Spatial and seasonal variations and ecotoxicological significance of sediment trace metal concentrations in Kebir-Rhumel basin (Northeast of Algeria)

Leila Sahli, Fatima-Zohra Afri-Mehennaoui, Mohamed El Hadef El Okki, Christian Blaise and Smail Mehennaoui

ABSTRACT

This study sought to assess sediment contamination by trace metals (cadmium, chromium, cobalt, copper, manganese, nickel, lead and zinc), to localize contaminated sites and to identify environmental risk for aquatic organisms in Wadis of Kebir Rhumel basin in the Northeast of Algeria. Water and surficial sediments (0–5 cm) were sampled in winter, spring, summer and autumn from 37 sites along permanent Wadis of the Kebir Rhumel basin. Sediment trace metal contents were measured by Flame Atomic Absorption Spectroscopy. Trace metals median concentrations in sediments followed a decreasing order: Mn > Zn > Pb > Cr > Cu > Ni > Co > Cd. Extreme values (dry weights) of the trace metals are as follows: 0.6–3.4 μg/g for Cd, 10–216 μg/g for Cr, 9–446 μg/g for Cu, 3–20 μg/g for Co, 105–576 μg/g for Mn, 10–46 μg/g for Ni, 11–167 μg/g for Pb, and 38–641 μg/g for Zn. According to world natural concentrations, all sediments collected were considered as contaminated by one or more elements. Comparing measured concentrations with American guidelines (Threshold Effect Level: TEL and Probable Effect Level: PEL) showed that biological effects could be occasionally observed for cadmium, chromium, lead and nickel levels but frequently observed for copper and zinc levels. Sediment quality was shown to be excellent for cobalt and manganese but medium to bad for cadmium, chromium, copper, lead, nickel and zinc regardless of sites.

Key words | contamination, ecotoxicological significance, Kebir Rhumel basin, sediments, trace metal

INTRODUCTION

Countries in North Africa are facing problems of water shortage because aquatic ecosystems are submitted in much of their areas to a semi-arid climate. In Algeria, pollution of water resources is beginning to reach alarming proportions, especially in the north where most of these resources are located. Situated in the Northeast of Algeria, between the littoral Kabyle mountain chain and the Southern massifs of the Tell, Kebir Rhumel basin covers an area of 8,815 km². Rhumel Wadi, one of the most important Wadis in Kebir Rhumel basin, supplies the Beni-Haroun dam (959,941 m³), which serves as a drinking-water supply for several cities, agricultural use and the new aquaculture program in the country (Afri-Mehennaoui et al. 2004). Throughout the Kebir Rhumel basin, there are 100 agglomerations with a total of 1.62 million inhabitants. Constantine City alone holds 750,000 inhabitants. Industrial activities have significantly increased during the past century in this area. The most important effluents are located within a radius of 20 km around Constantine City. Results published by the National Agency of Water Resources (Agency of Constantinois-Seybouse-Mellegue Basin, ABH 2004) reveal that large sections of Wadis in Kebir Rhumel basin are polluted. Wadis receive urban effluents, industrial discharges and surface runoff, mainly from agricultural land. They are thus exposed to pollution problems that might jeopardize Beni Haroun dam water and therefore the drinking water of nearly all the cities served. In addition, Kebir Rhumel Wadi in the North part of the basin pours into the...
Mediterranean sea at a total rate of wastewater of about 1.85 m³/s (159,840 m³/day). Fifty-two percent of the discharges are produced by Rhumel Smendou sub-basin (Mebarki 2000).

We had conducted a previous study on trace metal levels in Rhumel Wadi and its principal tributary, the Boumerzoug Wadi, in an urban area which showed that trace metal concentrations were higher in downstream stations under influence of anthropogenic activities (Afri-Mehennaoui et al. 2004). Moreover, the potential effects on macroinvertebrates were highlighted; besides the transfer of trace metal to the six sub-aquatic plants (Afri-Mehennaoui et al. 2007), especially Rorippa nasturtium aquaticum which can be used as a bioindicator of trace metals contamination of watercourses (Afri-Mehennaoui et al. 2009). To the authors’ knowledge, there is no information about the extent of trace metals contamination in Wadis of the Kebir Rhumel basin. Thus, the present study examined sediment contamination by trace metals (Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn) in principal Wadis and their tributaries of the Kebir Rhumel basin. Its objectives were to assess sediments contamination using trace metals, to localize contaminated sites as well as to identify environmental risks for aquatic organisms using American guidelines. Results could provide a baseline for future ecological environmental risks for countries in North Africa.

**SAMPLING, MATERIALS AND METHODS**

**Station location and sample collection**

Water and surficial sediment samples (0–5 cm) were collected in the Kebir Rhumel basin along their principal Wadis and in several small ones. Six sub-basins were considered: Kebir Wadi upstream Endja (sub-basin 10-02), upstream Rhumel Wadi (sub-basin 10-03), Rhumel-Seguen Wadi (sub-basin 10-04), Boumerzoug Wadi (sub-basin 10-05), Rhumel-Smendou Wadi (sub-basin 10-06) and Kebir maritime Wadi (sub-basin 10-07). Wadis of Dehemcha-Kebir sub-basin were not studied for reasons of accessibility. Thus, thirteen Wadis were studied, including three major (Rhumel Wadi, Endja Wadi and Kebir Wadi) and 10 secondary Wadis (Seguen, El Melah, El Kleb, El Berda, Boumerzoug, Hamimine, Smendou, El Ktone, Bou Selah and Siaba). Thirty-seven sampling stations were selected in locations considered relevant to the study; sediment accumulation areas were considered as well as upstream and downstream of industrial and urban discharges (Figure 1). Water and sediments were sampled on four occasions during base flow and flood in order to cover all seasons. Water samples were collected from a depth of 0.5 m and placed in 1 L polypropylene bottles. Five centimetres of surficial sediment (300–500 g), which would indicate a recent pollution, were collected manually at each station in a polypropylene jar previously treated with nitric acid (5N). Sediment samples were dried, crushed in an agate mortar and sieved through 65 μm nylon mesh screen for trace metals analysis and through 2 mm mesh screen for the other physico-chemical parameters.

**Physico-chemical and trace metal analysis**

Water temperature, pH (WTW model H 18014 pH meter) and conductivity (WTW model LF 90 conductimeter) were measured in situ. Suspended solids in water were determined according to ISO 11923 (1997). Sediment pH and conductivity were determined in the laboratory in a ratio of 1/2.5 and 1/5, respectively. The carbonates were measured by a volumetric method (NF ISO 10693 (X 31-105) 1995). Loss on ignition (LOI) was determined by calcination of 1 g of dry sediment in a furnace at 520 °C. The grain size distributions were measured on sediment samples by sieving, sedimentation and pipetting.

Water samples for trace metals analysis were pre-acidified in situ (at pH = 2) with concentrated nitric acid and filtered through a 0.45 μm Millipore membrane using a filtration apparatus. Sediment samples (0.5 g) were digested with 10 ml of aqua regia (3:1 mixture of HCl (12N) and HNO₃ (15N)) in teflon bombs in a microwave oven (model Speedwave MWS-2. BERGHOF B). This hot digestion was performed in two steps (step 1: power = 80%, temperature =150 °C, time = 15 min; step 2: power = 40%, temperature =100 °C, time = 15 min). Once cooled down, the solutions were filtered using an ash-free filter paper (Whatman 540) and their volume was adjusted to 50 ml with deionized water. These solutions were stored at 4 °C in polypropylene bottles until analysis. The concentrations determined are considered as the pseudo total trace metals fraction (Gupta et al. 1996); aqua regia does not mineralize silicate. This method is a widely used analytical procedure and is standardized for sediment analysis by NF ISO 11466 (1995). In addition, commercial certified sediment reference materials (Lake Sediment, LKSD1) from CANMET (Canadian Center for Minerals and Energy Technology) were used to control the analytical reliability. For all elements studied nearly 100% recoveries (95–107%) of the analytical method were obtained. Water and sediment samples were...
Figure 1  Study area and station localization.
analysed for Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn by flame atomic absorption spectroscopy (Perkin-Elmer A-Analyst 100). Trace metal concentrations (μg/g) in reference material were for Cd = 1.23 versus 1.2; Cr = 12.2 versus 12; Cu = 44.2 versus 44; Pb = 85.8 versus 84; Mn = 496 versus 460; Ni = 11.5 versus 11 and Zn = 319 versus 337.

ILLUSTRATIONS AND STATISTICAL ANALYSIS

Statistical analyses were conducted using Statistica 6.0 software. Minimum, 1st decile, median, 9th decile, maximum and standard deviation were calculated for water and sediment physico-chemical parameters, and trace metal in sediments. Spatial and temporal variations of sediment trace metal concentrations were tested by Anova followed by Newman-Keuls test. The level of significance was set at p value (5%).

RESULTS AND DISCUSSION

Water and sediment physico-chemical analysis results

Table 1 shows statistical results of water and sediments. The chemical quality of aquatic ecosystems varies according to local geology, climate, distance from the sea, and the amount of soil cover, among other factors (Meybeck & Helmer 1996). In this study, temperature of water ranges from 8.2°C to 28.6°C. Median pH of water and sediment indicates a slightly alkaline nature tending towards neutrality, which could be due to the calcareous nature of Kebir Rhumel basin but also to high temperature that reduces CO₂ solubility. For conductivity, 80% of values are included between 1 and 2.4 mS/cm for water. Values revealed a high mineralization, which can be attributed to pollution and also to presence of salt soils especially in the southern part of Kebir Rhumel basin. Water is loaded with suspended solids (SS) which could be attributed to industrial and urban discharges and run off from grounds neighbouring Wadis. Limestone contents could be attributed to the carbonate lithology of Kebir Rhumel basin, and higher values of loss on ignition compared to world averages (10%, Meybeck et al. 1998) could be attributed to disturbances in hydrological regimes and/or occasional pollution caused by industrial and urban discharges. Texture of sediments is variable; sediment grain size ranges from silty sand to sandy silt.

Trace metal analysis

Water analysis showed undetectable levels for the metals measured. This indicates that there might have been complete retention of trace metals by the suspended solids of sediments under different forms such as exchangeable ions, carbonates, or oxides/hydroxides or complexed with organic matter. Indeed, sediments act as sinks and sources of trace metal contaminants in aquatic ecosystems.

Statistical results of pseudo-total trace metal concentrations in sediments are illustrated in Table 1. Median concentrations followed the order: Mn > Zn > Pb > Cr > Cu > Ni > Co > Cd. The most variable concentrations (in percentage) were those of Cd, Cu and Zn (over 40%) while the least variable elements were Mn, Ni and Pb (less than 25%). According to the world natural concentrations specific to carbonate substrates proposed by Thomas &

Table 1 | Statistics of physico-chemical characteristics and trace metal concentrations

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<thead>
<tr>
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<th>Water</th>
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<tr>
<td></td>
<td>Tw (°C)</td>
<td>pH</td>
<td>CE (mS/cm)</td>
<td>SS (mg/l)</td>
</tr>
<tr>
<td>Min</td>
<td>8.2</td>
<td>7.0</td>
<td>0.4</td>
<td>10.1</td>
</tr>
<tr>
<td>1st decile</td>
<td>11.1</td>
<td>7.6</td>
<td>1.0</td>
<td>21.1</td>
</tr>
<tr>
<td>Mean</td>
<td>18.7</td>
<td>8.2</td>
<td>1.7</td>
<td>64.3</td>
</tr>
<tr>
<td>Median</td>
<td>19.2</td>
<td>8.2</td>
<td>1.7</td>
<td>38.7</td>
</tr>
<tr>
<td>9th decile</td>
<td>25.3</td>
<td>8.6</td>
<td>2.4</td>
<td>129.2</td>
</tr>
<tr>
<td>Max</td>
<td>28.6</td>
<td>8.9</td>
<td>4.7</td>
<td>742</td>
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<tr>
<td>Std. Dev</td>
<td>5.3</td>
<td>0.37</td>
<td>0.65</td>
<td>42.1</td>
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Meybeck (1992), sediments are considered contaminated if one or more concentration values exceed the corresponding reference level. This indicates the presence of an anthropogenic source of trace metals. For the 1,184 samples analysed, it was noted that Cd (0.6–3.4 $\mu$g/g of dry weight) exceeds the world natural concentration (0.3 $\mu$g/g) in all sites. The highest value was recorded at station 4, located in an area characterized by intensive agricultural activities. Cr (10–216 $\mu$g/g of dry weight) was close to the world natural concentration, which is about 120 $\mu$g/g in 98% of cases. However, Cr exceeded this reference value at station 34, located downstream El Milia City, revealing occasional discharge due to the tannery of this area. Pb concentrations (11–167 $\mu$g/g of dry weight) were higher compared to the world natural concentration (40 $\mu$g/g). Ninety-eight percent of sediments analysed exceeded the reference value against 32% of cases for Cu (9–446 $\mu$g/g of dry weight) for a world natural concentration of about 50 $\mu$g/g. The highest values for these two elements were recorded at station 15, located downstream of industrial and urban discharges, especially those of Ain M’lila City. Zn concentrations (38–641 $\mu$g/g of dry weight) followed those of Cd, Pb, and Cu, and exceeded the world natural concentration (110 $\mu$g/g) in 60% of cases. The highest value was recorded at station 15, located downstream of the confluence of Boumerzoug Wadi with two of its tributaries, El Kleb and Al Melah Wadis. Co (3–20 $\mu$g/g) and Ni (10–46 $\mu$g/g) concentrations were close to the world natural concentrations (20 and 80 $\mu$g/g) for Co and Ni, respectively. These concentrations may reflect the geochemical background of the study area. Although manganese is present in high concentrations (105–576 $\mu$g/g of dry weight), values were close to world natural concentration and the values reported in literature. This element is considered a natural component of the sediment, present in high concentrations in the earth’s crust. *Anova* showed a significant site effect ($p < 0.01$) with an effect intensity of about 43, 42, 59, 44 and 40% for Cd, Cr, Cu, Pb and Zn, respectively. Stations were divided into three groups for Cd, Pb and Zn contents, and into two groups for Cr and Cu contents according to the Newman-Keuls test. The most worrisome stations are located downstream of industrial discharges, especially those of Ain M’lila, El Khroub and Constantine cities. Industrial wastewater of those cities is treated and decontaminated in a wastewater treatment plant (WWTP) within industrial complexes before reaching the Wadis of Kebir Rhumel basin. However, polluted sludge stored in areas of industrial complexes is subject to weather changes and could be sources of Wadis contamination. This one may take place via water run-off especially during winter. Nevertheless, seasonal variations of trace metal contents were not statistically significant (*anova, p > 0.01*) as would be except for Cd and Pb, which showed considerable variation.

*Anova* showed a significant variation with an effect intensity of about 9.4 and 8.4% for Cd and Pb, respectively. The Newman-Keuls test showed that higher loads of Cd and Pb were found in winter and the lowest ones in summer. These disturbances could also be attributed to run-off of urban and agricultural edge soils of Wadis; run-off is most pronounced under intensive rain situations. These soils, especially agricultural ones, continue to receive waste gas rich in lead from cars and are the receptacle of phosphate fertilizers. Algerian phosphates are probably similar to Tunisian ones, which are rich in Cd. Their concentration is about 400 $\mu$g/g (Chiffreau et al. 2001). Algerian and Tunisian phosphates have the same origin; they are from a deposit located in the common border between Algeria and Tunisia. A significant proportion of discharges and metallic impurities could end up in sediments of Wadis in soluble form or adsorbed on suspended solids. Cd and Pb concentrations determined in soil borders of Rhumel Wadi by Ouahrani & Gheribi (2007) were about 5.8 ± 0.8 and 50.8 ± 7.5 $\mu$g/g, respectively.

Compared with the literature values reported for trace metal concentrations in sediments of watercourses in the North-east of Africa, the present study recorded concentration values close to and/or higher than those reported by Bouabdli et al. (2005) in sediments of Moulaya river in Morocco, which are considered contaminated especially by Pb and Zn. That article recorded the following concentrations: 0.2–0.8, 12.6–27.9, 19.2–710 and 86–949 $\mu$g/g for Cd, Cu, Pb and Zn, respectively. Sediment trace metal concentrations were also higher than those of contaminated surface sediment in the gulf of Tunis; concentrations of trace metals analysed were about 279–447, 39–67, 20–34, 9–20 and 56–142 $\mu$g/g for Zn, Ni, Co, Cu and Pb, respectively (Added et al. 2005).

Figure 2 shows views of the spatial distribution of sediment trace metal concentrations in studied sites according to Quality Assessment System (SEQ-France 2005) developed by French Basin Agencies. Results reveal a discrepancy between sediment qualities in sub-basins suggesting different origins of trace metals. As Co and Mn presented similar situations in all sub-basins, they could be considered as elements of natural origin. This is also the case for Ni; only the median concentration recorded at sub-basin 10-05 is higher; sediments are considered as moderately polluted, while similar situations were recorded for the remaining
sub-basins. Wadis of this sub-basin receive the most part of industrial and urban discharges, especially those of Ain M’illa, Ouled Rahmoune and El Khrout cities. Cd, Cr, Cu, Pb and Zn present higher concentrations for most samples. The highest ones were recorded in sub-basins 10-03, 10-05, 10-06 and 10-07, where most agglomerations, industries and agricultural lands are located. However, Anova showed significant sub-basin effect only for Cd ($p < 0.01$).

According to Sediment Quality Guidelines defined by Long et al. (1995), sediments were considered to be not polluted to moderately polluted for Cd concentrations, and moderately to heavily polluted for Cr, Cu, Pb and Zn concentrations (Table 2). These disturbances are due to anthropogenic origin of these metals in sediments. In addition, lower values seem to be very different from one sub-basin to another, in particular for Cr, Co, Ni, Mn, Pb and Zn. This variability is less pronounced for Cu and Cd; lower values are more or less stable. This could be partly explained by different natural background levels due to the earth crust’s metal levels.

Also, potential adverse effects of contaminated sediments on benthic fauna were evaluated by comparing our results to the American guideline developed by ‘Consensus-Based Sediment Quality Guidelines (CBSQG)’, (Mc Donald et al. 2000). Criteria (Threshold Effect Level ‘TEL’ and Probable Effect Level ‘PEL’) are shown in Table 2. The median concentrations, and even maximum, were lower than PEL for Cd and Ni but higher than TEL in 49 and 72% of cases, respectively. The most part of values were between the TEL and PEL; those concentrations were not predicted to be toxic or non-toxic (individual SQGs are not intended to provide guidance within this range of concentrations) (Mc Donald et al. 2000). However, we recorded concentrations higher than PEL for Cr (2%), Cu (2%), Pb (12%) and Zn (4%), indicating that harmful effects are likely to be observed for these elements. Risk concentrations for these elements were respectively recorded at stations 34, 13, 14 and 15, located downstream of industrial and urban discharges, especially those of Ain M’illa, Ouled Rahmoune, Sigus and Al Milia.
cities. For Pb, concentrations higher than PEL were recorded in stations near roads, especially those that are downstream of Constantine and Ain M’lila cities. Wadis continue to be the receptacle of run-off of bordering soils subject to waste gas rich in organic lead still used as additive in fuel for vehicles.

CONCLUSION

This study supplies valuable information about metal concentrations in surficial sediment from different sampling stations along Wadis of Kebir Rhumel basin. From the previous sections, it could be concluded that:

There exists a spatial variation in concentrations of Cd, Cr, Cu, Ni, Pb and Zn which is distinguished from other elements (Co and Mn) with high spatial disparity of concentrations across the region. Natural or anthropogenic activities that influence trace metal concentrations in the environment varied considerably along Wadis of the study area, confirming previous results for an urban area. However, some similarities were recorded for Co and Mn, whose levels were similar to the world background, reflecting a natural origin.

Comparing trace metal results with American guidelines (TEL/PEL) showed that biological effects on fauna could be frequently observed for Cr, Cu, Pb and Zn. Concentrations higher than the PEL were recorded for these elements in 2, 2, 12 and 4% of cases, respectively. Samples with trace metal concentrations higher than the TEL and lower than the PEL cannot be considered as non-toxic. More attention must be focused on these samples to confirm if they are false negative or false positive ones. A bioassay battery is recommended to confirm their toxicity or non-toxicity. Also, trace metals pseudo-total fraction does not assess the actual toxicity of sediments. Thus, for future studies it is recommended to assess different trace metal fractions (exchangeable, carbonates, Fe–Mn oxides, organic and residual) because their toxicity depends on their chemical form, including the nature of their links with the sediments.

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