

Assessment of Heavy Metal in Surface Sediments of Day River at Beni-Mellal Region, Morocco

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Abstract: The Day River receives domestic and industrial untreated wastewaters from Beni-Mellal city and surrounding villages during the last decades. The present study was to obtain a preliminary assessment about the level and distribution of six heavy metals (Cd, Cr, Cu, Pb, Zn and Fe) in its surface sediment collected from 13 stations. The metal concentrations (in mg/kg) ranged: Cd, 0.6-6.27; Cr, 52.34-311.69; Cu, 32.69-740.75; Pb, 72.93-140.36; Zn, 49.84-149.19; and Fe, 15670-36010. Significant spatial variation in concentrations was observed for all metals. Correlation analyses showed that metal content of sediment was controlled by organic matter and Fe contents. Pollution status was evaluated using the enrichment factor, geo-accumulation index and pollution load index and sediment quality guidelines. Based on geoaccumulation index and enrichment factors, Day sediment was treated as unpolluted to moderately polluted with Zn, Fe, Cr and Cu and moderate to considerable with Pb and Cd. Pollution load index and sediment quality guidelines showed that the metal levels exceed local and regional background concentrations, indicating contamination is high enough to be of risk to human health and ecosystem.

Keywords: Contamination, heavy metals, quantitative indexes, sediment, wastewater

INTRODUCTION

Environmental pollution is a big problem in modern society. Out of the various kinds of pollution, the high contamination of aquatic systems with toxic heavy metals is of major concern since these elements are not biodegradable and their elevated uptake by crops may also affect food quality and safety. Heavy metals enter these aquatic systems mainly through natural inputs such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal (Çevik *et al.*, 2009). Heavy metals discharged into aquatic systems may be immobilized within the stream sediment by main processes such as adsorption, flocculation and co-precipitation. Therefore, sediments in aquatic environments serve as a pool that can retain metals or release metals to the water column by various processes of remobilization (Caccia *et al.*, 2003; Pekey 2006; Marchand *et al.*, 2006). Numerous studies have demonstrated that the concentrations of metals in sediments can be sensitive indicators of contaminants in aquatic systems (Bellucci *et al.*, 2002; Bloundi *et al.*, 2009; Suthar *et al.*, 2009; Sekabira *et al.*, 2010; Mhamdi *et al.*, 2010).

Most rivers in the world flowing through the populated areas are highly vulnerable to heavy metal pollution due to urbanization and industrialization.

Anthropogenic impacts geogenic processes deteriorate sediment and water quality. Therefore, studies on the determination of the degree of anthropogenic impact on river sediment have been especially relevant over the last decades (Priju and Narayana, 2007; Nabi *et al.*, 2007; Dixit and Tiwari, 2008; Venugopal *et al.*, 2009; Biati *et al.*, 2010; Jayaprakash *et al.*, 2010). Many approaches have been applied in order to assess the severity of sediment contamination and to understand the natural and anthropogenic inputs in the river system. The metal assessment indices namely enrichment factor, geo-accumulation index, pollution load index and sediment quality guidelines were often used to screen the potential for contaminants within sediment.

In Morocco, most domestic and industrial wastewaters from urban and rural areas are released into the environment without prior treatment. Rivers and streams receive directly about 30% of the total human-generated-pollution. Various studies have demonstrated that several estuaries and watercourses are contaminated by heavy metals from discharged human waste (Azzaoui *et al.*, 2002; Bellucci *et al.*, 2003; Koukal *et al.*, 2004; Maanan *et al.*, 2004; Ben Bouih *et al.*, 2005; Gonzalez *et al.*, 2007; Achab *et al.*, 2007; Amri *et al.*, 2007; Anajjar *et al.*, 2008; Zourarah *et al.*, 2008; Bloundi *et al.*, 2009; Mhamdi *et al.*, 2010; Naoura *et al.*, 2011).

The Day River originates at Beni-Mellal city, passes through the Tadla plain and several rural areas and flows into the main river Oum er Rbia. For more than 3 decades, the Day River receives all domestic and industrial wastewater without any treatment directly from Beni-Mellal city. Further, wastewaters from rural agglomerations and runoff from agricultural fields in the catchment area enter into this river. Because this river is often used for irrigating agricultural lands, concerns have risen about heavy metal contamination in this area and the potential impact on food systems and human health. While there is strong evidence of pollution of this ecosystem, no investigation has been previously conducted to characterize heavy metal pollution status in Day River. Therefore, the aim of this study is to investigate heavy metal (Cd, Cr, Cu, Pb, Zn and Fe) concentration and distribution in sediments from Day River and to assess the contamination status using various metal assessment indices and sediment quality guidelines.

MATERIALS AND METHODS

Study area: The Beni-Mellal city is located in the center of Morocco (32°22'N, 6°21'39"W), on the north-atlasic piedmont. It is bordered by the central High-Atlas to the south and the Tadla plain to the north. The geology of the Atlas of Beni-Mellal is mainly composed of triassic red clay with salt-bearing levels and basalt, liasic limestone and dolomite and cretaceous marl and yellow limestone beds. The Tadla plain characterized by irrigated land is a broad depression filled with quaternary deposits that are marl and limestone covered by red loams. The region of Beni-Mellal is one of the areas in Morocco where the labor is owing to abundant underground and surface water

intensive agricultural sector is largely developed. This resources as well as the favorable climate for most crops grown in Morocco. The climate is continental semi-arid with a rainy season lasting from November to March and a dry season from April to October. The irregular annual rainfalls vary between 170 and 540 mm with an average of 280 mm. The average annual temperature is 18°C with peak periods of 38 to 40°C in August and 3 to 4°C in January. The annual potential evaporation is about 1800 mm. The Day River takes source in the base of travertine promontory on which the old medina of the Beni-Mellal city is built. The Day River flows 45 km through the Beni Moussa irrigated area, until its confluence with the largest Oum Er-Rbia River. Since its karstic source has long been dry, all of the water flowing in the Day River originates from its tributaries such as Sabek, Ain el Gahzi, Handak and Kikou rivers. These tributaries have seasonal water regime more heavily influenced by snowmelt and flood events. The Day River is known to be under contamination menace due to its role in carrying off the domestic and industrial wastewater and runoff from agricultural land in its drainage basin. These wastewaters raw or mixed are often used for irrigation of cereals, vegetables, fruit and beet.

Sediment sampling and analysis: Sediment sampling was conducted during the period (May, 2010) when water was in base flow regime. A total of 11 surface sediments samples (0-10 cm) were collected from main sampling points covering the full length of the Day River and the areas expected to be polluted (Fig. 1). The surface sediments were chosen as this layer controls the exchange of metals between sediments and water (El Nemr *et al.*, 2006). The sampling positions

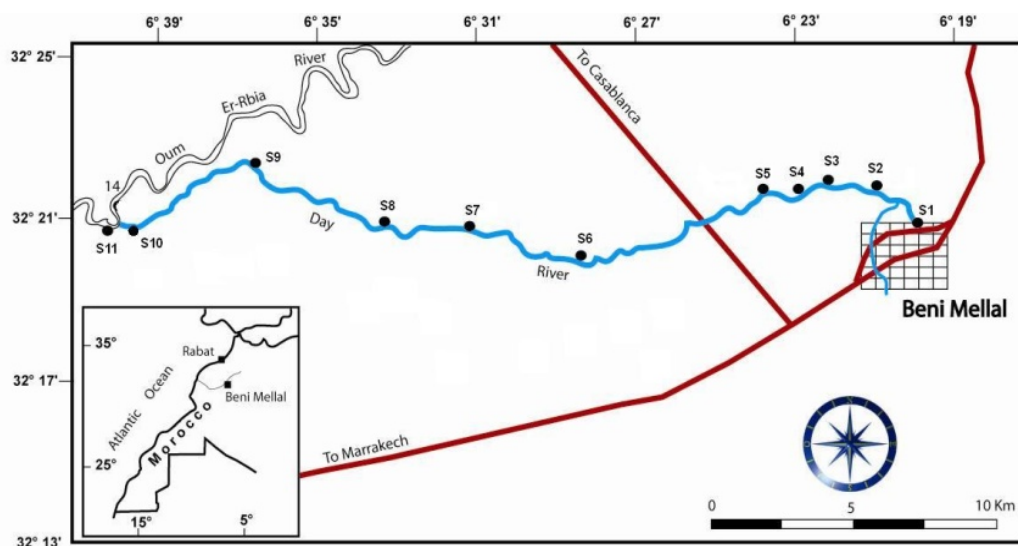


Fig. 1: Sampling locations of surface sediments in Day River

were recorded using GPS localization. Taken Samples were dried in the open air, crushed by hand in a porcelain mortar and sieved through a 2 mm screen. Air-dried <2 mm samples were stored in plastic bags for subsequent analysis. This fraction that concentrate iron oxide/hydroxide, organic matter, aluminum, clay minerals, will also have the largest capacity to bind particle reactive trace metal contaminants relative to coarser particles (>2 mm size). The <2 mm fraction was used for the evaluation of sediment physicochemical parameters namely pH, conductivity, organic matter and bicarbonates of calcium. Sediment's pH was measured in a suspension of 25 mL de-ionized water to 10 g of sediment after shaking for 2 h. Conductivity was evaluated from the suspension prepared by adding 50 mL de-ionized water to 10 g of sediment and shaken for 30 mn. Organic matter was determined by ignition at 550°C for 5 h in a muffle furnace. The percentage of loss on ignition was considered as Total Organic Matter (TOM). Carbonate content (CaCO₃) was analyzed by thoroughly ashing the oven-dried samples during 3 h at 930°C and comparing pre- and post-ashing weights. For heavy metal determination, tri-acid mixture (HNO₃-HF-HCl) was added to the beaker containing sediment sample and heated at 100-110°C until the solution became transparent (Allen *et al.*, 1986). The resulting solution was finally maintained to 50 mL using de-ionized water and stored at room temperature for further analysis of heavy metal. The samples were then analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) type ULTIMA2 at UATRS (Centre National pour la Recherche Scientifique et Techniques).

RESULTS AND DISCUSSION

Physicochemical analysis: Results of the physicochemical analyses are reported in Table 1. Sediment of the Day River exhibits a small fluctuation in pH values that range from 6.84 to 8.89 with an average at 8. The neutral to slightly alkaline pH,

Table 1: Physicochemical parameters of sediments from different stations

Stations	TOM (%)	CaCO ₃	pH	CE (μS/cm)
S1	13.51	25.03	6.84	1433
S2	8.96	14.05	7.72	789
S3	3.25	20.62	8.01	499
S4	7.05	13.21	7.80	575
S5	4.04	16.98	7.97	550
S6	6.70	10.96	7.96	416
S7	8.59	10.87	7.96	372
S8	8.60	10.90	8.89	284.5
S9	10.86	8.81	8.04	511
S10	5.48	11.86	8.29	396
S11	5.59	19.66	7.90	524
Minimum	3.25	8.81	6.84	284.5
Maximum	13.51	25.03	8.89	1433
Mean	7.51	14.81	7.94	577.23
S.D.	3.01	5.10	0.48	312.72

probably related to carbonate nature of the sediment and the organic matter accumulation in sediment, seems to be favorable for the immobilization of heavy metals (Chuan *et al.*, 1996; Thornton, 1996). Conductivity (EC) shows higher values in all samples (372-1433 μS/Cm) compared to Sabek background values (168.4 μS/cm).

This increase in conductivity is attributed to the high content of soluble salts in sediment (Mohammad and Mazahreh, 2003). TOM is measured as 3.25-13.51% with an average of 7.51%. The relatively high content of TOM is mainly related to the high organic matter flux to sediments due to direct discharge of domestic and industrial wastewaters. Overall, CaCO₃ content varies from 8.81 to 25.03% with an average of 14.8%. This relatively high carbonate content is mainly derived from the carbonate rocks exposed at the Atlas of Beni-Mellal and in the catchment area.

Heavy metals distribution: Concentrations of heavy metals (Cd, Cr, Cu, Pb, Zn and Fe) in Day River sediment are presented in Table 2 and Fig. 2. Metal concentrations are compared with values reported from other local and regional metal-contaminated rivers in order to further evaluate the likely contamination in Day River (Table 3). Pb concentrations varied from

Table 2: Heavy metal concentrations (mg/kg) in surface sediments

Stations	Cd	Cr	Cu	Pb	Zn	Fe
S1	6.27	311.69	740.75	135.29	145.48	36010
S1	0.74	97.10	68.79	118.49	131.65	23670
S3	0.66	52.73	39.62	72.93	62.67	17470
S4	0.74	87.97	46.48	96.01	86.04	24950
S5	0.80	67.83	39.05	84.83	70.07	21280
S6	0.78	94.12	42.83	115.78	101.29	28290
S7	0.77	101.44	38.55	121.10	96.61	28510
S8	0.82	81.24	39.12	131.28	80.29	32320
S9	0.87	97.08	52.61	140.36	149.19	33780
S10	0.83	81.48	54.38	108.04	128.32	26700
S11	0.70	52.34	32.69	75.02	49.84	15670
Minimum	0.67	52.34	32.69	72.93	49.84	15670
Maximum	6.27	311.69	740.75	140.36	149.19	36010
Mean	1.27	102.27	108.62	109.01	100.13	26241
S.D.	1.66	71.55	209.89	23.80	34.20	6483
Average conc. in Sabek river	0.36	36.01	22.21	16.93	47.08	25039

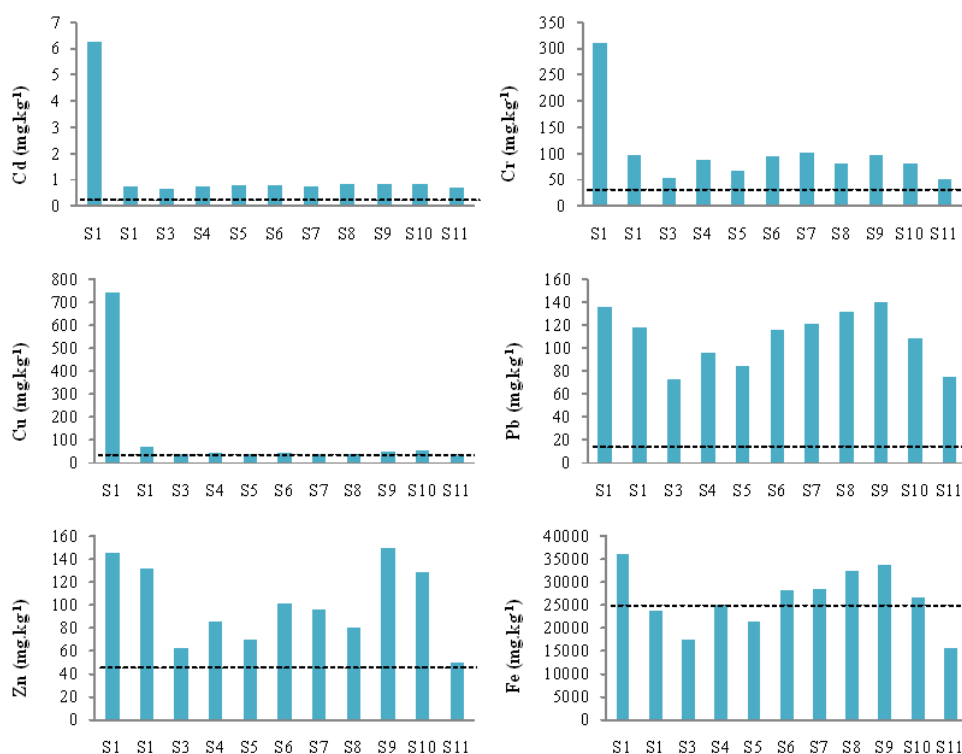


Fig. 2: Heavy metal concentrations in sediment from Day River. Horizontal dash line represents a reference level from Sabek River

Table 3: Heavy metal concentrations (mg/kg) in the sediment from different regions of the world

Rivers	Cd	Cr	Cu	Pb	Zn	Fe	Reference
This study	0.6-6.27	52.34-11.69	32.69-40.75	72.93-140.36	49.84-149.19	15670-36010	
Bas Oum Erbia	0.08	20.7	80	0.4	178	3730	Jadal <i>et al.</i> (2002)
Martil river	0.06-0.12	21.9-45.2	10.4-732	10.1-36.6	33.0-105	-	Bellucci <i>et al.</i> (2003)
Bouregreg river	0.02	39	21	17	61	1200	Tahiri <i>et al.</i> (2005)
Oum er Rbia estuary	2.2-3.2		30-40.4		135-211	9400-18600	Cheggour <i>et al.</i> (2005)
Sebou river	0.08-0.57	30-170	35-112	14-167	70-220		Amri <i>et al.</i> (2007)
Souss Estuary	0.28-0.38	65-89	29-59	18-46	62-106		Moukrim <i>et al.</i> (2008)
Nador Lagoon		9-139	4-466	11-297	4-1190		Bloundi <i>et al.</i> (2009)
Mghogha river	0.1-0.4	7.0-149.4	5.1-67.1	3.8-56.1	37.2-757.8	-	Rodriguez-Barroso <i>et al.</i> (2009)
Suani river	0.1-0.5	8.8-113.6	6.5-65.3	4.9-58.8	41.5-216.5	-	Rodriguez-Barroso <i>et al.</i> (2009)
Moulay Bousselham Lagoon	0.02-0.84	18.9-113	2-310.7	6.2-31.7	167-758.9	25600-59000	Mhamdi Alaoui <i>et al.</i> (2010)
Wadi Al-Arab dam (Jordan)	6.0-13		20-190		170-960	7780-15750	Ghrefat and Yusuf (2006)
Lianshan river (China)	1.25-19.4		29.0-106	59.3-164	114-797		Zheng <i>et al.</i> (2008)
Hindon river (India)	1.15-3.47	42.9-250.4	9.42-195.1	5.07-59.1	3.98-85.0	221.2-237.9	Suthar <i>et al.</i> (2009)
Han River (Korea)	0.05-1.02	25.2-13	7.64-14	14.2-96.6	34.3-55	14100-51200	Kim <i>et al.</i> (2011)

2003). High Pb levels observed in some stations (S1, S2, S4, S6, S8, S9 and S10) that very close to residential areas indicate that the source of this element could be the urban and rural discharges. Pb concentrations are significantly elevated than those observed in some moroccan contaminated rivers such as Bas Oum er Rbia (Jadal *et al.*, 2002), Martil River (Bellucci *et al.*, 2003), Bouregreg River (Tahiri *et al.*, 2005), Souss Estuary (Moukrim *et al.*, 2008), Mghogha and Suani Rivers (Rodríguez-Barroso 2009) (Table 3). When it is compared to regional rivers, Pb values were

higher than those reported for Hindon River (Suthar *et al.*, 2009) and Han River system (Kim *et al.*, 2011).

Zn concentrations ranged from 49.84 to 149.19 mg/kg with an average of 100.13 mg/kg. Higher Zn concentrations were close to values reported for Martil River, Oum er Rbia River, Sebou River and Souss estuary and slightly higher than that of Bouregreg River. Compared to regional studies, the Zn ranges were lower than those of Lianshan River (Zheng *et al.*, 2008) and Wadi Al-Arab Dam (Ghrefat and Yusuf, 2006).

Cd content fluctuated between 0.66 to 6.27 mg/kg with an average of 1.27 mg/kg which is higher than the natural levels (0.3-0.38 mg/kg) (Bervoets and Blust, 2003). High Cd values observed in all samples suggest an anthropogenic contribution to Cd mean concentrations. Nevertheless, these values are lower than Lianshan River and Wadi Al-Arab Dam.

Fe is the major element in all sediment samples, ranging from 15600 to 36000 mg/kg. Elevated Fe concentrations may be related in part to the Day iron-calcareous-rich sediments. However, contamination of anthropogenic origin cannot be excluded since the Fe content in Day River is higher than the values reported in the contaminated rivers such as Oum er Rbia, Sebou and Bouregreg (Table 3).

Cu concentrations varied from 32.69 to 740.75 mg/kg. The highest Cu content was detected in the upstream samples (S1 and S2) close to main wastewater discharge point suggesting an anthropogenic contribution to total Cu concentrations in Day sediment. The ranges of all other stations recorded were comparable to those reported for local and regional rivers mentioned in Table 3.

Cr exhibited a significant concentrations varying between 52.34 and 311.69 mg/kg with an average of 102.27 mg/kg. These concentrations exceeded those recorded for moroccan rivers and within those obtained for Hindon River (India). The high Cr values detected at stations S1 and S2 suggesting that the major source of Cr appears to be anthropogenic probably from a tannery factory that uses chromium and its compounds. Based on investigation of heavy metal concentrations, the impact of human activities on sediment quality in Day River is clearly demonstrated. Concentrations of heavy metals in all sediment samples were higher or comparable to levels detected in sediments classified as contaminated from other rivers of the world. For this reason, the metal background value in the Day sediment could not be assessed from the sampled sediments. To evaluate the metal background value, tree surface sediment samples were obtained from presumed uncontaminated points of Sabek River which is tributary of the Day River. They were taken upstream from Beni-Mellal city, away from any liquid or solid discharges. The average metal background levels were determined as 0.36, 36.01, 22.21, 16.93, 47.08 and 25039 mg/kg for Cd, Cr, Cu, Pb and Zn, respectively. When compared with these local background values, it could be seen that high levels of heavy metals had accumulated in the Day sediments (Fig. 2).

Generally, Pb, Zn, Cd, Fe, Cu and Cr concentrations showed similar evolution patterns along the Day River, with much variation from one station to another (Fig. 2). Maximum concentrations of these metals were observed at stations S1 and S2 suggesting that the most severe pollution occurred at outfall where urban wastewater is discharged. The wastewater is loaded in

Day river with metals derived from toxic discharges such as motor oil, printing, waste steel, chemical, solid waste disposal, transport, paintings, leather tanning, traffic, batteries, pesticides, etc. El-Baghdadi *et al.* (2011) studied the heavy metal pollution in urban soil of Beni-Mellal city. They reported that the traffic density in Beni-Mellal has a strong influence on metal pollution. Moreover, evidence for high concentration of heavy metal in municipal wastewater from Beni-Mellal city has been reported by Kassaoui *et al.* (2009). Metal concentrations founded in sewage sludge were 1971 mg/kg for Cr, 134 mg/kg for Cu, 155 mg/kg for Pb and 775 mg/kg for Zn. One other possible source of pollution may be the heavy metal leaching of solid wastes of the open dump located beside Sabek River. Relatively higher heavy metal values were also observed at stations S4, S6, S7, S9 and S10 that are close to rural areas suggesting that rural activities carried out at the wide lands surrounding the Day River might contribute to the observed metal pollution in Day sediment.

Correlation analysis: To discuss the factors controlling the precipitation of heavy metals in Day River, a correlation matrix was also calculated for heavy metals in sediments (Table 4). As organic matter can be bounded with some fractions of metals and can affect the metal enrichment rates of river sediment (Eimers *et al.*, 2002), we correlated the sediment organic matter content with sediment metal levels for different stations. Besides organic matter, iron oxides play an important role in heavy metal retention in surface sediment (Jones-Lee and Lee, 2005; L  v  que *et al.*, 2006). Also, it is well established that the co-precipitation with carbonate minerals is of importance for many metals (Sipos *et al.*, 2008). As illustrated in Table 4, most of metals showed a close relationship with TOM and Fe. Thus, the results suggested that Fe and organic pollution load in Day River should enhance the metal enrichment in sediments. Positive and significant correlation among Cd, Cr and Cu and CaCO₃ reveals the affinity of these metals to carbonate minerals. Negative correlation observed for Pb, Zn and Fe with CaCO₃, indicates that these metals are not associated with carbonate minerals. Also, correlation matrix shows significant and positive correlation among Cd, Cr, Cu, Pb, Zn and Fe. These correlations possibly reflect the same or similar source input for these metals and the difference in their distribution and concentration may be controlled by organic matter, Fe compounds and carbonate minerals and by pollution load.

Sediment contamination assessment: In view of geochemistry results, the heavy metals in the Day sediments show anomalous concentrations which are derived from natural inputs and human activities. For

Table 4: Correlation matrix of heavy metals in sediments

Variable	Cd	Cr	Cu	Pb	Zn	Fe	TOC	CaCO ₃
Cd	1							
Cr	0.98	1						
Cu	1.00	0.98	1					
Pb	0.40	0.55	0.39	1				
Zn	0.46	0.60	0.47	0.80	1			
Fe	0.53	0.65	0.51	0.95	0.74	1		
TOM	0.68	0.79	0.68	0.87	0.74	0.83	1	
CaCO ₃	0.64	0.49	0.65	-0.40	-0.20	-0.29	0.00	1

Significant correlation are indicated in bold where $p < 0.05$

abetter estimation of anthropogenic input, Enrichment Factor (EF), geo-accumulation Index (Igeo) and Pollution Load Index (PLI) should be considered. Since the bedrocks in the study area were terrigenous sedimentary and carbonate rocks, quantitative indexes values were calculated with respect to background values (as mg/kg) described by Taylor and McLennan (1995) (Table 2) (0.098 for Cd, 35.0 for Cr, 25.0 for Cu, 600 for Mn, 20.0 for Ni, 20.0 for Pb, 71.0 for Zn).

Commonly, Igeo index (Muller, 1981) is employed in order to determine and define metal contamination in sediments by comparing current concentrations with background levels. Geo accumulation index is expressed as in followed equation:

$$I_{geo} = \log_2 (C_n / 1.5 \cdot B_n)$$

where,

C_n: The measured concentration of the examined metal (n) in the sediment samples

B_n: The geochemical background concentration of the metal (n)

1.5: The background matrix correction factor due to lithogenic effects

Based on the Igeo value, Müller (1981) has distinguished seven classes:

- Igeo < 0, unpolluted
- 0 < Igeo < 1, unpolluted to moderately polluted
- 1 < Igeo < 2, moderately polluted
- 2 < Igeo < 3, moderately to strongly polluted
- 3 < Igeo < 4, strongly polluted
- 4 < Igeo < 5, strongly to very strongly polluted
- Igeo > 5, very strongly polluted.

The highest grade reflects 100-fold enrichment above the background values (Singh *et al.*, 2003).

Calculated Igeo index for heavy metal concentrations in Day sediment ranged from -1.04 to 2.66 (Table 5) suggesting a pronounced metallic pollution. Based on the Müller scale, the sediments in all sampling stations, except S1, were partially polluted rate for Zn (-1.1/0.49) and Fe (-1.74/-0.64), polluted in unpolluted to moderately rate for Cr (0.005/0.95) and

Cu (0.04/0.88), moderately polluted rate for Pb (1.28/2.23) and moderately to strongly polluted rate for Cd (2.17/2.56). Igeo index in station S1 was 5.41 for Cd, 2.57 for Cr, 4.30 for Cu, 2.17 for Pb, 0.45 for Zn and -0.54 for Fe. It is suggested that the station S1 is very strongly polluted by Cd, strongly to very strongly polluted by Cu, moderately to strongly polluted by Cr and Pb, unpolluted to moderately polluted by Zn and partially polluted by Fe. This relatively high pollution in S1 indicates that untreated wastewater and rubbish discharged into river were the major pollution source of heavy metal in Day sediment. Also, to identify anomalous metal concentration, geochemical normalization of heavy metal data to a conservative element, such as Al, Fe and Si were employed. Several authors have successfully used Fe to normalize heavy metals contaminants (Mucha *et al.*, 2003; Ghrefat and Yusuf, 2006; Zhang *et al.*, 2007; Çevik *et al.*, 2009; Esen *et al.*, 2011). In this study, Fe was selected as the normalize because it had a strong correlation with all heavy metals as mentioned above. The Enrichment Factor (EF) is defined as follows (Ergin *et al.*, 1991):

$$EF = (M/Fe)_{\text{sample}} / (M/Fe)_{\text{background}}$$

where,

(M/Fe)_{Sample}: The ratio of metal and Fe concentration of the sample

(M/Fe)_{background}: The ration of metal and Fe concentration of the background

According to Zhang and Liu (2002), EF values smaller than 1.5 suggest that heavy metals derived from mainly natural source such as weather processes while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. Han *et al.* (2006) divided the contamination into different categories based on EF values. If EF < 2, it suggests deficiency to minimal metal enrichment. However, if a value of EF is greater than 2 (i.e., EF > 2), it suggests various degrees of metal enrichment. The results of EF factor reveal that that the mean EF values for all elements were below 1.5, suggesting that a significant portion of heavy metal in Day sediment is delivered from non-crustal materials or non-natural weathering processes. As shown in Table 5, EF (Cd) ranges from 9.07 to 62, EF (Cr) from 2.51 to 8.63, EF (Cu) from 1.69 to 28.80, EF (Pb) from 6.56 to

Table 5: Geoaccumulation index (Igeo) and Enrichment Factor (EF) of heavy metals in sediments

Stations	Igeo						EF					
	Cd	Cr	Cu	Pb	Zn	Fe	Cd	Cr	Cu	Pb	Zn	PLI
S1	5.41	2.57	4.30	2.17	0.45	-0.54	62.00	8.63	28.72	6.56	1.99	2.20
S1	2.33	0.89	0.88	1.98	0.31	-1.15	11.14	4.09	4.06	8.74	2.73	1.67
S3	2.17	0.01	0.08	1.28	-0.76	-1.58	13.52	3.01	3.17	7.28	1.76	1.57
S4	2.33	0.74	0.31	1.68	-0.31	-1.07	10.56	3.52	2.60	6.72	1.70	1.63
S5	2.45	0.37	0.06	1.50	-0.60	-1.30	13.45	3.18	2.56	6.96	1.62	1.61
S6	2.41	0.84	0.19	1.95	-0.07	-0.89	9.84	3.32	2.11	7.14	1.76	1.65
S7	2.39	0.95	0.04	2.01	-0.14	-0.88	9.63	3.55	1.89	7.41	1.67	1.65
S8	2.49	0.63	0.06	2.13	-0.41	-0.70	9.07	2.51	1.69	7.09	1.22	1.66
S9	2.56	0.89	0.49	2.23	0.49	-0.63	9.13	2.87	2.17	7.25	2.17	1.70
S10	2.49	0.63	0.54	1.85	0.27	-0.97	11.01	3.04	2.84	7.06	2.36	1.66
S11	2.24	0.00	-0.20	1.32	-1.10	-1.74	15.83	3.33	2.91	8.35	1.56	1.57
Minimum	5.41	2.57	4.30	2.23	0.49	-0.54	9.07	2.51	1.69	6.56	1.22	1.57
Maximum	2.66	0.77	0.61	1.83	-0.17	-1.04	62.00	8.63	28.72	8.74	2.73	2.20
Mean	2.17	0.00	-0.20	1.28	-1.10	-1.74	15.92	3.73	4.97	7.32	1.87	1.69
S.D.	0.92	0.68	1.26	0.34	0.52	0.38	16.26	1.76	8.30	0.59	0.43	0.17

Table 6: SQG by USEPA and TEL/PEL guideline values for trace elements

	Cd	Cr	Cu	Pb	Zn
SQG non- polluted ^a		<25	<25	<40	<90
SQG moderate polluted ^a	>6	>75	>50	>60	>200
SQG heavily polluted ^a	>6	>75	>50	>60	>200
TEL ^b	0.68	52.3	18.7	30.2	124
PEL ^b	4.2	160.4	108.2	112.2	271

Concentrations are in mg/kg; ^a: Perin *et al.* (1997); ^b: Long *et al.* (1995)

8.74 and EF (Zn) from 1.22 to 2.73. The mean EF values of heavy metals from Day River follows the sequence:

Cd (15.92) > Pb (7.32) > Cr (3.73) > Cu (4.97) > Zn (1.87)

Overall, the average enrichment factors of Pb, Cr and Cd are greater than 2 (EF > 2), suggesting various degrees of metal enrichment, according to the recommendation by Han *et al.* (2006). In contrast, the average EF values of Zn and Cu are less than 2 (EF < 2), suggesting deficiency to minimal metal enrichment. Also, the contamination of these metals could be correlated to local point discharges. The highest EF values were observed in station S1 which is near a large wastewater outfall for the Beni-Mellal city. A decrease in the enrichment factor with distance from the pollution sources is observed and confirms that discharge of industrial and urban effluents is a major source of heavy metals pollution in Day River.

Another commonly used criterion to evaluate the heavy metal pollution in sediments is the Pollution Load Index (PLI). The Pollution Load Index (PLI) proposed by Tomlinson *et al.* (1980) is obtained as a Concentration Factor (CF) of each metal with respect to the background value in the sediment (Angulo, 1996), by applying the following equation:

$$CF = C_{\text{metal}} / C_{\text{background}}$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

n = number of metals

The PLI represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The PLI value of >1 is polluted whereas <1 indicates no pollution. The values of PLI obtained in Day sediments are summarized in Table 5. They ranged from 1.57 to 2.20 indicating that the concentration levels of Cd, Cr, Cu, Pb and Zn in most of the stations exceeded the background values. Sediments of the Day River have also been polluted overall by these metals which are a result of anthropogenic activities in the catchment area. To further examine the extent of metal contamination in the study area and to make an initial assessment of sediment ecotoxicity, USEPA Sediment Quality Guidelines (SQGs) (Perin *et al.*, 1997) and TEL/PEL sediment quality guidelines (Long *et al.*, 1995; MacDonald *et al.*, 2000) have been used because the sediment quality guideline in Morocco does not exist (Table 6). According to the numerical USEPA-SQGs, sediments in Day River were moderately polluted to heavily polluted for Cd, Cu, Cr and Pb, non-polluted to moderately polluted moderate for Zn. This suggests serious anthropogenic pollution at all stations. TEL/PEL guidelines are based on TEL (Threshold Effect Level) values below which adverse biological effects would infrequently be expected and on PEL (Probable Effect Level) values above which adverse biological effects would frequently occur. Compared to

TEL and PEL values given in Table 6, Day sediments from station S1 where one the main sewer empties are most toxic due to Cd, Cr, Cu and Pb concentrations exceeded the PEL values. For all other stations, sediments are less toxic because all Cd, Cr, Cu and Zn metals have concentrations ranged between TEL and PEL and only in few cases, i.e., for Cd and Zn, some of the samples lie below TEL values. In contrast, Pb concentration of most stations exceeded the PEL level. This Pb exceedance of the PEL level is clearly associated with local point pollution sources such as solid and liquid discharge from the surrounding villages.

CONCLUSION

In the present study, sediment analysis was made for assessment of heavy metal pollution status in Day River. Geochemical analysis showed significant heavy metal concentration in sediments indicating a clear pattern of anthropogenic impact on Day River. The abundance of heavy metals measured decreases as follows: Fe>Cu>Cr>Zn>Pb>Cd. Most of the elements show a similar distribution pattern, thus suggesting a common source and similar enrichment mechanisms. Correlation matrix suggested that Fe content and organic matter should enhance the metal enrichment in sediments. In contrast, carbonates seem to exert some control on Cd, Cr and Cu deposition. Also, a significant correlation between Cd, Cr, Cu, Pb, Zn and Fe implies that they have the same origin. Based on Igeo index and EF factors, the contamination degree can be defined as unpolluted to moderately polluted of Zn, Fe, Cr and Cu and moderate to considerable of Pb and Cd. With respect to PLI and SQGs, the metal levels exceed local and regional background concentrations indicating contamination sufficiently high to attract attention and to constitute risk to the ecosystem. Higher degree of pollution was generally observed at sampling stations close to Beni-Mellal city and this confirms that the major source of heavy metals is industrial and urban wastewater discharges. Moreover, relatively higher heavy metal contamination at other stations close to rural areas suggest that agricultural and rural activities carried out at the wide lands surrounding the Day River might contribute to the observed metal pollution in sediment.

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