Global evaluation of heavy metal content in surface water bodies: a meta-analysis using heavy metal pollution indices and multivariate statistical analyses

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ABSTRACT

Water is polluted by increasing activities of population and the necessity to provide them with goods and services that use water as a vital resource. The contamination of water due to heavy metals (HMs) is a big concern for humankind; however, global studies related to this topic are scarce. Thus, the current review assesses the content of HMs in surface water bodies throughout the world from 1994 to 2019. To achieve this goal, multivariate analyses were applied in order to determine the possible sources of HMs. Among the analyzed HMs in a total of 147 publications, the average content of Cr, Mn, Co, Ni, As and Cd exceeded the permissible limits suggested by WHO and USEPA. The results of the heavy metal pollution index, evaluation index, the degree of contamination, water pollution and toxicity load showed that the examined water bodies are highly polluted by HMs. The results of median lethal toxicity index showed maximum toxicity in As, Co, Cr and Ni in the surface water bodies. Results of ingestion and dermal pathways for adults and children in the current analyzed review showed that As is the major contaminant. Moreover, Cr, Ni, As and Cd showed values that could be considered as a high risk for cancer generation via the ingestion pathway as compared to the dermal route. It is recommended that remediation techniques such as the introduction of aquatic phytoremediation plant species and adsorbents should be included in land management plans in order to reduce human risks.

Keywords: Surface water; heavy metals; human health; water management; pollution indices; multivariate analysis.

1. Introduction

Contamination of aquatic environment by heavy metals (HMs) is a critical concern due to their potential toxicity and accumulation in aquatic habitats (Jordan et al., 2014; Tscheikner-Gratl et al., 2019). These are produced from numerous natural and anthropogenic sources. In freshwater ecosystems, metal contamination may result from direct atmospheric precipitation, geologic weathering or through the discharge of agricultural, municipal, domestic or industrial waste products (Dawson and Macklin, 1998; Salomons and Förstner, 2012). Specifically, the literature highlights coal combustion as one of the most important anthropogenic emission sources of trace elements and an important source of a number of HMs in surface water (Wagner and Boman, 2003; Tsai et al., 2003). Trace elements such as uranium (U), arsenic (As), antimony (Sb), thorium (Th), beryllium (Be), radon (Rn), cadmium (Cd), selenium (Se), chlorine (Cl), phosphorus (P), chromium (Cr), nickel (Ni), cobalt (Co), mercury (Hg), fluorine (F), manganese (Mn) and lead (Pb), and their compounds, are commonly found in coal and classified as potentially ‘hazardous air pollutants’ by the US Clean Air Act Amendments of 1990. Concentrations of HMs and their actual impacts can be greatly modified due to interaction with natural water ingredients (Pettersson et al., 1993; Klavinš et al., 2000). Under certain environmental conditions, HMs could accumulate to a toxic concentration level and cause significant ecological impacts and problems for human health (Wongsasuluk et al., 2014; Jaishankar et al., 2014).

HMs have a particular significance in ecotoxicology due to their long persistence, bioaccumulation and biomagnification in the food chain (Yin et al., 2018). They are non-degradable and continuously increasing in freshwater bodies (Salomons and Förstner, 2012). Being non-degradable, they bioaccumulate along the food chain, causing toxic effects at points far from the source of pollution (Strom, 2008; Ebrahimpour and Mushrifah, 2010; Weber et al., 2013).

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27 When HMs remain in contact with freshwater ecosystems, they are ultimately
28 adsorbed onto the sediments. Consequently, organisms living in these sediments accumulate
29 these metals at varying degrees (Varol, 2011). Li et al. (2015) in their studies on HM
30 pollution in China reported that several highly populated urban areas, such as Kunming,
31 Zhuzhou, Chenzhou, Shaoguan and Chongqing, are highly polluted, and need special HMs
32 control measures in order to reduce their impact on human health. They further reported that
33 high levels of HMs in water bodies are mainly linked to human activities like urbanization
34 and industrialization. Qu et al. (2018) reported levels of As (1.71 µg/L), Cr (7.7 µg/L), Pb
35 (30.1 µg/L), Cd (16.0 µg/L), Hg (46.1 µg/L), Cu (copper, 96.8 µg/L) and Zn (zinc, 98.3 µg/L)
36 in the Wen-Rui Tang River in China, electroplating and leather tanning industries being
37 mainly responsible for the HMs contents. They suggested that remediation and management
38 efforts should be developed to protect human health in these rapidly developing areas. The
39 Regulations of the People's Republic of China on Nature Reserves and the Administration
40 Regulations of Marine Natural Reserves have ban activities that affect the water bodies
41 (Wang et al. 2015), and remediation measures are needed to reduce the HMs levels (Mitsch et
42 al., 2015).

43 The environmental regulatory authority of India, the Central Pollution Control Board
44 (CPCB), has recognized 43 industrial groups in India where industrial and human activities
45 are responsible for contaminating the water bodies (CPCB 2009). The eastern parts of India,
46 mainly the states of Orissa, Jharkhand and West Bengal, and Durgapur industrial city, are
47 recognized as highly polluted regions (CPCB 2009). For example, Kumar et al. (2017), in
48 their studies on Indian rivers, showed that upper stretches of the rivers are less polluted
49 compared to the lower reaches. This may be attributed to industrial and wastewater
50 discharges into the upper river reaches that accumulate towards the lower reaches.

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52 For developing efficient protection and management plans for surface water
53 ecosystems, the potential contamination risks should be disseminated from the scientific
54 community to local managers and decision-makers (Daily, 2000; Mitchell, 2006; Richter et
55 al., 2018). Environmental quality indicators and contamination indices are powerful tools for
56 processing, analyzing and conveying raw environmental information to decision-makers,
57 managers, technicians or the public (Kumar et al., 2018a, 2018b). During the last decades,
58 several heavy metal assessment indices have been applied to the aquatic environment
59 (Hakanson, 1980; Yegemova et al., 2018). There are several examples of these studies that
60 have provided valuable information for land managers and policymakers such as the
61 investigations carried out in Durgapur city in West Bengal (Saha and Paul, 2018); Yangtze
62 River in China (Wu et al., 2009); Phewa and remote Gosainkunda lakes in Nepal (Rupakheti
63 et al., 2017); Port Jackson, Botany, Kembla, Newcastle, Yamba and Eden in Australia (Jahan
64 and Strezov, 2017) and Khanpur Lake in Pakistan (Iqbal and Shah, 2013). However, to date,
65 global studies that consider a general perspective of the heavy metal contents in surface water
66 bodies are limited in the scientific literature.

67 The main aim of this literature review is to evaluate the heavy metal content of
68 surface water bodies throughout the world from 1994 to 2019. Since water quality changes
69 over time, data for years before this period may not reflect the scope of this research.
70 Moreover, assessment methods are being modernised each year, and to make the results
71 comparable, the chosen period of study is considered appropriate. To assess the different
72 results, and to integrate them into a comprehensive dataset, a multivariate analysis was
73 applied to determine the probable sources of HMs in the water bodies. Moreover, pollution
74 indices such as heavy metal pollution index (HPI), heavy metal evaluation index (HEI),
75 degree of contamination (C_d), water pollution index (WPI), and heavy metal toxicity load

(HMTL) were also calculated to evaluate the overall surface water quality of the examined water bodies. Also, the median lethal toxicity index was developed to assess the toxicity of HMs in water bodies. Finally, a human health risk assessment was also considered using ingestion and dermal pathways for adults and children. Our hypothesis is that water quality is a well-known problem over the world, although there is a lack of information in the literature about a clear global perspective about this issue. Water quality of surface water bodies has been very well-studied in isolated regions, but has not received much attention like other environmental problems such as climate change or plastic contamination.

2. Material and methods

2.1. Data collection

A total of 147 indexed publications and proceedings in the English language on HMs in surface water bodies throughout the world were gathered. Because English language is the main language to transfer our results to the international audience of Chemosphere, our literature search was limited to this language. We searched the keywords “heavy metals content”+ “surface water”+ “lake water”+ “river water” + “concentrations of heavy metals” from ISI of Web of Science, Science Direct, Google Scholar, ResearchGate and PubMed. Fe (iron), Cu, Zn, Cr, Mn, Co, Ni, Cd, As and Hg were analysed for this review paper. Out of the studied literature, China recorded the maximum number of sites for assessment of HMs in surface water bodies (102), followed by India (93), Greece (37), Spain (34), South Africa (30), Iran (21) and Turkey (20), as depicted in Fig. 1. It is important to highlight that only the papers that presented results in surface water bodies were taken into consideration to allow for homogeneity in the same database.

Fig. 2 shows the distribution of the journal papers: Environmental Monitoring Assessment Journal (20), Marine Pollution Bulletin (5), Environmental Earth Sciences (5), Science of the Total Environment (5), Bulletin of Environmental Contamination and

Toxicology (4), Applied Water Science (3), and Archives of Environmental Contamination and Toxicology (3). In Fig. S1 is presented the instruments used for the HMs analysis in the surface water bodies. Atomic absorption spectrometry (AAS) has the maximum amount of usage (90) followed by inductively coupled plasma mass spectrometry (ICP-MS, 28), inductively coupled plasma atomic emission spectroscopy (ICP-AES, 12), inductively coupled plasma optical emission spectroscopy (ICP-OES, 6) and X-ray fluorescence (XRF, 2).

Fig. S2 depicts the methodologies adapted for digestion of HMs in surface waters. Digestion is a mandatory process carried out in order to dissolve various impurities present in water samples (Fang et al., 1991). The most commonly used methodology for HM digestion is acidification of water with nitric acid (41) (Klavinš et al., 2000; Turgut, 2003; Dippner and Pohl, 2004; Bolormaa et al., 2006; Huang et al., 2008; Edokpayi et al., 2016; Khan et al., 2017; Zhou et al., 2018). The second most applied method is filtration (20), where the surface water is filtered prior to analysis (Karadede and Ünlü, 2000; Kumar et al., 2016; Arefin et al., 2016). Next in line is aqua-regia (16) (Sedykh et al., 2000; Majhi and Biswal, 2016). Moreover, there are other methods adapted for digestion of surface waters including 0.5 N HCl, HCl and 2.5% HNO₃. Finally, a database where the concentrations of all the HMs published during the above-mentioned literature review period was created (Supplementary Table S1).

2.2. Pollution assessment indices

Several pollution indices were employed to determine the pollution status of HMs in the surface water bodies.

2.2.1. Heavy metal pollution index (HPI)

This index gives the combined effect of individual HMs on surface water quality (Sheykhi and Moore, 2012). For this index, a rating is given to each HM based on

their relative significance and defined as inversely proportional to the recommended standard value for each HM. It is computed as:

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad eq.(1)$$

where W_i is the unit weighting of the i^{th} HM, Q_i is the sub-index for the i^{th} HM, and n is the number of HMs which equals 10 (Fe, Cu, Zn, Cr, Mn, Co, Ni, Cd, As and Hg) for this study. The sub-index (Q_i) is computed as:

$$Q_i = \sum_{i=1}^n \frac{|M_i - I_i|}{S_i - I_i} 100 \quad eq.(2)$$

where M_i ($\mu\text{g/L}$) is the examined value of the i^{th} HM. In eq.(2) S_i and I_i are the standards and ideal values, respectively, for drinking water taken from WHO (2017) and USEPA (2009) for the HMs ($\mu\text{g/L}$). A value of HPI below 100 represents low pollution of HMs, while 100 is the threshold value at which harmful health consequences are probable. An HPI value greater than 100 indicates the water is unsuitable for consumption.

2.2.2. Heavy metal evaluation index (HEI)

HEI presents the overall surface water quality with respect to HMs content, and is computed by the following equation (Al-Ani et al., 1987; Ameh, 2013):

$$HEI = \sum_{i=1}^n \frac{M_i}{MAC_i} \quad eq.(3)$$

where MAC_i is the monitored value and maximum admissible concentration of the i^{th} HM. Classifications of surface water quality based upon HEI are: <10 for low, 10-20 for moderate and >20 is high pollutions

2.2.3. Degree of contamination (C_d)

C_d indicates the collective detrimental impact of the HMs on surface water (Backman et al., 1998) and determined as:

$$C_d = \sum_{i=1}^n Cf_i \quad eq.(4)$$

$$Cf_i = \frac{M_i}{MAC_i} - 1 \quad eq.(5)$$

where Cf_i is the contamination factor for the i^{th} HM. The categories used to represent HM pollution on the basis of C_d are: <1 for low, 1-3 for moderate and >3 for high pollutions of HMs in the surface water body (Backman et al., 1998).

2.2.4. Water pollution index (WPI_i)

WPI is applied to all types of water use including water pollution control and management (Thukral et al., 2005). This index provides a relative number with respect to the minimum acceptable limit for a particular HM, and is computed as:

$$WPI_i = \frac{(M_i - Min_i)}{R_i} \quad eq.(6)$$

where Min_i is the minimum acceptable limit, and R_i is the range of the acceptable limits for a particular HM taken from WHO (2017).

2.2.5. Heavy metal toxicity load (HMTL)

HMTL index evaluates the content of HMs found in water bodies that affect human health (Saha and Paul, 2018). It is computed by multiplying the examined content of the HMs with their hazard intensity, and calculated as:

$$HMTL = \sum_{i=1}^n M_i \times HIS_i \quad eq.(7)$$

where HIS_i is the hazard intensity score of the i^{th} HM adopted from ATSDR (2017). HIS is allocated based on the frequency of incidence of the HM as a harmful substance on the National Priorities List (NPL) sites maintained by ATSDR, the toxicity level of these substances, and the prospect of human contact. The maximum HIS for HMs is 1800, where 600 points are allotted for each of the NPL frequency, the toxicity, and the prospect of human contact.

2.2.6. Median Lethal Toxicity (MLT)

The toxicity of a metal or its salt is reciprocal to its median lethal dose (MLD or LD_{50}), i.e., the lesser the MLD the more is the toxicity (Shetty Akhila et al., 2007). HMs present in inland waters is of direct concern to human or animal use. The toxicity of an HM in water may be expressed as its concentration in terms of MLD units (LD_{50} mg/kg, rat or mouse, oral). In the current research, an index to measure the toxicity of HMs in water is proposed on the basis of their MLD values. Safety data sheets of LD_{50} values of most of the commonly occurring HMs are available in the literature. It is evident that the toxicity of an HM salt may be attributed to the HM ions present in it. Therefore, the MLD values of an HM is calculated from the MLD of its commonly occurring salt as:

$$MLD(metal) = \frac{MLD_{ms} \times M_{m.m}}{ms_{m.m}} \quad eq.(8)$$

where MLD_{ms} is the median lethal toxicity of the metal salt, $M_{m.m}$ is the molar mass of metal and $ms_{m.m}$ is the molar mass of the metal salt.

We define the median lethal toxicity (MLT) of a metal in water as the amount of metal present in 1000 litres of water in units of its LD_{50} (mg/kg, rat or mouse, oral) as:

$$MLD(metal) = \frac{\text{Amount of metal (mg / kl)}}{MLD(\text{mg / kg rat or mouse, oral})} \quad eq.(9)$$

In terms of metal concentration in water, the equation is,

$$MLD(metal) = \frac{\text{Amount of metal}(\mu\text{g} / \text{l})}{MLD(\text{mg} / \text{kg rat or mouse, oral})} \quad eq.(10)$$

The total median lethal toxicity (TMLT) due to all HMs in a water source is the sum of all the individual MLT values.

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2.3. Human health risk assessment

The human health risk evaluation, as computed by USEPA, involves data compilation and examination, exposure and toxicity determination, and risk categorization (US Environmental Protection Agency, 2013). Exposure determination is estimated by involving the daily exposure value of a human body to HMs. The key exposure routes include direct ingestion, inhalation and dermal absorption (Koki et al., 2015; Mahato et al., 2016). We have determined exposure by employing ingestion and dermal routes since these are the two important routes of HM exposure from an aquatic ecosystem (USEPA, 2004). The exposure assessment was computed as:

$$ADD_i = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \quad eq.(11)$$

$$ADD_d = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad eq.(12)$$

where ADD_i ($\mu\text{g}/\text{Kg}/\text{day}$) and ADD_d ($\mu\text{g}/\text{Kg}/\text{day}$) are the average daily doses through ingestion and dermal absorption of water, respectively. In eqs. (11) and (12) C_i is the concentration of the HMs ($\mu\text{g}/\text{L}$), IR is the ingestion rate, EF represents exposure frequency, ED is exposure duration, BW indicates body weight, AT is the average time for non-carcinogens, SA represents exposed skin area, K_p is the skin adherence factor, ET represents exposure time, and CF is the conversion factor.

The non-carcinogenic risks were determined by applying the hazard quotient (HQ) of USEPA (2013). The summation of the non-carcinogenic risk of an individual HM is presented as a hazard index (HI) for the two exposure routes, and computed as:

$$HQ_i = \frac{ADD_i}{RfD_i} \quad eq.(13)$$

$$HQ_d = \frac{ADD_d}{RfD_d} \quad eq.(14)$$

$$HI = HQ_i + HQ_d \quad eq.(15)$$

where RfD_i and RfD_d are the ingestion and oral/dermal reference doses ($\mu\text{g/kg/d}$), respectively, HQ_i is the hazard quotient through ingestion, and HQ_d is the hazard quotient through dermal absorption. This index categorizes health risks into two types; $HI < 1$ indicates a low detrimental impact of HMs on human health, while $HI \geq 1$ represents greater chances of harmful health effects.

The carcinogenic risks (CR) of HMs were calculated to evaluate the chances of an individual developing cancer during their life span due to their contact with potential carcinogens. The slope factor (SF) is a toxicity value that describes the association between dose and response and was adopted from USEPA (2005). The range for CR certified by the USEPA (1989, 2004) is 1×10^{-6} to 1×10^{-4} . CR was computed as:

$$CR_i = ADD_i \times SF \quad eq.(16)$$

$$CR_d = ADD_d \times SF \quad eq.(17)$$

$$CI = \sum CR_i + CR_d \quad eq.(18)$$

where CI is the cancer index, and CR_i and CR_d are the carcinogenic risks for ingestion and dermal absorption pathways, respectively.

2.4. Data analysis

Firstly, Pearson's correlation analysis was applied to find the possible linear relationships among the different HMs in surface waters. Secondly, a cluster analysis (CA) was conducted by using varimax rotation and Euclidean distance in order to find the associations among the HMs. The results were presented in the form of a dendrogram. Then, we considered the importance of reducing the amount of a factor that could show the origin of the HM using a principal component analysis (PCA). Finally, non-metric multidimensional scaling (NMDS) was performed. This final analysis was selected in order to find performance data reduction and rank based approach for graphical representation of the associations between the HMs in a multidimensional space. This analysis is able to generate an ordination plot using the Euclidean distance, and to determine the level to which distance among the HMs in decreased dimensional space corresponds with the original multivariate distance between the samples. The statistical analysis of the data was performed using PAST v.3.21 (Hammer et al., 2001), SPSS v.16 software (IBM, USA) and Minitab v.14.

3. Results

3.1. Statistical analysis of HMs

The statistics of the concentrations of HMs detected in the surface water bodies of this review are given in Table 1. Among the investigated HMs, the highest mean values detected were of Co (3995 µg/L) followed by As (3982 µg/L), while the lowest mean concentration was observed for Hg (1.01 µg/L). The coefficient of variation results showed that Ni exhibited the maximum variation followed by Cd, while the minimum variation was reported for Hg (Table 1). Comparing the average values of HMs with drinking water guidelines as recommended by WHO (2017), it was observed that all HMs except Cu and Zn exceeded the highest permitted values for drinking water (Table 2). The average contents of

Cr, Mn, Co, Ni, As and Cd were found to be higher than the highest permitted values prescribed by USEPA (2009) for drinking water (Table 3).

Fig. 3 shows the average concentration of HMs in different countries. It was observed that the average values of Fe and Mn, and Mn, Co, As and Ni in China exceeded the highest permitted values of drinking water for WHO (2017) and USEPA (2009), respectively. In India, the mean values of Fe, As and Cr exceeded the values of drinking water as recommended by WHO (2017), while Mn, Ni, Cd and As recorded higher than the permitted values of USEPA (2009). In Greece, Hg values exceeded both WHO (2017) and USEPA (2009) guidelines. The average values of Cr and Ni in South Africa were found to be higher than the highest permitted values prescribed by WHO (2017) and USEPA (2009). In Iran, Ni and Cr exceeded both WHO (2017) and USEPA (2009) guidelines for drinking water. In Turkey, Ni values were found to be greater than the WHO (2017) and USEPA (2009) guideline values. The average values of Ni, Cd and Cr in the USA were found to be higher than the values recommended by WHO (2017) and USEPA (2009) for drinking water. In Pakistan, the mean values of Mn, Co, Cu, Ni, Cd, Cr and As recorded higher than the values prescribed by WHO (2017) and USEPA (2009) for drinking water, respectively. It is observed for Bangladesh and Nigeria the the Co, Ni, Cr and As content exceeded the highest permitted values recommended by WHO (2017) and USEPA (2009) for drinking water, respectively. In Germany, Mn and Ni contents were recorded higher than the USEPA (2009) guidelines for drinking water.

3.2. Multivariate analyses

The results of the Pearson's correlation analysis (Fig. 4) indicate that Cr is significantly correlated with Mn and Hg. Statistically, a significant correlation was also found between Mn, Hg and Fe. Co and Hg were also highly correlated with each other, whereas no

significant correlation was found with the remaining HMs. This is an indication of multiple point source apportionment for the HMs.

A cluster analysis (CA) conducted divided the HMs into two main groups (Fig. 5): Group I (Fe, Cd, Zn, Co and Ni), and Group II (Mn, Cr, Cu, Hg and As). From the results of the CA, it was found that Co and Ni have similar sources of origin, so do Mn and Cr, while Cu, Hg and As are contributed to by similar sources.

Finally, PCA was conducted in order to analyse the separation of the key HMs into four principal components. In general, the PCA accounted for a total of 83.2% of the variance with Eigenvalues above 1 (Table 4). The loadings of PCA after the varimax rotation (Fig. 6 and Table 4) showed that PC1 accounted for 42.7% of the variance and obtained maximum loadings for Fe, Ni, Cu, Zn and Cd, while Cr and Mn are in PC2 that accounted for 16.3% of the variance. PC3 registered the maximum loadings for Co and Hg (12.9%), while PC4 was dominated by As and accounted for 11.2% of the variation. NMDS was conducted to see the ordination based on distance matrix and presented in Fig. 7 (left). In the scatterplot of Fig. 7 (right), Mn, As and Co showed relative significant distance from the other HMs. The Shepard plot showed well-correlated dataset with low ordination stress (0.046) and high linear correlation ($R^2 = 0.903$).

3.3. Pollution assessment using HM pollution indices

HPI findings on the basis of WHO (2017) guidelines for drinking water indicate that the surface water bodies examined in our study are highly contaminated by HMs and unsuitable for potable uses. The HPI value was found above 100 (Table 2). HPI determined on the basis of the guidelines given by USEPA (2009) (Table 3), also indicated the unsuitability of the surface water bodies for consumption.

The HEI was determined to assess the quality of surface waters with respect to HM contents (Table 5). HEI value was found to be higher than 20, indicating high pollution of HMs in the examined surface waters. The degree of contamination (C_d) value was found to be greater than 3, indicating very high contamination of surface waters by the HMs (Table 5). The WPI indicates how many times the polluted water has to be diluted with good quality water to bring its quality to within the permissible limits (Thukral et al., 2005). WPI results showed that Cr, followed by As and Co, had caused high pollution of HMs in surface waters (Table 5). The tested water with a Cr value of 413.27 $\mu\text{g/L}$ was diluted with 82.65 L of good quality water to bring it to the minimum permissible value of 5 $\mu\text{g/L}$. Similarly, the tested water having As value of 3981.78 $\mu\text{g/L}$ and Co value of 3994.8 $\mu\text{g/L}$ was diluted with 79.64 L and 39.95 L of water, respectively, to bring these HMs to the lowest permissible value of 0 $\mu\text{g/L}$. It is worth noting that WPI values of all the HMs studied were greater than 1.

HMTL quantifies the pollution load or content in a water body and indicates the necessary elimination percentage of the HMs from the rivers to make it safe for human use. HMTL evaluates the HMs level found in the rivers that affect human health. It gives an indication to the regulatory authority about the level of treatment needed to treat the rivers to acceptable levels for consumption purposes. This index helps in providing an efficient treatment and management plan. HMTL determines the pollutant levels in the water that results in non-carcinogenic health risk. Agency for Toxic Substances and Disease Registry (ATSDR) and the United States Environmental Protection Agency (USEPA) list diverse substances that exist in large levels at NPL sites and are harmful to human health. The HMTL values were observed higher than the permissible level (5888.527 mg/L, Table 6). HM As showed the maximum value of HMTL, while the lowest value was recorded for Hg. The HMTL load of Cr, Mn, Co, Ni, As and Cd were found to be higher than their permissible toxicity load.

The total median lethal toxicity (TMLT) due to all HMs in a water source is the sum of all the individual MLT values. The average MLT values due to the metals reviewed in various water bodies are given in Table 7. HM As showed the highest value of MLT, whereas the lowest value was observed for Hg. Since HMs present in surface waters are of direct concern with regard to human or animal use, the toxicity of an HM in water may be expressed as its concentration presented in terms of MLD units (LD_{50} mg/kg, rat or mouse, oral) as indicated in Table 7.

3.4. Human health risk assessment

The health risks associated with the HMs in surface water were calculated by using ingestion and dermal routes because these are the two major exposure pathways of HMs. Table 8 indicates the health risks presented by the various HMs found in the surface water bodies. The results for children and adults indicated that As, followed by Co and Mn, showed higher risks via the ingestion route from the water bodies. For the dermal route As, Fe and Mn exhibit the highest risks of contamination. The hazard quotient results of the ingestion pathway for children and adults indicated that As, Cd and Co have high risks of contamination. As, Cd, Co and Cr display the highest human health risks through the dermal route. The hazard index was found to be higher than 1 for Cr, Mn, Co, As and Cd, indicating a detrimental effect of such HMs on the health of both children and adults. The carcinogenic risks determined for Cr, Ni, As and Cd (Table 9) showed a high risk of cancer via the ingestion pathway for both children and adults as compared to the dermal route. The cancer index values for Cr, Ni, As and Cd were found higher than the ranges recommended by USEPA (1989, 2004) of 1×10^{-6} to 1×10^{-4} for both adults and children.

4. Discussion

HMs are usually widespread in aquatic environments and understanding their distribution at the global scale is necessary to advise environmental protection policymakers. The high content of HMs in water bodies underlines the necessity of regular monitoring for aquatic biodiversity and human health protection (Ayenimo et al., 2005). Pekey et al. (2004) in their studies on the Dil Deresi stream, observed loadings of Cu and Cr on PC1 and indicated that effluents from a paint industry were responsible for the source apportionment of these HMs. Krishna et al. (2009) reported loadings of Fe and Zn on PC1 and observed that anthropogenic activities are responsible for the origin of these metals. Cd and Cu loadings were observed by Varol (2011) on PC1 while working on the surface water of the Tigris River and reported that these HMs originated from human activities. The atmospheric discharge of Cd, Zn, As, Hg and Pb that originated from human activities were likely to be between 527 and 22,320 t in 2012, released mainly from non-ferrous metal smelting and coal utilization (Tian et al., 2015).

The results of different contamination indices like heavy metal toxicity load (HMTL) find support from Saha and Paul (2018) who, in their studies on the surface water of urban and industrial cities of West Bengal, reported that Co, Mn, Zn and Cu are the main contaminants responsible for polluting the water bodies. They further concluded that Co (70%), Mn (85%) and Pb (63%) removal is required to make the water suitable for human purposes. Our results indicated that Cr (99%), Mn (61%), Co (97%), Ni (93%), As (99%), Cd (44%) and Hg (1%) removal is needed to make the water suitable for human uses. Yegemova et al. (2018) while working on Syr Darya River in Kazakhstan reported HPI values above 100, indicating high contamination of HMs in this river. The results of the current study also correlate with these findings. Kumar et al. (2018) also reported HPI values greater than 100 in the Sutlej River and Harike wetland, Punjab, representing high pollution of HMs in these

water bodies. Our results confirm these studies. The HEI and degree of contamination (C_d) results also showed high contamination of HMs in the water bodies. HEI values above 20 and C_d values higher than 3 represent high contamination of HMs in water bodies. The different indices were applied in this review paper on the basis that HPI, HEI, WPI and C_d were indicative of pollution levels of HMs in water bodies. All these indices confirmed that the examined water bodies are highly contaminated and need serious attention for the protection of human and animal users of these water bodies. Further, the HMTL index showed the significant removal rate of HMs required to make these water bodies safe for human uses. The median lethal toxicity index developed and applied for the first time in this study may be helpful for assessment of lethal toxicity of other contaminants in the environment.

The key issue for water contamination is the scarcity of basic sanitation and it is linked to vulnerable areas of population that do not have any option other than polluted rivers as sources for personal hygiene, food preparation, and sewage discharge (Chaggu et al., 2002; Qadir et al., 2010). Such types of studies are regularly required, and more knowledge and techniques are needed to help policymakers mitigate water pollution and fast environment degradation. This may be possible by introducing specific aquatic phytoremediation plants that will help in minimizing concentrations of HMs from the surface water bodies (Cicero-Fernández et al., 2016). For example, Bang et al. (2015) used *Miscanthus* sp. Goedae-Uksae 1 for phytoremediation of As, Cu, Ni, Cd, and Zn from contaminated water and reported that this plant species has a high potential for phytoremediation of HMs in polluted water bodies. Stricter rules should be designed for adequate integration of wastewater treatment systems in urban, agricultural and industrial areas (Capodaglio, 2017). Wastewater treatment requires massive expenditure and reduces economic revenue due to the installation of costly treatment units (Renzetti and Kushner, 2004). Consequently, available adsorbents have proved to be cost-effective and environmentally friendly treatment options (Sadegh et al., 2017). HMs can

be eliminated from wastewater by employing waste produced from industrial and agricultural activities, e.g., fly ash, lemon peel, barley straw, orange and mango peels, coir pitch, wheat bran and jute fiber (Parab et al., 2006; Sud et al., 2008; Bhatnagar et al., 2010; Pahade and Sharma, 2015; Malik et al., 2017). In addition to these adsorbents, sugarcane bagasse, rice husk and wheat straw have also been discovered as low cost and efficient adsorbents for the elimination of HMs (Bhatnagar and Sillanpaa, 2010; Beh et al., 2012; Tadeipalli et al., 2016).

For better management and safeguarding of water resources, identification of spatiotemporal alterations and distribution of contamination origins in water bodies is paramount (Ghadouani and Coggins, 2011). Among the water bodies, rivers are highly susceptible to contamination due to sewage and industrial discharge, and agricultural runoff. Su et al. (2011) illustrated the dynamics of water quality, mainly spatiotemporal variations and pollution distribution, and presented information for the advancement of river contamination management practice. This study may be useful in environmental management to recognize policies for the regulation of water bodies (Su et al., 2011). Increasing anthropogenic land pollution has led to the degradation of the river ecosystem of the Yamuna River in Delhi. This river has been highly contaminated due to the release of wastewater and untreated sewerage overflow from the national capital area, representing about 79% of the contamination load (Upadhyay et al., 2011). Such types of pollution in water bodies need efficient management such as enhancing the efficiency of sewage treatment plants (STPs), and introducing regulations for operation and maintenance of STPs and forming a sewage master plan (Upadhyay et al., 2011).

The inadequate use of participatory practice involving policymakers, environmentalists, decision-makers and the general public has been recognized in the management of water bodies, particularly when addressing information related to water bodies (Fölster et al., 2014; Timmerman and Langaas, 2005; Timmerman et al., 2010). The

lack of participatory approaches may be attributed to the fact that they are complex and vary depending on the research requirement, scope and stakeholder participation (Reed, 2008). Consequently, adaptable participative practices should be introduced, consisting of public involvement and GIS monitoring in order to tap into local information, as well as to recognize facts and information requirements (Behmel et al., 2016). The regular assessment of water bodies is also needed in addition to these techniques for documentation of efficient management plans. Awareness campaigns are also required for active participation of the public to safeguard the water bodies. This paper has underlined HMs in water bodies that should be reduced because they pose harmful hazards to human health. The data and methods applied in this paper present insight into the quality of water bodies and will be helpful for planning authorities in the execution of adequate management and treatment plans.

5. Conclusions

This review paper concludes that Cr, Mn, Co, Ni, As and Cd average values exceeded the WHO and USEPA guidelines for drinking water in the water bodies studied. The results of HPI, HEI, C_d , WPI and HMTL also indicated that the water bodies are highly contaminated by HMs. Hence, removal of HMs from surface water bodies is necessary to make them safe for consumption. For As, Cr, Co, Ni, Mn and Cd, 99%, 99%, 97%, 93%, 61% and 44% removal, respectively, is required to make the surface water bodies appropriate for human activities. The MLT index developed in this paper showed that As, Co, Cr and Ni exhibit maximum toxicity in the water bodies. HM As is the major contaminant that affects human health via ingestion and dermal pathways. Cr, Ni, As and Cd showed high cancer risks through the ingestion pathway. The results of this paper will be helpful to environmentalists in developing strategies to mitigate the problems of HMs pollution in water bodies.

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Table 1. Statistics of the concentrations of various heavy metals ($\mu\text{g/L}$) in surface water bodies.

	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Hg
Minimum	0.001	0.15	0.001	0.06	0.001	0.00067	0.01	0.22	0.003	0.007
Maximum	21800	77000	63500	42970	38100	27400	54000	86100	13700	8
Mean	413.27	2562.15	1654.05	3994.82	945.86	537.87	723.11	3981.78	180.88	1.01
Standard Deviation	128.24	747.74	541.75	135.24	191.84	138.71	213.10	145.96	62.80	0.54
Coefficient of variation	478.71	432.87	322.94	292.32	669.54	500.72	579.3	440.66	614.25	168.34

Table 2. HPI for various heavy metals in surface water bodies based on WHO (2017) guidelines for drinking water.

[illegible]

Table 3. HPI for various heavy metals in surface waters based on USEPA (2009) guidelines for drinking water.

Heavy metals	Mean ($\mu\text{g/L}$)	Highest permitted value for drinking water (S_i)	Sub-index (Q_i)	Unit weight $W_i = (K/S_i)$	$W_i \times Q_i$
Cr	413.27	100	413.3	0.01	4.1
Mn	2562.15	50	5124.3	0.02	102.5
Fe	1654.05	3000	55.1	0.0003	0.02
Co	3994.82	110	57068.9	0.142	8152.7
Ni	945.86	15	6305.7	0.067	420.4
Cu	537.87	1300	537.9	0.01	5.4
Zn	723.11	5000	14.5	0.0002	0.0
As	3981.78	10	39817.8	0.1	3981.9
Cd	180.88	5	3617.6	0.2	723.5
Hg	1.01	2	50.5	0.5	25.3
$\sum W_i = 1.05$; $\sum W_i \times Q_i = 13415.64$ and $HPI = 12776.10$					

Table 4. Principal component analysis of various heavy metals in surface water bodies.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.45	44.5	44.5	4.45	44.5	44.5	4.27	42.7	42.7
2	1.56	15.6	60.1	1.56	15.6	60.1	1.63	16.3	59.0
3	1.26	12.6	72.8	1.26	12.6	72.8	1.29	12.9	72.0
4	1.04	10.4	83.2	1.04	10.4	83.2	1.12	11.2	83.2
Variables	Component matrix				Rotated component matrix				
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	
Cr	0.762	0.625	0.135	0.051	Cr	0.630	0.765	0.093	0.043
Mn	0.138	0.913	0.305	0.099	Mn	0.058	0.973	0.009	0.074
Fe	0.944	0.042	0.144	0.179	Fe	0.957	0.088	0.148	0.016
Co	0.272	0.026	0.758	0.214	Co	0.264	0.218	0.679	0.342
Ni	0.954	0.060	0.120	0.160	Ni	0.966	0.081	0.118	0.001
Cu	0.674	0.367	0.384	0.265	Cu	0.665	0.082	0.506	0.318
Zn	0.774	0.303	0.281	0.164	Zn	0.770	0.040	0.376	0.246
As	0.179	0.108	0.142	0.888	As	0.022	0.103	0.070	0.914
Cd	0.946	0.043	0.140	0.183	Cd	0.960	0.089	0.145	0.020
Hg	0.013	0.306	0.526	0.088	Hg	0.009	0.111	0.604	0.024

*Bold values: Variables that conform to that component.

Table 5. Heavy metal evaluation index (HEI), degree of contamination (C_d), and water pollution index (WPI) for various heavy metals in surface waters.

Heavy metals	Mean ($\mu\text{g/L}$) M_i	MAC	M_i/MAC	S_i	$Cf = \frac{M_i}{S_i} - 1$	WPI
Cr	413.27	50	8.27	50	7.27	82.65
Mn	2562.15	50	51.24	50	50.24	2.56
Fe	1654.05	200	8.27	200	7.27	1.65
Co	3994.82	100	39.95	100	38.95	39.95
Ni	945.86	20	47.29	20	46.29	13.51
Cu	537.87	1000	0.54	1000	0.46	0.18
Zn	723.11	5000	0.14	5000	0.86	0.14
As	3981.78	50	79.64	50	78.64	79.64
Cd	180.88	3	60.29	3	59.29	1.81
Hg	1.01	1	1.01	1	0.01	1.01
$\text{HEI} = \sum \frac{M_i}{MAC} = 296.64 C_d = \sum Cf = 286.64$						

* MAC values adopted from Siegel (2002)

Table 6. Heavy metal toxicity load (HMTL) of surface water bodies following ATSDR (2017) relative toxicity level of heavy metals responsible for human health hazards.

Heavy metals	Hazard intensity score (HIS)	Recorded HMTL (mg/L)	Permissible HMTL (mg/L)	%age removal of HM to reduce pollution load
Cr	895	366.9	4.47	99
Mn	798	2042.9	798	61
Co	1013	4041.9	101.3	97
Ni	996	936.2	69.72	93
Cu	807	427.7	2421	PTL
Zn	915	658.8	4575	PTL
As	1674	6662.5	83.7	99
Cd	1320	237.6	132	44
Hg	1458	1.5	1.45	1
Heavy metal toxicity load (HMTL) (mg/L) = 15376.02				

Table 7. Median lethal toxicity (MLT) of various heavy metals in surface water bodies.

[illegible]

Table 8. Assessment of potential health risks posed by various heavy metals in surface water bodies.

Heavy metals	RfD (ingestion) $\mu\text{g/kg/d}$	RfD (dermal) $\mu\text{g/kg/d}$	Children		Adults		Children		Adults		Hazard index (HI)	
			ADD (ingestion)	ADD (dermal)	ADD (ingestion)	ADD (dermal)	HQ (ingestion)	HQ (dermal)	HQ (ingestion)	HQ (dermal)	HI (child)	HI (adult)
Cr	3	0.08	16.9	0.4	11.3	0.1	5.6	4.6	3.8	1.6	26.2	5.9
Mn	24	0.96	104.8	1.1	70.2	0.4	4.4	1.1	2.9	0.4	4.9	1.1
Fe	700	140	67.8	0.7	45.3	0.2	0.1	0.0	0.1	0.0	0.0	0.0
Co	0.3	0.06	163.4	0.7	109.5	0.2	544.8	11.2	364.8	3.8	6121.7	1389.5
Ni	20	0.8	38.7	0.1	25.9	0.0	1.9	0.1	1.3	0.0	0.2	0.0
Cu	40	8	22.0	0.2	14.7	0.1	0.6	0.0	0.4	0.0	0.0	0.0
Zn	300	60	29.6	0.0	19.8	0.0	0.1	0.0	0.1	0.0	0.0	0.0
As	0.3	0.12	162.9	1.7	109.1	0.6	543.0	13.7	363.6	4.6	7416.7	1683.5
Cd	0.5	0.03	7.4	0.1	4.9	0.0	14.8	3.1	9.9	1.0	45.2	10.3
Hg	0.3	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0

*ADD = average daily dose; HQ = Hazard quotient and RfD = oral/dermal reference dose.

Table 9. Carcinogenic risk (CR) of various heavy metals in surface water bodies.

Heavy metals	SF (mg/kg)/day	Children		Adults		Cancer index (CI)	
		CR (ingestion)	CR (dermal)	CR (ingestion)	CR (dermal)	CI (child)	CI (adult)
Cr	0.5	8.5	0.2	5.7	0.1	8.6	5.7
Ni	1.7	65.8	0.1	44.1	0.1	65.9	44.1
As	1.5	244.4	2.5	163.6	0.9	246.9	164.5
Cd	15	111.0	1.2	74.4	0.5	112.2	74.9

Fig. 1.The number of sampling sites per country used for the assessment of the heavy metal contamination of the surface water bodies.

Fig. 2. Distribution of journal papers on heavy metals in the surface water bodies.

Fig. 3 Average values of heavy metals content in the surface water bodies of different countries.

Fig. 4 Pearson's correlation analysis.

Fig. 5. Cluster analysis of heavy metals in surface water bodies.

Fig. 6 Loading plot of PCA

Fig. 7. Left: non-metric multidimensional scaling (NMDS) scatter plot (95% eclipse) and Right: NMDS Shepard 2-D plot of heavy metals in surface water using correlation as a similarity measure (NMDS Shepard 2-D plot: Stress = 0.04585, R^2 for Axis 1 = 0.9032, Axis 2 = 0.0901)

Highlights

- A global evaluation of heavy metals (HMs) from 1994 to 2019 in global surface water bodies.
- The global average values of Cr, Mn, Co, Ni, As and Cd exceeded WHO and USEPA guidelines.
- Results of heavy metal pollution indices showed that surface water bodies are generally highly polluted.
- Ingestion and dermal routes indicated that As is the major contaminant affecting human health.
- Cr, Ni, As and Cd exhibited high cancer risk via the ingestion route considering HMs in surface water bodies.