfD values, CSF values, allowable Monthly fish consumption for As, Cd, Ni and Cr are summarized in Table 3.

Based on CR_{mm} value, maximum allowable consumption of Barbel and *L. cephalus* fishes for carcinogenic health of As is two meals per month (Approximately 0.5 kg).

Table 3. Monthly fish consumption limits for carcinogenic and noncarcinogenic health endpoints and other parameters of PTEs in fish species

| Fish species | PTEs | C _m | RfD | CSF | Noncancer | | cancer | |
|--------------------|------|----------------|--------|-----|-------------------|------------------|-------------------|------------------|
| | | | | | CR _{lim} | CR _{mm} | CR _{lim} | CR _{mm} |
| Barbel | As | 0.0325 | 0.0003 | 1.5 | 0.65 | 87 | 0.01 | 2 |
| | Cd | 0.018 | 0.001 | NA | 3.89 | 521 | - | - |
| | Ni | 1.44 | 0.02 | NA | 0.97 | 130 | - | - |
| | Cr | 1.39 | 0.02 | NA | 1.01 | 135 | - | - |
| Leuciscus cephalus | As | 0.035 | 0.0003 | 1.5 | 0.6 | 80 | 0.01 | 2 |
| | Cd | 0.04 | 0.001 | NA | 1.75 | 235 | - | - |
| | Ni | 0.065 | 0.02 | NA | 21.54 | 2888 | - | - |
| | Cr | 0.91 | 0.02 | NA | 1.54 | 206 | - | - |

Conclusions

The selected elements concentration in sediment samples with sediment quality indices revealed that the average concentration of As, Cr and Ni in the present sediments is higher than threshold effect level. Abundance of some toxic metals in water samples and fishes are similar. This represents that the contamination in water can be transferred into some fish species.

Keywords: Iran, potentially toxic elements, risk assessment, sediment quality guidelines, Shahid Rajaei Dam.