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Assessment of Heavy Metals Pollution in Water and Sediments of Djendjen River, North Eastern Algeria

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ABSTRACT: Water and sediment samples have been collected from five different stations, located along Djendjen River between February and June, 2016 so that the concentrations of Cd, Ni, Zn, and Cu could be determined. The extent of the sediment pollution has been assessed, using the multiple pollution indices, namely Contamination Factor (CF), Pollution Load Index (PLI), and the geoaccumulation index (Igeo). The distribution of trace elements in water and sediment follows Ni>Zn>Cd>Cu and Zn>Ni>Cu>Cd, respectively. The water sample analysis from Djendjen River shows that the total concentrations of Cu, Ni, Cd, and Zn have been lower according to the references. In comparison, sediment mean metal concentrations with several environmental contamination parameters, like probable effect level (PEC) and background levels, indicates that the concentrations of all investigated elements are lesser than PEC, except for Ni, but higher than the background levels. The Igeo values reveal that Cd has been the most accumulated compared to the other metals. Contamination Factor (CF) confirms that the sediment samples have been moderate in terms of all studied metals contamination. The Pollution Load Index (PLI) values have been above one (>1), indicating an advanced decline of the sediment quality.

Keywords: heavy metals, Djendjen River, sediment, water, Algeria

INTRODUCTION

Various kinds of contaminations have been affecting aquatic ecosystems around the world in the recent few years (Nazeer et al., 2014) with trace elements being reported as one of the major pollutants to seriously deteriorate the ecosystems (Sakakibara et al., 2011; Ali et al., 2013; Nasrabadi et al., 2010). They can be either from natural or human activities, though anthropogenic sources of metals exceed the natural ones, as a matter of fact (Karbassi et al., 2014). Elevated concentrations of Cd, Cu, Pb, and Fe can proceed as ecological pollutants in aquatic and terrestrial environments (Balsberg-Pahlsson, 1989; Guilizzoni, 1991; Islam et al., 2016). Excessive metal concentrations in surface water can pose a health problem to both humans and the ecosystem, thus it is necessary to restore and conserve surface water resources for the sake of their inevitable role in sustaining both aquatic and terrestrial life forms (Nazeer et al., 2014).

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Sediments are the main place for heavy metals' accumulation; the heavy metals, pulled into the water body of rivers, lakes, and bays, eventually accumulate in the sediments (Scheibye et al., 2014; Esmaeilzadeh et al., 2016). However, assessment of sediments quality is often considered most crucial in determining anthropogenic input of trace metals in aquatic ecosystems due to their long residence time, being hence capable of reflecting history of pollution in aquatic ecosystems (Tuna et al., 2007; Karbassi et al., 2008). Usually, concentrations of heavy metals in aquatic ecosystem are determined by measuring their concentration in water and sediments (Camusso et al., 1995) that generally exist at lower levels in water, attaining a considerable concentration in the sediments (Namminga & Wilhm, 1976). The geoaccumulation index (Igeo), Contamination Factor (CF), and Pollution Load Index (PLI) are among different statistical indices that can be used to determine the source and magnitude of metal pollution. These pollution index methods have been widely utilized in river and marine sediments (Müller, 1969 ; Bryan and Langston, 1992 ; Buccolieri et al., 2006 ; Vaezi et al., 2016). Djendjen River, studied in this study, is a major riverine system in the alluvial plain of Djendjen, north east of Algeria, continuously affected by direct human activities (urban effluents and fertilizers). The deteriorating quality of its surface water has become a major concern for managers and users of this precious resource.

The objectives of this study are to (i) assess the pollution status of Djendjen River by estimating the levels of heavy metals in water and sediment; (ii) explore the degree of contamination and pollution impacts by means of pollution indicators, including Contamination Factor (CF), Pollution Load Index (PLI), and geo-accumulation index (Igeo); and (iii) establish baseline data on the present status of the river that can be used by relevant authorities as well as other researchers.

MATERIALS AND METHODS

Djendjen River basin is located north-east of Algeria (Fig. 1) between 5°30’ and 5°58’E longitude and 36°22’ and 36°48’ N latitude. Characterized by humid Mediterranean climate. the average annual air temperature and precipitation is 18.4°C and 970.6 mm, respectively, with the rainfall season between November and March. The total study area is 525 km^2. Agricultural wastes, fertilizers, and raw sewage effluents constitute the predominant anthropogenic sources in the area.

The study used three indices of geo-accumulation index (Igeo), Contamination Factor (CF), and Pollution load index (PLI) in order to gain information about the sources of metal pollutants and to assess the metal pollution status.

According to Müller (1981), geoaccumulation index (Igeo) for metals was determined using the following equation:

$$I_{geo} = Log_2 \frac{C_n}{1.5 \times B_n} \quad (1)$$

where C_n is the measured concentration of the examined metal (n) in the sediment and B_n, the geochemical background concentration of the metal (n). The number 1.5 is the background matrix correction factor due to lithogenic effects. The crustal abundance data of Turekian & Wedepohl (1961) were used as background data. The geoaccumulation index consisted of seven grades or classes (Table 1).

Contamination Factor (CF) of a single trace element was calculated, as suggested by Min et al. (2013) and Kerolli-Mustafa et al. (2015). It was used to evaluate the contamination of the single heavy metal in the present samples.

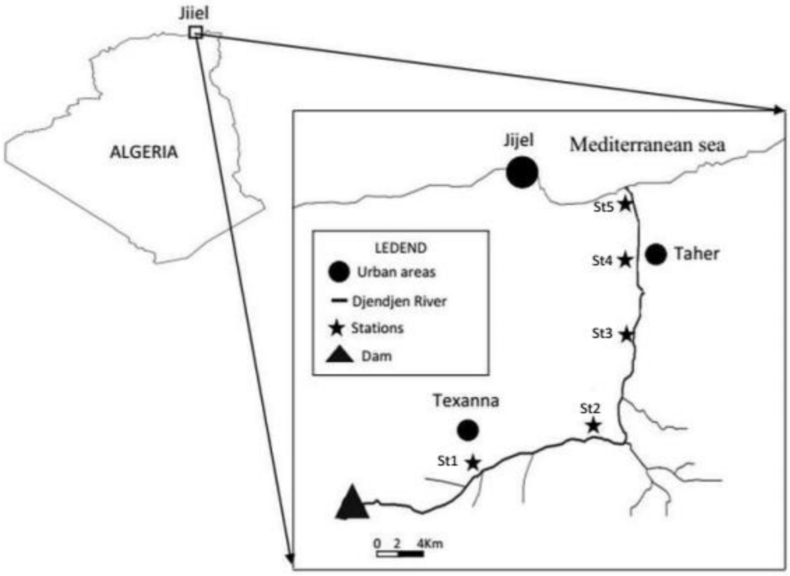

Fig.1. Location of different sampling sites of Djendjen River.

Table 1. Descriptive classes for Igeo values (Müller, 1981)

Sediment quality	I_{geo}	I_{geo} Class
Unpolluted	$I_{geo}<0$	0
Unpolluted to moderate polluted	$0< I_{geo}\leq 1$	1
Moderately polluted	$1< I_{geo}\leq 2$	2
Moderately to heavily polluted	$2< I_{geo}\leq 3$	3
Heavily polluted	$3< I_{geo}\leq 4$	4
Heavily to extremely polluted	$4< I_{geo}\leq 5$	5
Extremely polluted	$I_{geo}>5$	6

The formula to calculate Contamination Factor (CF) used to evaluate the pollution of the single heavy metal in our sediment samples is:

$$CF = \frac{C^{i}_{sample}}{C^{i}_{reference}} \quad (2)$$

where CF is the Contamination Factor for a heavy metal; C^{i}_{sample}, the measured value of the heavy metal in the sediment; and $C^{i}_{reference}$, the parameter for calculation.

Table 2. Sediments contamination level based on Contamination Factor (CF) value (Hakanson, 1980)

Contamination Factor level	CF value
Low contamination	CF<1
Moderate contamination	1< CF≤3
considerable contamination	3< CF≤6
Very high contamination	CF >6

The contamination levels were classified, based on their intensities, on a scale of 1 to 6 as shown in Table 2.

PLI was originally used to determine the pollution load of the sediments. It can also give a simple and relative means for evaluation of the degree of metal pollution (Tomlinson et al., 1980). This parameter is expressed as:

$$PLI = \sqrt[n]{Cf_1 \times Cf_2 \times Cf_3 \times \ldots Cf_n} \quad (3)$$

where n is the number of metals and Cf, the contamination factor. The pollution load index can be classified as no pollution (PLI < 1), moderate pollution (1 < PLI < 2), heavy pollution (2 < PLI < 3), and extremely heavy pollution (3 < PLI) (Tomlinson et al., 1980).

Samples of sediment and water were collected from five sites, namely St 01 to

St 05, located along Djendjen River and used by the local people for domestic and agricultural purposes. All samples were collected from February to June 2016 in three replicates at each sampling site. Water samples were collected from a depth of 30 cm, with the sampling bottles pre-cleaned with nitric acid HNO_3(v/v), stored in ice boxes conserved at 4 °C, and were immediately filtered through 0.45 mm membrane filters. For trace element analysis, the filtrates were immediately acidified to pH = 3 with concentrated nitric acid, HNO_3, then to be brought to the laboratory and stored in refrigerator (Jain et al., 2005).

In order to avoid metal contamination, sediment samples were taken from each location, using plastic sampling spatula and plastic gloves. After the collection, each sediment was placed in polyethylene bags and immediately refrigerated. Sediment samples were oven dried until reaching a constant dry weight at 60°C, and sieved with a 63-µm stainless steel sieve. Generally, fine fractions contain more trace elements than the coarser ones. This enrichment is mainly due to the high specific surface area of the smaller particles (Szefer et al., 1996). For trace elements analysis, 0.1 g of dry sediment was digested, using 10 ml HCl-HNO_3-HF (Bai et al., 2011). Finally, the solution was diluted to a final volume of 25 ml with deionized distilled water.

The elemental state of trace elements was analysed by a flame atomic absorption spectrometer (AAS, PerkinElmer model 2380, USA) as prescribed in Standard Methods (APHA et al., 2005). To assess the contamination levels of heavy metals, the mean values were calculated for water and sediments. Data analysis was carried out by means of the packaged Statistica software program version 8.0.

RESULTS AND DISCUSSION

Table 3 gives the concentration levels of priority toxic pollutants including: Cd, Cu, Ni, and Zn (listed in US EPA, 1999, for water quality criteria) in the water body of Djendjen River, comparing these heavy metals' concentrations with water quality standards, currently effective in Algeria (US EPA, 1999 and background concentrations world average), as well as the results, obtained from the literature.

As a whole, the observed concentration values were greater than the ones in Djendjen waters. The average concentrations of Cd, Cu, Ni and Zn, were lower than those revealed by US EPA water quality criteria (Table 3). Generally, average concentrations of these metals decreased in the following order: Ni> Zn > Cd> Cu. When compared with other rivers in the world, results from the present study demonstrated that Djendjen was an unpolluted river as world average background concentrations (Turekian & Wedepohl (1961) are higher than mean metal concentrations in Djendjen River water as well as other regions (Hu et al., 2012; Enguix-González et al., 2000 ; Bhuiyan et al., 2015).

Table 4 shows metal concentrations in the sediment. Generally, metal concentrations had the following order: Zn>Ni>Cu>Cd. To assess the impacts of trace elements in sediments, the metal levels in Djendjen River were compared with metal background concentrations along with other rivers' sediments and the probable effect concentrations for sediments (PEC), wherein the data, obtained by Turekian & Wedepohl (1961), formed the background data. The probable effect for sediment concentrations were developed by MacDonald et al. (2000). The results, presented in Table 4, showed that the concentrations of all studied elements in the water were lower than the element concentrations in the sediment. Results of many investigations show an increasing trend of the metals levels in sediment, compared with water (Samecka-Cymerman & Kempers, 2001; Brankovic et al., 2010; Demirezen & Aksoy, 2006). However, average sediment metal levels from Denjden River were higher than the background concentrations, but not exceeded the PEC, except for Ni, indicating low to moderate degrees of pollution. In addition, metal concentrations in the sediments of the study area were lower than those, reported by Varol & Şen (2012) and Mendez (2005). However, in contrast to the current investigation, Ahmad et al. (2010), Bai et al. (2001), and Hongyi et al. (2009) reported lesser values.

Table 3. Concentrations of heavy metals (µg/L) in surface water from Djendjen River, compared with reference values

	Cd	Cu	Ni	Zn
Water (µg/L)	0.24±0.008	2.3±0.004	3.63±0.02	17.9±0.01
[a]Water quality criteria				
CMC	2	13	470	120
CCC	0.25	9	52	120
[b]Background world average	0.3	45	68	95
[c]Honghu Lake (China)	1.71	1.93	1.20	2.13
[d]Guadaira River (Spain)	0.6	10	07	40
[e]Buriganga River(Bangladesh)	590	239	150	332

[a]US EPA (1999)
[b]Turekian and Wedepohl (1961)
[c]Hu et al. (2012)
[d]Enguix-González et al. (2000)
[e]Bhuiyan et al.(2015)

Table 4. Mean concentrations of trace element (µg/g) in sediment, compared to background world average and sediment quality guidelines (SQGs)

	Cd	Cu	Ni	Zn
Sediment (µg/gd)	1.101±0.07	121.56±4.50	140.68±2.52	196.51±4.73
[a]Background world average	0.3	45	68	95
[b] SQGs				
PEC	4.98	149	36	459
[c]Bangshi River (Bangladesh)	0.61	31.01	25.67	117.5
[d]Yilong Lake (China)	0.76	31.40	1.20	2.13
[e]Pearl River (China)	1.72	348	-	391
[f]Tigris River (Turkey)	7.9	860	-	1061
[g]Rimac River(Peru)	31	796	-	8076

[a]Turekian and Wedepohl (1961); [b]Sediment quality guideline (2000); [c]Varol and Şen (2012); [d]Mendez (2005); [e]Ahmad et al. (2010); [f]Bai et al. (2011); [g]Hongyi et al. (2009)

Table 5 offers the calculated Igeo of the metals in the sediments as well as their corresponding contamination intensity. On the basis of the mean values of Igeo, sediments were enriched for metals in the following order: Cd> Cu> Ni≈ Zn.

The Igeo values for Cd, calculated in the sediments, were constantly above 1. Based on the classification of Igeo, Djendjen sediments were in total moderately polluted. Otherwise, the calculated Igeo values for Ni, Zn, and Cu were constantly below 1, ranging from 0.43 to 0.49 for Ni, 0.42 to 0.52 for Zn, and 0.82 to 0.89 for Cu. Based on Igeo classification, the majority of the sediment samples were unpolluted to moderate polluted with respect to these elements.

Table 5. Geoaccumulation indexes (Igeo), Contamination Factors (CF), and Pollution Load Indices (PLI) of the studied metals in sediments of the studied area

Sites	I_{geo}				PLI	CF			
	Cd	Ni	Zn	Cu		Cd	Ni	Zn	Cu
S1	1.15	0.43	0.42	0.82	2.44	3.35	2.02	2.01	2.62
S2	1.29	0.44	0.44	0.84	2.52	3.68	2.04	2.03	2.68
S3	1.35	0.47	0.47	0.85	2.58	3.83	2.08	2.06	2.70
S4	1.30	0.47	0.47	0.86	2.56	3.70	2.08	2.08	2.71
S5	1.33	0.49	0.52	0.89	2.63	3.78	2.12	2.14	2.78
Total mean	**1.28**	**0.46**	**0.46**	**0.85**	**2.73**	**3.67**	**2.07**	**2.06**	**2.70**

Both CF and PLI are widely used to evaluate the degree of heavy metal pollution in the sediments (Bhuiyan et al., 2010). Table 5 presents CF values for heavy metals, recorded at different sampling locations. The mean CF values for metals in the studied area appeared in the following sequence Cd> Cu> Ni ≈ Cu. Results show that CF values for all metals were above 1 (CF>1), probably due to agricultural and domestic use of water and discharges to the river without any pre-treatment.

The values of PLI were high in all studied samples, varying between 2.44 and 2.63, indicating heavy pollution, with regards to the sum of the studied metals (Table 5). Sekabira et al. (2010) reported that PLI> 1 indicated anthropogenic inputs.

CONCLUSION

Studying the distribution of heavy metals in surface water and the sediment from the Djendjen River suggests that the river is currently facing heavy metal pollution. The present study revealed that the concentration of heavy metals in water and river sediments of Djendjen River is due to anthropogenic influences such as domestic sewage and agricultural activities. In surface water, abundance of heavy metals in water was ranked as the following: Ni> Zn > Cd> Cu. All heavy metals did not exceed background values, indicating that the water of Djendjen River was unpolluted with these heavy metals. As for the sediments, abundance of heavy metals was ranked as what follows: Zn>Ni>Cu>Cd. However, all metal concentrations exceeded background values. The contamination Factors (CFs) showed that contamination level of Cd was higher than other heavy metals in sediments, and the mean CF values for the metals in the studied area followed the sequence $CF_{Cd} > CF_{Cu} > CF_{Ni} \approx CF_{Zn}$. The mean Pollution Load Index (PLI), being within the range of 2.44-2.63, indicated heavy pollution of river sediments. The geo-accumulation index (Igeo) revealed that the pollution descended in accordance to the following order: Cd> Cu> Ni≈ Zn, with Cd causing the most pollution and Cu, Ni, and Zn, having nearly no pollution in river sediments. In order to protect the water and sediment from further contamination, it is recommended to design a monitoring network and reduce anthropogenic discharges.

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