Assessment of heavy metals contamination in surface water of the upstream Sardabrud River, North of Iran.

Parvin Reyhani [1], Mohammad Reza Ansari [2], Keivan Saeb [3]

[1]MSc student of Environmental Engineering Department, Tonekabon Branch, Islamic Azad University (IAU), Tonekabon, Iran
[2]Faculty of Geoscience Department, Chaloos Branch, Islamic Azad University (IAU), Chaloos, Iran.
[3]Faculty of Environmental Engineering Department, Tonekabon Branch, Islamic Azad University (IAU), Tonekabon, Iran
*Corresponding Author: reyhanparvin@yahoo.com

Abstract: The aim of this study was to assess the level of heavy metals (i.e Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the surface water of the Sardabrud River. This study was conducted at 2011 to determine the residues of heavy metals in surface water of Sardabrud River in North of Iran. Results for levels in water were compared with national and international water quality guidelines,as well as literature values were reported for streams and rivers, The results showed that Sardabrud River Mean metals concentrations (µg kg_1) were in the range of; Cu:0.70–8.2, Cd: 0.05–0.11, Fe: 10–6168, Zn: 3.4–29.2, Mo: 0.5–5.7, Mn: 1–187.5, Cr: 0.5–9.5 and Pb: 0.9–25.4 respectively, Cluster analysis (CA) was used in this study, so, Cluster analysis suggests all of heavy metals in most of sites are similar and derived from same natural sources.This study indicated the surface waters polluted very weak with heavy metals by natural sources, and the pollution was weak at all of sites.
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1. INTRODUCTION

The Sardabrud is one of the most important rivers in North of Iran. The Sardabrud River originates in the Kelardasht region of the Northen of Central Alborz mountains of Iran and follows a northeastern route to Caspian Sea near the Chaloos city.The total length of the river is approximately 100 km, in Mazandaran province. Previous investigations indicated that the concentrations of heavy metals such as Pb and Fe were very high in surface water of the Sardabrud River by natural and anthropogenic pollution in this river (Kazemnejad et al, 2010). In addition, there is a lack of information on the concentrations and distributions of heavy metals in water of the river. This paper describes research undertaken to explore the heavy metal pollution in upstream of the Sardabrud River. Numerous studies have demonstrated that the concentrations of metals in suspended and bedsediments can be sensitive indicators of contaminants in hydrological systems (Salomons and Fo¨rstner, 1980; Luoma, 1990; Singh et al, 2005). The presence of trace metals in sediments is affected by the particle size and composition of the sediments (Foster and Hunt, 1975; Throne and Nickless, 1981; Sakai et al., 1986; Singh et al., 2005). More than 97% of the mass transport of heavy metals to the oceans is associated with river sediments (Jain and Sharma, 2001; Singh et al., 2005). Heavy metals are produced from a variety of natural and anthropogenic sources and are introduced to the riverine sediment naturally through the weathering of rocks; however, most heavy metal contaminants originate from anthropogenic sources such as long-term discharge of untreated domestic and industrial wastewater runoff, accidental spills, and direct soil waste dumping. (Schropp and Windom, 1987; Windom et al., 1989; Alexander et al., 1993; Keller and Schell, 1993;Chang et al., 1998; Feng et al., 1998; Benoit et al., 1999; Breuer et al., 1999; Gobeil et al.,1999; Murray et al., 1999; Phuong et al., 1998; Turgut 2002; Ramos et al., 1999; Topcuoglu et al., 2002; Ouyang et al.,2001; Macklin et al., 2006; Martin, 2000; Nouri et al., 2008; Reza and Singh, 2010). In fluvial environments, however, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products (Dawson and Macklin, 1998; Demirak et al., 2005). Metal contamination in aquatic environments has received much concern due to its toxicity, abundance and persistence in the environment, and subsequent accumulation in aquatic environments. Heavy metal residues in contaminated environments may accumulate in microorganisms, aquatic flora and fauna, which, in turn, may enter into the human food chain and result in health problems (Cook et al., 1990; Deniseger et al., 1990; Sin et al., 2001; Varol and Sen., 2012). Usually in unaffected environments, the concentration of most of the metals in rivers is very low and is mostly derived from

weathering of rock and soil (Reza and Singh, 2010; Varol and Sen., 2012). Heavy metals discharged into a river system by natural or anthropogenic sources during their transport are distributed between the aqueous phase and bed sediments. Because of adsorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water and a large quantity of them are deposited in the sediment (Bradley and Cox, 1986; Gaur et al., 2005; Horowitz, 1991; Macklin, 1992; Varol and Sen., 2012). It is estimated that between 30 and 98% of the total metal load of a river can be transported in a sediment-associated form (Gibbs, 1973; Salomons and Förstner, 1984; Varol and Sen., 2012). Metals stored in floodplains and channel sediments have the potential to serve as future sources of pollution. The degree to which they become a source of pollution depends on factors such as the proximity of contaminated sediments to the active channel (lateral and vertical) and the intensity of geomorphic activity along the river (Bradley and Cox, 1986; Martin, 2000; Marcus, 1989; Varol and Sen., 2012). When channel banks or low elevation surfaces have high metal concentrations, or the river is geomorphically active, the storage of metalliferous sediments may be brief, posing a threat of metal pollution downstream (Hudson-Edwards et al., 1999; Marcus, 1989; Martin, 2004, Varol and Sen., 2012). In contrast, if metal concentrations are spread more widely and evenly across the floodplain, are present on higher topographic positions, or the river is geomorphically quiet, metalliferous sediments may remained stored for decades or centuries (Coulthard and Macklin, 2003; Hudson-Edwards et al., 1999; Martin, 2000).
Since multivariate statistical methods become very helpful to assess for interrelationships among the measured data, they have been widely used in geochemical and ecochemical studies (Li and Zhang, 2010; Sakan et al., 2009; Soares et al., 1999; Varol and Sen., 2012).

Furthermore statistical methods such as Cluster analysis (CA) can explore the relationship between constituents in surface waters to identify the geochemical behavior of heavy metals. Cluster analysis (CA) and correlation analysis have been used to identify the sources and typology of pollution, as well as to indicate associations between samples and/or variables (Casado-Martinez et al., 2009; Chung et al., 2011; Soares et al., 1999; Zhou et al., 2008). The spatial evaluation and visualization of pollutants is important to better understand how the sources of risk, the receptors and the exposure pathways are distributed in the space (Bien et al., 2004; Delgado et al 2010). This is the reason of the recent interest of using GIS techniques in studies of distribution of environmental pollution (i.e. Zhou et al., 2007).

In this study, we incorporated spatial interpolation in GIS to assess the spatial distributions of 14 heavy metals (Zn, Zr, Mn, Pb, Cu, Cd, As, Co, Fe, Cr, Al, Mo, U) in surface water samples. First, a GIS-based cluster analysis (CA) identified similar groups of monitoring sites on a global scale; last, the local spatial distributions of heavy metals in surface waters were determined based on significant variables was performed to assess the spatial influences of natural and anthropogenic impacts in different areas.(Zhou et al., 2007)

2. SAMPLING SITES

Surface water samples were collected from 31 sites along the Sardabrud River (Fig. 1). The sampling sites were chosen to entry from the drains into the Sardabrud River. Thus, heavy metal concentrations in water at the sites upstream up to downstream of Sardabrud River were compared. Considering the sample accessibility and representative ness, 31 sampling points were selected in the Sardabrud River, covering the 28 km in downstream direction (Fig. 1). These locations were affected by different natural and anthropogenic sources of pollution (Table 1). The samples were collected at spring of 2012.

3. SAMPLE COLLECTION

The water samples were collected in polyethylene bottles from 1⁄4, 1⁄2, 3⁄4 width across the river at each of the 31 sites for variation of metal concentration. Temperature, pH, and conductivity were determined in the field. The 'total metal' water samples were collected in plastic bottles previously soaked and washed with 10% nitric acid and double distilled water. The water samples were acidified in the field with concentrated HNO3 (5 ml per litre of water, to reduce the pH of the sample below 2.0 (Duncan and Harrison, 1981; singh et al 2005).

4. CHEMICAL ANALYSIS

A 200 mL aliquot of each water sample was filtered through Whatman No 42 filter paper for analysis of heavy metals. The elements' concentrations were analyzed by Acme Analytical Laboratories Ltd (Vancouver, Canada), accredited under ISO 9002, a number of trace elements evidencing possible environmental impact, among which As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb,y Zn are outstanding, were determined by optical (ICP-AES) and mass (ICP-MS) spectrometry. Aqua regia extractable metal and metalloids (Ag, As, Au, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Rb, Sc, Sr, Zn and Zr) were also determined by digestion of 0.5 g of sample with aqua regia extracts (3:1 HCl-HNO3) at 95 ºC for 1 h, follow by ICP-AES analysis. This extraction is commonly used to determine the

pseudototal metal content in environmental samples, which is considered as a measure of the maximum potential hazard that could occur in long term or in extreme environmental regimes (McGrath and Cunliffe, 198.

5. QUALITY CONTROL

As it can be seen in Table 1 the measured concentrations of all the 31 analytes overlap or are much closer to the relative certified values for this standard. The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of known additions and analysis of replicates. All analyses were carried out in triplicate, and the results were expressed as the mean. In addition, to check the quality of the analysis, a total of 2 replicates were analyzed. From them the Relative Percentage Difference (% RPD) has been calculated as shown in Eq. (1). The results for % RPD (Table 1) are reasonably good and the expected value close to zero. Most values are below 1.5%, such as Al = 0%, AS = 0.001%, Co = 0%, Cr = 0%, Cu = 0%, Cd= 0%, Mn =0.001 %, Mo = 0.004%, Ni= 0%, Pb = 0%, U= 0%, Zn = 0.005%, Fe= -0.005%.

However these values are never higher than 5% RPD.

% RPD=(S-D)/[(S+D)/2] ×100 (Eq: 1) (Delgado et al., 2010)

Where: S=determinate value of the samples, D = value of the duplicates.

6. RESULT AND DISCUSSION

6.1. STATISTICAL ANALYSIS

Cluster analysis (CA) was used to group the similar sampling sites (spatial variability) and to identify specific areas of contamination (Casado-Martinez et al., 2009; Chung et al., 2011; Rath et al., 2009; Simeonov et al., 2000; Sundaray et al., 2011; Yang et al., 2009). Hierarchical agglomerative CA was performed on the normalised data set using Ward's method with Euclidean distances as a measure of similarity. Relationships among the considered variables were tested using correlation analysis with statistical significance, Cluster analysis (CA),is an unsupervised pattern recognition technique, reveals the intrinsic structure of a data set without making a priori assumptions about the data to classify the objects of the system into categories or clusters based on their nearness or similarity (Varol and Şen, 2009).

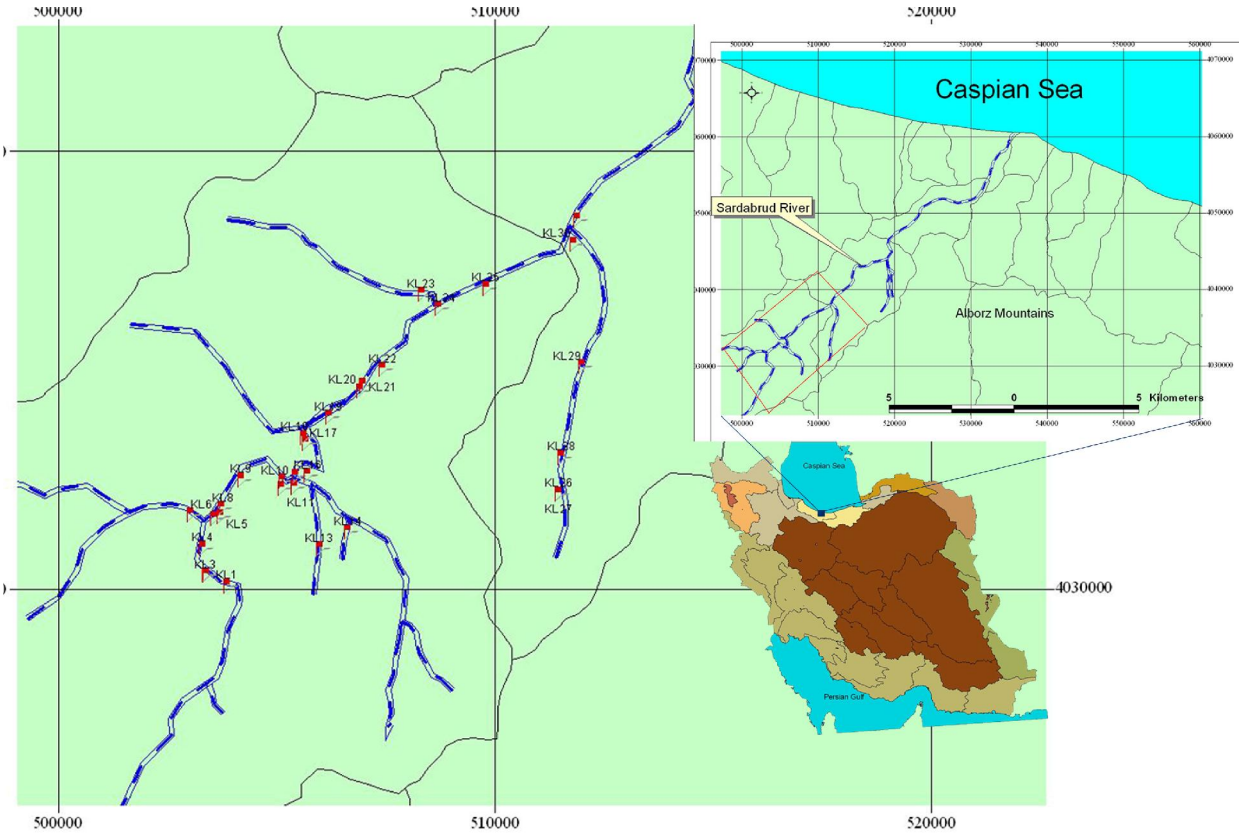

Figure 1. Map showing sampling sites on the Sardabrud River

Table 1 Heavy metal concentration in 31 sites of water samples of upstream of Sardabrud River, North of Iran. (Concentration unit is in µg/l)

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Pb	U	Zn	Σ (heavy metals)
KL1	125	0.9	0.05	0.12	1.1	1.4	128	12.96	1.9	1.4	0.33	4.8	278
KL2	78	0.8	0.05	0.10	0.9	0.7	100	13.03	1.8	1.3	0.33	4.5	202
KL3	50	0.5	0.05	0.05	0.5	1.0	24	2.38	2.5	1.0	0.65	3.4	86
KL4	109	0.7	0.05	0.14	0.9	0.9	143	15.09	1.9	1.0	0.35	3.9	277
KL5	75	0.8	0.05	0.07	0.8	0.9	69	8.22	2.2	1.3	0.41	3.7	162
KL6	1269	2.9	0.07	1.66	4.8	3.8	1782	78.89	2.0	6.1	2.08	13.8	3167
KL7	1370	2.8	0.07	1.74	5.1	3.6	1911	81.27	2.1	6.3	2.02	13.2	3399
KL8	549	1.4	0.05	0.76	2.7	1.6	764	35.82	1.9	4.4	0.90	8.0	1371
KL9	635	1.5	0.05	0.79	2.6	2.3	934	42.73	2.0	4.1	1.00	7.9	1634
KL10	574	1.4	0.05	0.67	2.4	1.8	793	35.59	2.1	3.0	0.97	8.0	1423
KL11	203	0.5	0.05	0.30	1.0	1.6	272	12.53	5.7	0.9	0.62	4.1	502
KL12	581	1.4	0.05	0.73	2.9	2.9	822	37.86	2.2	4.7	1.03	8.2	1465
KL13	562	0.5	0.05	0.81	1.5	1.5	853	26.37	1.8	1.4	1.04	6.3	1456
KL14	463	0.5	0.05	0.58	1.6	1.6	612	20.39	1.8	2.3	0.78	5.0	1110
KL15	4030	2.8	0.11	6.09	9.5	8.2	6168	187.51	0.9	8.9	2.24	29.2	10453
KL16	1104	2.0	0.06	1.43	4.3	3.6	1563	64.69	1.7	5.3	1.01	11.9	2763
KL17	966	1.8	0.05	1.08	3.5	2.5	1311	51.06	1.9	3.6	1.02	9.3	2353
KL18	293	0.7	0.05	0.39	1.3	3.5	282	26.36	0.6	3.1	0.60	5.5	617
KL19	1456	2.3	0.05	1.68	5.4	3.9	2046	76.71	1.9	5.9	1.11	13.0	3614
KL20	29	0.9	0.05	0.06	1.2	5.1	10	7.00	3.1	1.9	1.99	5.1	65
KL21	883	1.6	0.05	1.00	3.4	2.2	1172	44.97	2.0	3.0	1.03	7.9	2122
KL22	999	1.7	0.05	1.16	3.7	2.6	1342	51.41	2.1	3.5	1.03	10.0	2418
KL23	1068	1.8	0.06	1.08	3.5	5.4	1266	53.47	2.1	4.4	1.07	15.5	2422
KL24	681	0.8	0.05	0.62	2.3	2.2	545	41.94	0.5	25.4	0.92	12.6	1313
KL25	1174	1.7	0.05	1.16	4.1	3.6	1434	56.40	2.2	4.8	1.16	11.3	2694
KL26	24	0.8	0.05	0.02	0.8	0.7	10	1.11	7.6	0.2	1.36	1.6	48
KL27	109	0.5	0.05	0.13	1.1	1.3	91	6.41	6.4	1.1	0.95	2.8	221
KL28	187	0.5	0.05	0.21	1.0	1.6	232	13.29	3.5	1.7	0.19	4.0	445
KL29	126	0.5	0.05	0.13	2.3	2.4	71	8.17	5.0	8.5	0.90	7.7	233
KL30	315	0.6	0.05	0.32	1.6	1.7	319	16.38	4.0	2.0	0.93	4.9	666
KL31	957	1.3	0.05	1.18	3.8	3.8	1493	54.89	2.5	5.0	1.14	14.3	2538

Table 2 Maximum permitted heavy metal concentrations (mg/L) for drinking water quality and protection of freshwater aquatic life.

Water quality guidelines	As	Cd	Cr	Cu	Fe	Mn	M0	Pb	Zn
Drinking water quality									
EC (1998)	0.01	0.005	0.05	2	0.2	0.05	-	0.01	0.1
WHO (2004)	0.01	0.003	0.05	2	-	0.4	0.07	0.01	-
USEPA (2009)	0.01	0.005	0.1	1.3	0.3	0.05	-	0.015	5
Acute values for protection of freshwater aquatic life									
USEPA (2006)	0.34	0.002	-	0.013	1	-	-	-	0.12

Hierarchical clustering is the most common approach, where clusters are formed sequentially by starting with the most similar pair of objects and forming higher clusters in a step-by-step fashion. The Euclidean distance usually gives similarities between two samples, and a 'distance' can be represented by the 'difference' between analytical values from both of the samples (Otto, 1998). In this study, hierarchical agglomerative CA was performed on the normalized data set using Ward's method with Euclidean distances as a measure of similarity (Ward, 1963). This method uses the analysis of variance approach to evaluate the distances between clusters while attempting to minimize the sum of squares of any two clusters that can be formed at each step. The linkage distance is reported as Dlink/Dmax, which represents the quotient between the linkage distances multiplied by 100, as a way to standardise the linkage distance represented on the y-axis (Shrestha and Kazama, 2007; Simeonov et al., 2000; Varol and Şen, 2009). Multiplied by 100, as a way to standardise the linkage distance represented on the y-axis (Shrestha and Kazama, 2007; Simeonov et al., 2000; Varol and Şen, 2009). For a particular case divided by the maximal distance, multiplied by 100, as a way to standardise the linkage distance represented on the y-axis (Shrestha and Kazama, 2007; Simeonov et al., 2000; Varol and Şen, 2009).

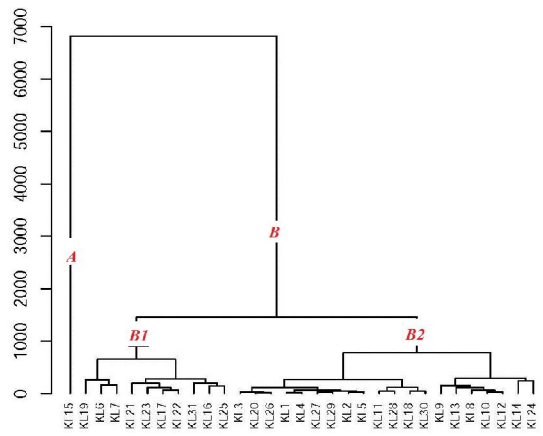

Figure 2. Dendrogram showing clustering of Water sampling sites on the Sardabrud River.

Spatial CA rendered a dendrogram (Fig. 2) where all 31 sampling sites on the river were grouped into two statistically significant clusters. Cluster A consisted of one site (site-15), and cluster B consisted of 30 sites. The cluster classifications varied with significance level because the sites in these clusters had similar characteristic features and natural background source types. Cluster A corresponded to high contaminated sample and cluster B corresponded to lower than Cluster A contaminated samples, in this cluster some samples corresponded with B1 cluster have higher than concentration of heavy metals against B2 cluster. Similarly, CA was performed to identify the relationships among the analysed parameters and their possible sources (Casado-Martinez et al., 2009; Chung et al., 2011; Goorzadi et al., 2009; Li et al., 2009). Cluster A includes Al, Cu, Cd, Cr, Fe, Mn, U and Zn, were identified as contaminants derived from lithogenic sources, although they are greatly impacted by recycling of deposed sediments into surface water.

6.2. HEAVY METALS IN WATER

The results of heavy metal concentrations in surface waters of the Sardabrud River are shown in Tables 1, of this study on the upstream to midstream reaches of the river. In our study, we found that the river water heavy metal concentrations such as (Al,As,Co,Cd,Cr,Cu,Mn,U,Zn,Fe) at site15 situated in upstream higher than concentrations measured at other sites. At site -15 two major drains of Sardabrud River coupled together and increase water load of this river and caused recycling of sediments in fluvial trust into the river. After site-15, a significant decrease was observed in metal concentrations toward downstream direction by dilution and sedimentation processes of fine grain size of sediments into the river bed, channel bank and fluvial trusts. So, Pb and Mo concentrations at sites 24, 25 and 26 were higher than concentrations measured at other sites, these sites were in Ojabit valley, On this valley the Guret Pb mine and granitoied viens derivation of Alam kuh and Akapol granitoied plutons are present, so, Pb and Mo discharge into the Ojabit valley, thus, these sites have high concentration of those metals. Total metal concentrations followed the order of site-15> site-19>site-7 site-6> site-16>site-25 >site-31>site-23>site-22 to site-5>site-2>site-3. As shown in Table 1, the dissolved heavy metal concentrations at the 1-5 and 9-14 sites situated upstream and 16-23 and 26-30sites toward downstream of the Sardabrud river were very low in comparative with 6,7,15,24,25,26 and 31 sites, indicating that the major sources of the contamination were natural and related to quaternary sediments deposit into the channel banks, Guret Pb-Zn mine and granitoied viens derivation of Alam kuh and Akapol granitoied plutons. Therefore, we concluded that the contamination of heavy metals in the river could be attributed to the natural pollutant discharges from the lithogenic and recycling of sediments into the surface water by exchange geomorphologic structure and lithology around Sardabrud basin. This can be supported by the fact that the concentrations of heavy metals were the highest at some sites such as 6,7 and15, when increase slope of basin or coupled the main drainages, the surface water can recycling the sediments bearing heavy metals and dissolution those metals into the surface water and / or the concentrations of heavy metals closest to lithogenic process, such as 24,25 and 26 sites. Metal concentrations were compared with water quality guidelines (or standards) for drinking water (EC, 1998; USEPA, 2009; WHO, 2004) and the protection of freshwater aquatic life (USEPA, 2006) (Table 2). The concentrations of As, Cd, Cr, Fe, Mn, Mo, u, Pb and Zn at all sites were lower than to the maximum permitted concentration for drinking water quality guidelines (EC, 1998; USEPA, 2009; WHO, 2004).

Cu concentration in surface water against to the maximum permitted concentration for drinking water quality guidelines at most sites such as 1,2,3,4,5,8,10,11,13,14,27,28 and 30 was below and in other sites was higher than to the maximum permitted concentration for drinking water quality guidelines (EC, 1998; USEPA, 2009; WHO, 2004).

Concentrations of the heavy metals (As, Cd, Cr, Fe, Mn, Pb and Zn) in surface waters of the Sardabrud River were much lower than and comparable to the findings from other rivers. Dundar and Altundag (2007), Karageorgis et al. (2003),Frankowski et al. (2009), Salati and Moore (2010), Levkov and Krstic (2002), Ahmad et al.

(2010), Dan'azumi and Bichi (2010), Gutierrez et al. (2008), Adamiec and Helios-Rybicka (2002), Aguasanta et al. (2005), Sinha and Kumar (2006), Kikuchi et al. (2009), Mohiuddin et al. (2010), Budambula and Mwachiro (2006)

7. CONCLUSION

The purpose of this study was to assess levels of heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, U, Mo, Pb and Zn) in surface water samples from the upper Sardabrud River. The results indicated that concentrations of heavy metals were Low in water samples, and the highest concentrations were recorded at sites 15, 6, 7, 25, 26 and 27 due to dissolution of heavy metals in surface waters from natural sources and recycling deposed sediments in channel banks.

Concentrations of the heavy metals in surface waters of the Sardabrud River were much lower than and comparable to the findings from other rivers. All metal concentrations in water samples, except Cu, were lower than the maximum permitted concentration for protection of aquatic life.

Cluster analysis (CA) was used in this study, so, Cluster analysis suggests all of heavy metals in most of sites excepted are similar and derived from same natural sources.

This study indicated the surface waters polluted very weak with heavy metals by natural sources, and the pollution was weak at all of sites.

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