Metal contamination assessment in water column and surface sediments of a warm monomictic man-made lake: Sabalan Dam Reservoir, Iran
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ABSTRACT
In this study, metal concentrations in the water column and surface sediment of the Sabalan Dam Reservoir (SDR) were determined. Moreover, heavy metal pollution index (HPI), contamination index (CI), heavy metal evaluation index (HEI), enrichment factor (EF), geo-accumulation index ($I_{geo}$), sediment quality guidelines (SQGs), consensus-based SQGs (C-BSQGs), and mean probable effect concentration quotients (mPECQs) were evaluated for water and sediments of SDR. It was observed that metal concentrations in river entry sediment were lower, but those in river entry water were higher than corresponding values in the vicinity of the dam structure. The HPI values of water samples taken from 10 m depth in the center of SDR exceeded the critical limit, due to high concentrations of arsenic. However, according to CI, the reservoir water was not contaminated. The HEI values indicated contamination of SDR water with metals at 10 m depth. A comparison of water quality indices revealed that HEI was the most reliable index in water quality assessment, while CI and HPI were not sufficiently accurate. For SQGs, As and Cu concentrations in sediments were high, but mPECQ, $I_{geo}$, and EF revealed some degree of sediment pollution in SDR. The calculated EF values suggested minor anthropogenic enrichment of sediment with Fe, Co, V, and Ni; moderate anthropogenic enrichment with As and Mn; and moderate to severe anthropogenic enrichment with Cu. A comparison of SQG values revealed that the threshold effect and probable effect levels were the most reliable metrics in the assessment of sediment toxicity. Statistical analysis indicated similarities between metal concentrations in the center of the reservoir and near to the dam structure, as a result of similar sediment deposition behavior at these points, while higher flow velocity at the river entry point limited deposition of fine particles and associated metals.

Key words | arsenic, contamination index, copper, sediment pollution, water quality

HIGHLIGHTS
- This study aimed to determine metal concentrations in the water column and surface sediment of the Sabalan Dam Reservoir (SDR), Iran.
- It was observed that metal concentrations in river entry sediment were lower, but those in river entry water were higher than corresponding values in the vicinity of the dam structure.

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A comparison of metallic pollution indices in water revealed that heavy metal evaluation index was the most reliable index, while contamination index and heavy metal pollution index were not sufficiently accurate.

The calculated enrichment factor values suggested minor anthropogenic enrichment of surface sediment in the SDR with Fe, Co, V, and Ni; moderate anthropogenic enrichment with As and Mn; and moderate to severe anthropogenic enrichment with Cu.

**GRAPHICAL ABSTRACT**

**INTRODUCTION**

Metal contamination, toxicity, and accumulation in the aquatic environments have attracted major global attention (Purves 1985; Valls & Lorenzo 2002; Gochfeld 2003; Vesali Naseh et al. 2018). Metals in the environment originate from both natural and anthropogenic sources, with the latter being more important. When metals are discharged into aquatic ecosystems, they redistribute into water and sediment strata. Due to adsorption, hydrolysis, and co-precipitation, large proportions of metals settle in bottom sediments, while only small proportions of free metal ions remain dissolved in the water column (Gaur et al. 2005). In general, metal concentrations in sediments of an aquatic ecosystem are usually three- to five-fold greater than those in the water column (Luoma 1989). Therefore, concentrations of metals in sediments are a good indicator of the health and contamination status of water bodies (Pekey 2006). On the other hand, sediments act as a substantial sink and source of metals in water bodies (Morillo et al. 2002). Accordingly, settled metals may be resuspended and released into the water column, causing ecological and health-related problems in aquatic ecosystems such as lakes and reservoirs (Saha et al. 2017; Tiwari & De Maio 2017). Therefore, in addition to studying metals in sediments, analyzing these pollutants in the water column provides important information for effective water quality management of aquatic environments, particularly dams, which are usually constructed to supply drinking water.

Many studies have examined the distribution of dissolved metals in water and sediments of natural lakes (Hou et al. 2013; Rahman et al. 2014; Makokha et al. 2016; Matta et al. 2018). However, dam reservoirs, as man-made lakes, have received less attention than natural lakes. Manipulation of inflow/outflow makes dam reservoirs different from natural lakes, as they undergo large water level fluctuations. This increases the variability of hydrodynamic conditions, an important factor affecting the distribution of metals in dam reservoirs (Ford 1990; Noori et al. 2018). Therefore, information on metal distribution in dam reservoirs is needed to enable effective and sustainable water quality management.

Analyzing the degree of contamination of metals in water resources is complicated. Hence, a number of indices have been proposed to analyze the toxicity of metals in the
water column and sediment of water bodies (Horton 1965; Mohan et al. 1996; MacDonald et al. 2000; Edet & Offiong 2002; Prasad & Jaiprakas 2009). To evaluate the degree of metal pollution in water, many indices and guidelines are proposed, including World Health Organization guidelines for drinking water quality (WHO 2017), heavy metal pollution index (HPI; Prasad & Bose 2001), contamination index (CI; Backman et al. 1998), and heavy metal evaluation index (HEI; Edet & Offiong 2002). Guidelines and indices developed to study the toxicity of sediments include sediment quality guidelines (SQGs; Persaud et al. 1995; Long et al. 1995; Smith et al. 1996), consensus-based SQGs (C-BSQGs; MacDonald et al. 2000), mean probable effect concentration quotients (mPECQs; MacDonald et al. 2000; Ingersoll et al. 2001), enrichment factor (EF; Pekey 2006), and geochemical accumulation index ($I_{geo}$; Muller 1979).

In this study, metal concentrations in the water column of a warm monomictic man-made lake, Sabalan Dam Reservoir (SDR) in Iran, were assessed using guidelines on drinking water quality. SDR water and sediment quality were then evaluated using well-known metal pollution indices to answer the research question: ‘What is the level of metal pollution in SDR after around 15 years since impoundment?’ Additionally, water/sediment quality guidelines and indices were compared to determine which provided the most accurate results.

**MATERIALS AND METHODS**

**Study area**

Sabalan Dam Reservoir, a warm monomictic man-made lake, is located at a mean elevation of around 1,000 m above sea level on the Qareh-Su river in Ardebil Province, Iran, 55 km north-west of the city of Ardebil and 40 km north-east of the city of Meshkin Shahr (Figure 1). The total volume of water in the reservoir is 105 million cubic meters (MCM), with a surface area of 4.4 km$^2$ at a normal water level. The Qareh-Su river originates in the Sabalan and Baghroo Mountains, Iran.

The Sabalan Dam was constructed in 2006 to supply water for drinking and agricultural purposes. The reservoir

![Figure 1](http://iwaponline.com/hr/article-pdf/51/4/799/730785/nh0510799.pdf)
supplies water for irrigation of around 15,000 hectares (ha) of agricultural land downstream of the dam and provides around 10 MCM of potable water annually for Meshkin Shahr City (population 150,000). In addition, the reservoir supplies water for 89 villages downstream of the dam.

Since the Qareh-Su river runs through different urban and rural areas and a wide range of agricultural and industrial land, it is exposed to large pollution loads, which makes SDR susceptible to water quality deterioration. Since the Sabalan Dam was built only recently, there is no water quality information available regarding metals in the reservoir. Therefore, this study evaluated metal concentrations in the water column and sediments of the reservoir to determine reservoir water quality 13 years after impoundment.

Water and sediment samples were taken in early January 2018, at a time when the reservoir was thermally mixed (Figure 2). Water/sediment samples were taken at six different distances from the entrance to the dam structure, at points where the water depth was about 12 m (Points E and F), 15 m (Point D), 36 m (Point C), 39 m (Point B), and 45 m (Point A) (Figure 1).

Water samples were taken from surface water and at 10 m depth in the water column. All water samples were filtered using 0.45 μm membrane, transferred to polyethylene bottles previously cleaned with 50% HNO₃, acidified with 50% HNO₃ to maintain pH < 2, and then stored in gray boxes at 4°C. Surface sediment samples were taken and transported to the laboratory, oven-dried at 80°C for 12 h, and then digested using a combination of HNO₃, HCl, HF, and HClO₄. Water and sediment samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) to measure the concentration of 13 metals. Analysis of the water samples was carried out using the U.S. EPA Method 3005A, Revision 1 (USEPA 1992), and analysis of the sediment samples was carried out using the U.S. EPA Method 3050B (USEPA 1996). Blanks and certified reference material (NIST 1640 and NIST 2709a for water and sediment, respectively) were used to assure quality control of the procedures. Duplicate analysis of blanks, samples, and certified reference materials revealed an acceptable recovery rate (92–104%) and relative standard deviation (SRD ≤ 5%).

Approaches for water/sediment evaluation

Analyzing the degree of metal contamination is complicated, as described in Supplementary Material, Appendix A. Metals in the water column of the reservoir were assessed using guidelines on drinking water quality drawn up by the WHO (2017) and the Institute of Standards and Industrial Research of Iran (ISIRI). Thereafter, SDR water quality was evaluated using HPI (Mohan et al. 1996), CI (Backman et al. 1998), and HEI (Edet & Offiong 2002) (see Supplementary Material, Appendix A). Sediment pollution was assessed using EF (Selvaraj et al. 2004; Pekey 2006), Igeo (Muller 1979), SQGs (Persaud et al. 1993; Long et al. 1995; Smith et al. 1996), C-BSQGs (MacDonald et al. 2000), and mPECQs (MacDonald et al. 2000; Long et al. 2006) (see Supplementary Material, Appendix A). Note that C-BSQGs are important reliable guidelines for assessing sediment quality in freshwater ecosystems, as they offer a combination of guidelines (SQGs) accounting for the interactive effects of

Figure 2 | Depth profiles of water temperature at Points A to F in SDR, Iran, in early January 2018.
contaminants in sediment (MacDonald et al. 2000). Finally, correlation and cluster analyses were used to identify relationships between metals in water and surface sediments of SDR. Cluster analysis (CA) has been widely applied in different fields of science and engineering, but estimating the number of clusters is challenging, and poor choice in selecting the number of clusters strongly affects the final results (Bostan-maneshrad et al. 2018), leading to inaccurate interpretations. In this study, the Dunn index (DI; Dunn 1974; see Supplementary Material, Appendix B) and Baker–Hubert Gamma index (BHGI; Baker & Hubert 1975; see Supplementary Material, Appendix B) were applied to determine the optimum number of clusters.

RESULTS AND DISCUSSION

Water quality analysis

Metal detection limits, permissible values, and ideal and shale values are presented in Supplementary Material, Table S1. The metal concentrations detected in surface water and water samples taken from 10 m depth in SDR are shown in Figure 3.

The concentrations of metals in surface water and at 10 m depth followed the order: Fe > Al > Mn > As > Cu. Concentrations of Cd, Co, Cr, Cu, Ni, Pb, V, and Zn were below the detection limit at all water sampling locations.
It was found that the concentration of most dissolved metals was higher at 10 m depth than in surface water. In general, the SDR is thermally stratified during most months of the year and only mixes in late December to early March, i.e., it was thermally mixed during the sampling period. However, it was chemically stratified for various reasons. Compared with the thermal dynamics, the cycle of elements in SDR displays a lag, due to anoxic conditions in deep layers (see Supplementary Material, Figure S1), a common phenomenon in deep lakes/reservoirs (Calamita et al. 2019; Noori et al. 2019). Under anoxic conditions, most metals are released from sediment to the water column (De Jonge et al. 2012; Li et al. 2013). Therefore, metal concentrations are higher in deep layers (e.g., 10 m depth) than at the water surface where water is saturated by oxygen. In addition to anoxic conditions, pH contributes to metal solubility in lakes/reservoirs, with the solubility of most metals generally decreasing with increasing pH (Avila-Perez et al. 2013). Moreover, high pH values intensify sorption onto clay minerals, which results in the deposition of some metals such as Cd and Pb in sediments (Tao et al. 2012; Hou et al. 2013). These processes, along with a decreasing trend in pH with depth in SDR (Supplementary Material, Figure S2), result in higher concentrations of metals at 10 m depth than in surface water.

To further assess the level of metal pollution, metal concentrations in SDR water were compared with those reported in other studies conducted on the Jose Antonio Alzate reservoir, Mexico (Avila-Perez et al. 1999), Lake Volvi, Greece (Fytianos & Lourantou 2003), Lake Balaton, Hungary (Nguyen et al. 2005), Avsar reservoir, Turkey (Ozturk et al. 2009), the Chah Nimeh reservoirs, Iran (Bazrafshan et al. 2016), Lake Manzala, Egypt (Zahran et al. 2015), and East Dongting and Hongu lakes, China (Makokha et al. 2016) (Table 1). More details about the lakes/reservoirs are given in the Supplementary Material. It seems that Zn and Fe are generally the most abundant metals in reservoir/lake water (Table 1). Comparisons revealed that concentrations of As in SDR are rather high compared with those in other water bodies worldwide. Concerns about As contamination of water resources resulting

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**Table 1 | Metal concentrations (μg/L) in water in some lakes and reservoirs worldwide**

| Site                              | Water body type | Al  | As  | Cd  | Co  | Cr  | Cu  | Fe* | Mn  | Ni  | Pb  | Zn* |
|-----------------------------------|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Present study                     | Reservoir       | 100 | 16  | ND  | ND  | 10  | 0.10| 20  | ND  | ND  | ND  | ND  |
| Avsar reservoir (Ozturk et al. 2009) | Reservoir      | 50  | ND  | 1.2 | 12  | 20  | 2.40| 12  | 19  | ND  | ND  | ND  |
| Chah Nimeh (Bazrafshan et al. 2016) | Reservoir      | 1   | 1   | 10  | 0.28| 0.3 | ND  | ND  | ND  | ND  | ND  | ND  |
| Jose Antonio Alzate Reservoir (Avila-Perez et al. 1999) | Reservoir  | 17  | 38  | 217 | 0.12| 38  | 8  | 8  | 1.56 | ND  | ND  | ND  |
| Lake Manzala (Zahran et al. 2015)  | Freshwater lake | 9.2 | 7.2 | 22  | 4.9 | 0.18| ND  | 9.15| ND  | ND  | ND  | ND  |
| East Dongting lake (Makokha et al. 2016)  | Freshwater lake | 6.1 | 0.17| ND  | 1.38| ND  | 0.89| ND  | 0.09| ND  | ND  | ND  |
| Hongu lake (Makokha et al. 2016)    | Freshwater lake | 6.7 | 0.06| ND  | 4.0 | 0.17| ND  | 0.71| ND  | ND  | ND  | ND  |
| Lake Volvi (Fytianos & Lourantou 2003) | Freshwater lake | 2.8 | 0.00| ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  |
| Lake Balaton (Nguyen et al. 2005)   | Freshwater lake | 0.1 | 0.1 | 0.6 | 0.71| 0.33| ND  | 0.33| ND  | ND  | ND  | ND  |

ND, Non-detectable.

*Fe and Zn are in mg/L.
from lithogenic sources in Ardabil Province have been reported previously (Mehrnews 2017). However, further studies are required to determine background level and anthropogenic sources of metals such as As in the region. Therefore, it is of great importance to re-evaluate As concentrations in SDR water before starting water withdrawal, especially for drinking purposes.

**Water quality guidelines**

The concentration of Fe ranged from 40 (Point A) to 130 μg/L (Points B and C), that of Al from 50 to 100 μg/L, that of Mn from 10 (Point C) to 20 μg/L, and that of Cu from 5 (Point B) to 10 μg/L (Point C). Compared with guideline values (Supplementary Material, Table S1), the concentrations of all these metals were below the standard permissible or ideal value. At two locations (Points A and C), the As concentrations were found to be higher than the permissible limit set in drinking water quality guidelines (WHO 2017). These concentrations were detected at 10 m depth at Point A (11 μg/L) and Point C (16 μg/L). In general, redox conditions can influence the mobility of metals such as As (Masscheleyn et al. 1991; Miao et al. 2006) with higher concentrations of As found in anoxic conditions (Barringer et al. 2011). Since the bottom layers of SDR were found to be anoxic in deep areas (e.g., Points A and B), As diffusion from sediment to water may increase its concentrations in the reservoir. Similar results have been reported for Union Lake, USA, by Keimowitz et al. (2017).

Given the location of Point A close to the water gate, it is essential to take appropriate caution in the water withdrawal of SDR. In emergency cases, water should be withdrawn from the surface of the reservoir, where there is no concern about elevated As concentration.

**Sediment analysis**

Metal concentrations in sediment are shown in Figure 3. The metal concentrations at Point A decreased in the order: Al > Fe > Mn > Cu > V > Zn = Cr = Ni > As > Co > Pb, while the concentrations of Cd and Hg were below the detection limit. The order was similar at other sampling locations, as shown in Figure 3.

Metal concentrations were higher at Point A than at other sediment sampling locations (Figure 4). In general, hydrodynamic conditions are the main contributor to sedimentation of suspended particles at Point A, the deepest point in SDR. Suspended particles usually carry large nutrient and metal loads from land upstream in the basin to the reservoir (Pietron’ et al. 2018). In addition, low turbulence at Point A (and other deep points located far from the river entry point) usually provides suitable conditions for sedimentation of fine suspended particulates in a large specific area that contains the highest pollution loads. However, concentrations of metals in sediments were generally higher than those in surface water or water at 10 m depth. These observations are in line with findings by Morillo et al. (2002) and...
This could be a result of metal separation and combination with dissolved organic carbon since metals readily combine with dissolved organic carbon and settle in sediment (Tao et al. 2012; Hou et al. 2013).

Table 2 shows the metal concentrations in the sediment of different lakes and reservoirs around the world. A comparison indicated that the concentrations of Ni, Pb, and Zn in SDR were lower than those measured in Jose Antonio Alzate reservoir, Mexico (Avila-Perez et al. 1999), Lake Ontario, Canada (Marvin et al. 2004), Lake Volvi, Greece (Fytianos & Lourantou 2005), Lake Balaton, Hungary (Nguyen et al. 2005), Lake Onbe and Lake Hamahara, Japan (Bibi et al. 2007), Avsar reservoir, Turkey (Ozturk et al. 2009), Yilong lake, China (Bai et al. 2011), Three Gorges Reservoir, China (Tang et al. 2014), the Chah Nimeh reservoirs, Iran (Bazrafshan et al. 2016), Lake Manzala, Egypt (Zahran et al. 2015), and East Dongting and Hongu lakes, China (Makokha et al. 2016). (See ‘Lakes/Reservoirs’ in the Supplementary Material for details.) East Dongting and Hongu lakes are known to be polluted with Zn and As (Makokha et al. 2016). Comparing the concentration of As in sediment of SDR with that in these two lakes, and also in the Earth’s crust, showed that SDR sediments are slightly polluted with As (Table 2).

Table 2 | Metal concentrations (μg/kg) in sediment in some lakes and reservoirs worldwide

| Site | Water body type | Metal concentration (max/min) |
|------|----------------|------------------------------|
|      |                | Al<sup>a</sup> | As | Cd | Co | Cr | Cu | Fe<sup>a</sup> | Mn<sup>a</sup> | Ni | Pb | Zn<sup>a</sup> |
| Present study | Reservoir | 25.3 | 12 | ND | 7 | 20 | 70 | 21 | 1 | 20 | 5 | 0.02 |
|                |            | 18 | 10 | 5 | 10 | 60 | 17.2 | 0.7 | 10 | 2 | 0.01 |
| Avsar reservoir (Ozturk et al. 2009) | Reservoir | – | – | 1.2 | – | 20 | 38 | 29 | – | 39 | 6 | – |
|                |            | 0.3 | 9 | 18 | 20 | 20 | 0.64 |
| Chah Nimeh (Bazrafshan et al. 2016) | Reservoir | – | – | 8.8 | – | 14 | 5.2 | 0.3 | 0.12 | 38 | 29 | 0.1 |
|                |            | 5 | 10 | 3 | 0.2 | 1 | 28 | 19 | 0.09 |
| Three Gorges reservoir (Tang et al. 2014) | Reservoir | – | 21 | 1.2 | – | 106 | 103 | – | 58 | 81 | 0.19 |
|                |            | 11 | 0.6 | 76 | 54 | 41 | 37 | 0.11 |
| Jose Antonio Alzate Reservoir (Avila-Perez et al. 1999) | Reservoir | – | – | 2.8 | – | 145 | 61 | 44 | – | 43 | 76 | 0.23 |
|                |            | 2.0 | <5 | 51 | 30 | 15 | 12 | 0.09 |
| Onbe (Bibi et al. 2007) | Freshwater lake | – | 34 | – | – | 89 | 50 | – | – | 57 | 65 | 0.18 |
|                |            | 29 | 57 | 39 | 30 | 45 | 17 | 0.17 |
| Hamahara (Bibi et al. 2007) | Freshwater lake | – | 27 | – | – | 78 | 36 | – | – | 62 | 47 | 0.24 |
|                |            | 5 | 20 | 14 | 3 | 15 | 0.04 |
| Ontario (Marvin et al. 2004) | Freshwater lake | – | – | 5.8 | – | ND | 110 | – | – | ND | 200 | 1.3 |
|                |            | 0 | ND | 3.7 | ND | 5 | 0.01 |
| Yilong lake (Bai et al. 2011) | Freshwater lake | – | 26 | 1.6 | – | 125 | 67 | – | – | 73 | 89 | 0.12 |
|                |            | 7.8 | 0.3 | 40 | 15 | 14 | 31 | 0.03 |
| Lake Manzala (Zahran et al. 2015) | Freshwater lake | – | 2.8 | 19.9 | 102 | 53 | 0.7 | – | – | 66 | 0.16 |
|                |            | 0.6 | 3.0 | 3 | 2.5 | 0.3 | 3.4 | 0.00 |
| East Dongting lake (Makokha et al. 2016) | Freshwater lake | – | 102 | 24.0 | – | 54 | 294 | – | – | 56 | 114 | 0.47 |
|                |            | 25 | 0 | 2 | 2.4 | 4 | 10 | 0.02 |
| Hongu lake (Makokha et al. 2016) | Freshwater lake | – | 48 | 0.7 | – | 53 | 558 | – | – | 50.0 | 35 | 0.47 |
|                |            | 24 | 0 | 0.0 | 12.6 | 9.3 | 5.6 | 0.02 |
| Lake Volvi (Fytianos & Lourantou 2003) | Freshwater lake | – | – | 1 | – | 25 | 16 | 0.0 | 0.16 | – | 14 | 0.08 |
|                |            | 0.7 | 20 | 12 | 0.0 | 0.08 | 11 | 0.05 |
| Lake Balaton (Nguyen et al. 2005) | Freshwater lake | – | – | 0.7 | – | 66 | 36 | – | 0.76 | 55 | 160 | 0.15 |
|                |            | 0.1 | 5.7 | 0.7 | 0.16 | 4 | 2 | 0.01 |

ND, Non-detectable.

<sup>a</sup>Al, Fe, Mn, and Zn are in mg/L.
Indexing approaches

Water indices

The HPI values calculated for samples of surface water and water at 10 m depth are shown in Figure 5. In calculating the HPI values, only Al, As, Cu, Fe, and Mn were considered, as metals with concentrations below the detection limit were excluded. The HPI value at 10 m depth at Point C (∼146.5) was higher than the critical index value of 100, mainly due to the concentration of As exceeding the permissible level. The HPI values at 10 m depth at Points A and E were 94 and 93, respectively. In surface water, the HPI value at Points A to F was 51, 51, 60, 50, 57, and 66, respectively. It can, thus, be concluded that surface water is generally less contaminated by metals than deep water layers in SDR. As discussed above, this is a result of hydrodynamic conditions and the decrease in pH with depth in SDR.

The HPI values indicated that SDR water was polluted only at Point C, but the WHO and ISIRI guidelines were exceeded for As, with higher concentrations than the permissible limit, at Points A and C. Therefore, it can be concluded that HPI results should be verified using water quality standard guidelines before practical application, especially for drinking water.

The CI values in surface water and at 10 m depth in SDR were <1 at all sampling locations (Figure 5), indicating no problem with metal contamination in SDR water. Therefore, the CI results were inconsistent with the HPI results and...
with the WHO and ISIRI guidelines. A similar discrepancy has been reported previously by Edet & Offiong (2002), who concluded that, despite the significant correlation between HPI and CI data, the final classification could give different results.

To overcome the discrepancy between HPI and CI values, we calculated HEI values for SDR water samples (Figure 5). The mean HEI value was around 1.2, so the contamination level at 10 m depth was in the medium category (1.2 ≤ HEI ≤ 2.4). All surface water samples were in the low contamination range (HEI < 1.2).

Comparing the HPI, CI, and HEI results, it can be concluded that CI is the least reliable index. In contrast, the HPI value failed to account for high concentrations of As in Point A. Overall, HEI results showed the best agreement with the observations and with the WHO and ISIRI guidelines. Noted that research works revealed that despite a significant correlation between HPI and CI data, the final classification could give very different results (Edet & Offiong 2002). To overcome this discrepancy, Edet & Offiong (2002) recommend the use of HEI.

**Sediment indices**

The $I_{geo}$ values for each element detected at the sampling locations are shown in Figure 6(a). The pollution status of sediments is evaluated using Supplementary Material, Table S2. Since the concentrations of Cd and Hg were below the detection limit, they were excluded from the calculation of $I_{geo}$. From Figure 6(a), it can be concluded that sediments in SDR are generally not polluted with metals. However, for Cu at Points A to C ($I_{geo} ≈ 0.05$), sediments in SDR were found to be unpolluted to moderately polluted.

The calculated EF values were generally higher at Point C than at Points A and E (Figure 6(a)). The EF values for Pb, Zn, and Cr were approximately <1 at all sampling locations, indicating no anthropogenic enrichment of these metals in SDR sediments (Zhang & Liu 2002). Higher EF values were observed for Fe, Co, V, and Ni, showing minor anthropogenic enrichment (Birch 2003). The EF values for As and Mn were within the range 3–5, classified as moderate anthropogenic enrichment (Birch 2003). This may be due to agricultural and industrial activities upstream of SDR.

![Figure 6](http://iwaponline.com/hr/article-pdf/51/4/799/730785/nh0510799.pdf)
The EF value calculated for Cu was $>5$, indicating moderate to severe anthropogenic enrichment in the surface sediments in SDR.

Comparing metal concentrations with the threshold level (TEL) and the probable effect level (PEL) values revealed that all the metal concentrations were below the PEL values. However, the As and Cu concentrations were above TEL and below PEL at all sampling locations, so adverse biological effects can be expected to occur occasionally as a result of these As and Cu concentrations (Smith et al. 1996). The Ni concentration was also below the TEL value at Points A to C but was below the TEL value at Points D to F. So sediment-dwelling organisms at Points D to F are less likely to experience the adverse effects of Ni than those at Points A to C.

The concentrations of As and Cu were between the lowest effect level (LEL) and severe effect level (SEL) values, indicating that they might have adverse effects on sediment-dwelling organisms. The concentrations of Ni were above LEL at Points A to C, but below LEL at Points D to F, indicating no significant effect on benthic biological resources at the latter locations.

Comparing metal concentrations in SDR sediments with the effect range median (ERM) and effect range low (ERL) values revealed that concentrations of As and Cu were within the ERM–ERL values, and other trace metal concentrations were not likely to be troublesome.

The concentrations of Cd, Cr, Hg, Ni, Pb, and Zn were lower than the threshold effect concentration (TEC) values stated in C-BSQGs, suggesting that they are present at levels that are not hazardous to biota (Supplementary Material, Table S3). On the other hand, the observed concentrations of As and Cu fell between the TEC and probable effect concentration (PEC) values, where concentrations are commonly considered to be neither toxic nor non-toxic (MacDonald et al. 2000). Therefore, concentrations of metals in sediments of SDR appear not to be hazardous to sediment-dwelling organisms.

The evaluation of sediments using the proposed SQGs revealed that As and Cu concentrations in sediments were a concern. The SQG values were also compared with each other to estimate the precision of each method (Figure 6(b)). The comparison revealed that PEL values were lower than other upper boundaries in SQGs in all cases except for Cu. This result shows that the PEL–TEL approach sets the most extreme boundaries for sediment toxicity and, hence, could be more reliable than other approaches. As seen in Figure 6(b), if a metal concentration was found to be non-toxic using PEL and TEL, it fulfilled the other two SQGs (LEL and SEL) in most cases. It can be concluded that PEL–TEL has a higher safety factor than the other two SQGs. On the other hand, the TEC values in most cases (except for Cu and Zn) were higher than the threshold effect values for the other SQGs. Hence, it is necessary to apply appropriate caution when using the TEC–PEC approach.

The mPECQ values were calculated for As, Cr, Cu, Ni, Pb, and Zn concentrations at sampling stations across SDR (Figure 6(a)), while Cd and Hg were below the detection limit and were excluded from the analysis. According to the mPECQ-based classification by Long et al. (2006), SDR is a low–medium priority site with a 15–29% probability of toxicity. However, the results are only valid for these six metals, which were used to get an indication of the toxicity risk in SDR sediments.

The mPECQ values declined on moving from the dam structure (Point A) to the river entry to SDR (Point F) (Figure 6(a)). This finding means that the sediments located near the dam structure are more polluted with heavy metals than those at the point where the river enters SDR.

**Statistical analysis**

The normality of the data was checked by the Kolmogorov–Smirnov test ($p < 0.05$) before the application of statistical analyses. The results of statistical analyses are given below.

**Water samples**

The results of hierarchical CA by Ward’s method for SDR water samples are given in Figure 7(a). Metals at Point A and B (surface water and 10 m depth) were grouped in one cluster and those at Points C to E in another cluster. The third cluster included metals in surface water of Point F. These findings are a result of hydrodynamic conditions at the sampling points, as the turbulence declines from the river entry (Point F) to the dam structure (Point A).

The results of Pearson correlation analysis of metals in surface water and at 10 m depth are given in Table 3. Note
that metals with concentrations below the detection limit were excluded from the correlation analysis. The results showed strong correlations between metals in surface water at Points A to D. Strong correlations were also observed for metals in surface water at Points D to F. Interestingly, it was found that on moving from Point A (dame structure) toward Point F (river entry), the correlation coefficient between concentrations in surface water and at 10 m depth increased. As discussed, differences in hydrodynamic conditions at the sampling points may have contributed to these differences.

Table 3 | Results of Pearson correlation analysis of metal concentrations (Al, As, Cu, Fe, and Mn) at the water surface and water samples from 10 m depth (water column) at sampling Points A to F in SDR

| Water surface (Point A) | Water column (Point A) | Water surface (Point B) | Water surface (Point C) | Water column (Point C) | Water surface (Point D) | Water surface (Point E) | Water column (Point E) | Water surface (Point F) | Water surface (Point F) |
|-------------------------|------------------------|-------------------------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Water surface (Point A) | 1                      |                         |                         |                         |                         |                         |                         |                         |                         |
| Water column (Point A)  | 0.52                   | 1.00                    |                         |                         |                         |                         |                         |                         |                         |
| Water surface (Point B) | 0.999**                | 0.54                    | 1.00                    |                         |                         |                         |                         |                         |                         |
| Water surface (Point C) | 0.987**                | 0.64                    | 0.987**                 | 1.00                   |                         |                         |                         |                         |                         |
| Water column (Point C)  | 0.912*                 | 0.55                    | 0.908*                  | 0.930*                 | 1.00                   |                         |                         |                         |                         |
| Water surface (Point D) | 0.991**                | 0.61                    | 0.991**                 | 0.998**                | 0.943*                 | 1.00                    |                         |                         |                         |
| Water surface (Point E) | 0.950*                 | 0.65                    | 0.950*                  | 0.972**                | 0.985**                | 0.979**                 | 1.00                   |                         |                         |
| Water column (Point E)  | 0.910*                 | 0.63                    | 0.908*                  | 0.937*                 | 0.995**                | 0.947*                  | 0.992**                | 1.00                   |                         |
| Water surface (Point F) | 0.951*                 | 0.64                    | 0.950*                  | 0.972**                | 0.987**                | 0.979**                 | 1.000**                | 0.993**                | 1.00                   |

*Correlation significant at \( p < 0.05 \) (two-tailed).
**Correlation significant at \( p < 0.01 \) (two-tailed).
**Sediment samples**

The results of hierarchical CA using Ward’s method for metals in sediments of SDR are shown in Figure 7(b). Two clusters were observed, indicating similarities between metal concentrations at Points A to C (Figure 7(b)). This similarity is likely caused by similar deposition behavior of sediments at Points A to C, whereas higher flow velocity at Points D to F somewhat limits the deposition of fine particles, which are much more strongly associated with metals than coarse particles. The metals in the two clusters were (i) Al and Fe and (ii) Mn, V, Cu, As, Pb, Co, Cr, Zn, and Ni (Figure 7(c)). Since Fe was classified in the same group as Al (cluster (i)), it can be concluded that it derives from lithogenic sources (Karbassi et al. 2005). The fact that Cu, Zn, Ni, and Cr were strongly correlated with each other (Table 4), and were classified in one cluster along with As, Pb, Co, V, and Mn, indicates that they may derive from the same source.

Pearson correlation was used to evaluate the sources of metals. Arsenic and V were excluded from correlation analysis due to their constant values in sediment. Correlation coefficients for metals in sediment (Table 4) revealed that Cu, Zn, Ni, and Cr were strongly correlated with each other but showed no significant correlation with other metals, indicating that Cu, Zn, Ni, and Cr may derive from the same source. The strong negative correlation of Fe with Mn, and the fact that they were classified in different clusters, may indicate that Fe and Mn have different sources.

**CONCLUSION**

Analysis of metal concentrations in water and sediment in SDR, a drinking water supply, revealed arsenic (As) to be the main concern in both water and sediment. Therefore, water withdrawal should be delayed until further analysis is performed to ensure that the As concentration meets the permissible value for drinking water. In emergency cases, water should be withdrawn from the surface of the reservoir, where the As concentration is lower.

Comparisons of various indices/guidelines for assessing metal pollution in water in SDR revealed that HEI was most reliable because both CI and HPI were unable to account for the effect of high concentrations in water of As, a critical pollutant. A comparison of SQGs revealed that the threshold effect and the probable effect were the most reliable guidelines for sediment quality assessment. This novel information can be used for effective water quality assessment/management in SDR.

**AUTHOR CONTRIBUTIONS**

Conceptualization, R.N. and Q.T.; methodology, S.A. and R.N.; formal analysis, S.A. and A.T.H.; investigation, R.N.; data curation, R.N.; writing – original draft preparation, S.A.; writing – review and editing, R.N., R.B., M.H., and F.H.; supervision, R.B. and B.K.; project administration, R.N.; funding acquisition, R.N. and Q.T.

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**Table 4** Correlation analysis between metals in sediments in SDR

|     | Al   | Co   | Cr   | Cu   | Fe     | Mn     | Ni   | Pb   | Zn   |
|-----|------|------|------|------|--------|--------|------|------|------|
| Al  | 1.00 |      |      |      |        |        |      |      |      |
| Co  | −0.20| 1.00 |      |      |        |        |      |      |      |
| Cr  | −0.70| 0.73 | 1.00 |      |        |        |      |      |      |
| Cu  | −0.70| 0.73 | 1.00 |      |        |        |      |      |      |
| Fe  | −0.842*| 0.63 | 0.911*| 0.911*| 1.00  |        |      |      |      |
| Mn  | 0.834*| −0.60| −0.894*| −0.894*| −0.996*| 1.00  |      |      |      |
| Ni  | −0.70| 0.73 | 1.00 |      | 1.000**| 0.911*| −0.894*| 1.00 |
| Pb  | −0.62| 0.19 | 0.16 | 0.16 | 0.16   | 0.19   | −0.14 | 0.16 | 1.00 |
| Zn  | −0.70| 0.73 | 1.00 | 1.00 | 1.000**| 0.911*| −0.894*| 1.00 |

*Correlation significant at p < 0.05 (two-tailed).
**Correlation significant at p < 0.01 (two-tailed).
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SUPPLEMENTARY MATERIAL

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