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Occurrence, contamination level and ecological risk assessment of dissolved and particulate trace elements in rivers entering the southwestern Mediterranean Sea

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Abstract.

Metal pollution in rivers should not be overlooked before their entry into the sea. However, there are few studies for estimating such contamination in rivers entering the Algerian coastal. Semimonthly quantification of dissolved and particulate metals, near the mouths of two industrial-tainted rivers, El Harrach and Mazafran rivers, was carried out during one-year. All analyzed metals are originating from anthropogenic sources ($EF > 1.5$), with higher contamination of dissolved Pb, Cd, Zn and Ni and slightly pollution of particulate Cu and Zn ($0 < I_{geo} < 1$). Particulate metals showing a stable complex with particulate phase ($e.g. 2 < \text{Log}K_d < 6$). The assessment results indicated that the particulate Pb and Zn have a potential of toxicity for adverse biological effects with a 33% likelihood. A significant toxicity effect ($\Sigma TU_i > 4$) of combined particulate metals (Pb, Cd, Cu, Zn, Cr, Ni and As) was due to the higher particulate Cd, Zn, and Cr availability.

Keywords: Pollution metals; River water quality; Index analysis approach; ICP-MS; Algerian coastal zone.

1 INTRODUCTION

Contamination by trace metals in the aquatic environment is a worldwide threat due to their abundance, toxicity, persistence and their resultant accumulation in aquatic ecosystems (Benedicto *et al.*, 2011; Guendouzi *et al.*, 2021; Guendouzi *et al.*, 2017; Jović and Stanković, 2014; Marengo *et al.*, 2018; Ternengo *et al.*, 2018). The analysis of trace elements in river waters is motivated by a number of research papers (Basooma *et al.*, 2021; Gaillardet *et al.*, 2003; Viers *et al.*, 2009; Xue *et al.*, 2022).

The rivers are considered as the essential transport pathways of the numerous metal containing effluents discharged from large cities and other anthropogenic activities which eventually enter the marine environment (Tomczak *et al.*, 2019). According to Chapman *et al.* (1996), the sediments are recognized as a source of many contaminants discharged into surface water bodies. In addition, the metal contaminated suspended particulate matter eventually settles and adds to the sediment contamination in rivers (Kern *et al.*, 1998).

The watershed of El-Harrach river (Fig. 1), which belongs to the large Algiers Coastal Watershed, covers an area of 1250 km², and stretches from north to south for 53 km, and from east to west for 31 km. This river, which is one of the main Ouadis that crisscross the Mitidja, has its source in the north part of the Blidéen Atlas mountains (Bouchelouche *et al.*, 2018; Boudjema *et al.*, 2014). The El Harrach river, which flows directly into the bay of Algiers, is a heavily contaminated, uncontrolled aquatic environment. According to Yoshida *et al.* (2005), extraordinarily high concentrations of Hg, Cu, Pb, Cr, and Cd were measured in sediments and water of El Harrach river, due mainly to the fact that the local wastewaters are discharged directly into the input streams without appropriate treatment.

According to the ANRH "Agence Nationale des Ressources Hydrauliques" basin subdivision, the Mazafran river watershed (Fig. 1) is one of the most important basins of the Algiers Coastal Watershed, covering roughly 1900 km². It is located in the Matidja's central region. The Mazafran river has three main tributaries which are: "Owad Djer", "Bou Roumi" and "Chiffa". All these Ouadis take their source in the Tellian Atlas mountains, and cross the Matidja plain to join downstream and form a single Ouadi "Mazfran" river (Bouras *et al.*, 2020). In Bou Ismail bay, the Mazafran river was considered as the major source of terrigenous inputs to the seawater (Guendouzi *et al.*, 2021), and is characterized by seasonal water flow with an approximate flow rate of 4.10⁷ m³/year (Benzohra, 1993).

Studies of particulate and dissolved metals in rivers of Algeria are rare and most are not published. To the best of our knowledge, no research has focused on the aspect of risk assessment of particulate trace metals in such river ecosystems in Algeria.

The aims of the present study are (1) to evaluate the concentrations of 11 trace metals in river water and suspended particulate matter of two polluted rivers which terminate in the central coastal region of Algeria, and to define the relationship between dissolved and particulate metals using the K_d approach; (2) to compare our data with those of other riverine studies around the world; (3) to assess the environmental risk of particulate metals through use of the geo-accumulation index (Igeo), enrichment factor (EF) and pollution load index (PLI) using Fe as a reference index; and (4) to assess the ecological risk of particulate metal toxicity comparing our results with the effect range low/median range values (ERL/ERM), and threshold /probable effect level (TEL/PEL), and using potential ecological risk index (RI), toxicity units (TU) and potential acute toxicity (ΣTU_i).

2 MATERIALS AND METHODS

2.1 Study areas

The region under study, *i.e.* El Harrach river and Mazafran river both terminate in the central Algerian coastal zone, a part of the southwestern Mediterranean Sea (Fig. 1).

The first monitoring station is located on the El Harrach river (S1: 36° 43' 51.31" N / 3° 7' 41.35" E). The sediments of El Harrach river are characterized by the presence of clay minerals such as mica-smectite mixed layer minerals, sulfide mineral; quartz; chlorite and calcite (Yoshida *et al.*, 2005). That composition has an important impact on the geochemical behavior of metals in this river.

The second station is on the Mazafran river (S2: 36° 39' 34.20" N / 2° 48' 36.57" E). The annual average flow rates of the Mazafran river range from 1 to 10 m³ s⁻¹, with an estimated annual average input of 10¹⁴ m³ s⁻¹ (Bouras *et al.*, 2021). Bouras *et al.* (2020) illustrate the seasonal variations of water flow; *e.g.* during the winter (350 m³ s⁻¹) and spring (170 m³ s⁻¹), high water flow rates are seen; whereas in the fall and summer, the river fluxes are less than 100 and 10 m³ s⁻¹, respectively. The Mazafran River watershed is composed of micaceous sandstone, metamorphosed limestone, detritic sediments and silty clays, which are the main source of the solids transported by Mazafran river.

In general, El Harrach and Mazafran basins have a typical Mediterranean two-season climate. Water inflow is fairly significant during the winter season, and sometimes quite violent floods occur, particularly in early autumn. During the summer, the river becomes a mere stream of water, fueled primarily by anthropic discharges (Bouras *et al.*, 2021).

Sampling was carried out in the downstream portion of each watershed in order to assess the pollutant trace element load (Pb, Cd, Cu, Zn, Cr, Ni, Co, Mn, As, V and Fe) that enters the sea, with a major condition governing the choice of sampling stations; *i.e.* the collected samples must be free from marine influence. At each of the two stations (1 & 2), two samples (one for particulate and one for dissolved metals) were collected twice per month over a period of one year from August 2017 to July 2018 giving a total of 96 samples for analyses.

2.1 Environmental parameters

Temperature, pH, and electric conductivity were all measured *in situ* using a multi-parameter Testr 35 series (PCSTestr 35) instrument that was calibrated for each sampling campaign. Rainfall was not included among these parameters because 1) reliable data are not available for these two river basins at that time, and 2) the semi-monthly sampling strategy would not be of sufficient frequency to obtain high resolution data needed.

2.2 Sampling strategy

Water samples were collected manually twice per month at the same station with a 1 L polyethylene bucket and a rope on a bridge. Afterwards, samples for dissolved trace metals analysis were filtered through a 0.2 μm syringe filter into 30 ml vials and acidified with nitric acid (3 drops of HNO_3 to make a pH of ~ 1). They were then stored in a freezer until analysis (Ollivier *et al.*, 2010).

For particulate trace metals, samples were collected in decontaminated polyethylene bottles and preserved at 4 °C. In the laboratory, 100 ml of the samples was rapidly filtered through pre-weighed 0.2 μm cellulose acetate filters (SARTORIUS). The filters with the suspended particulate matter (SPM) were weighed to determine the SPM concentration before acid digestion (Radakovitch *et al.*, 2008).

2.3 Chemical treatments and analysis

Eleven selected trace elements (Pb, Cd, Cu, Zn, Cr, Ni, Co, Mn, As, V and Fe) in the SPM were determined after a microwave acid digestion conducted in acid-cleaned Teflon tubes. For the samples collected on acetate filters, the filters were previously desiccated to estimate

the SPM weight, and they were then humidified in order to insert them into the tubes. All reagents were of analytical grade. Three mL of HCl (34 %), 4 mL HNO₃ (67 %), 20 drops of H₂O₂ (35%), and 0.5 mL of HF (47-51 %) were progressively added into the tubes. The mixtures were digested on a hotplate at 170 °C (2 hours), and then 250 °C for about 2 days. The sample solutions were all clear, indicating that the SPM samples had completely decomposed. The solutions were then diluted with ultrapure Milli-Q water and analyzed using an ICP-MS (Perkin Elmer, NexION 300X) against calibration curves and an internal standard of rhodium solution, except for the Fe which was analyzed by ICP-AES (Perkin Elmer 4300 dv) at the CEREGE Laboratory in France. The samples for the analysis of dissolved trace metals in both rivers were directly transferred into 15 ml vials and then analyzed by ICP-MS (Delile *et al.*, 2020; Ollivier *et al.*, 2010; Radakovitch *et al.*, 2008).

2.4 Quality control

Repeated analysis of procedural blanks and reference sediments such as: Light Sandy Soil n° 7002, STSD-3 (Stream Sediment Reference Materials) and MESS-4 (Canadian Certified Reference Materials Project) were used during the analysis and all results were consistent with the certified values (*i.e.* between 85 and 115% of the values certified).

2.5 Statistical analysis

All numerical data are presented as the mean ± standard deviation (mean ± s.d. and n=3). The Shapiro–Wick test was used to test the normal distribution of data.

To analyze the effect of temporal variation, using the Duncan’s post hoc (ANOVA), all the measured parameters, *e.g.* the environmental parameters, dissolved and particulate metal concentrations were tested and the significant differences considered at ($p < 0.05$) followed by a Tukey HSD test (honestly significant difference: pairwise comparison).

To identify the correlation between environmental parameters, dissolved and particulate metals concentrations, the Pearson’s correlation matrix was used.

2.6 Solid-solution partitioning

To define the solid-solution partitioning of trace elements, the distribution coefficient, K_d , was employed (Tomczak *et al.*, 2019) and expressed on a logarithmic scale (Pavoni *et al.*, 2022):

$$\text{Log } K_d = \text{Log} \left(\frac{C_s}{C_l} \right) \quad [L/kg]$$

where C_s (mg/kg) and C_l (mg/l) are the metal concentrations of any metal C in suspended particulate matter and in the dissolved phase, respectively, under the assumptions of equilibrium (Ollivier *et al.*, 2011).

2.7 Environment risk assessment of particulate metals

The geo-accumulation index (Igeo) introduced by Muller (1969) was used to assess the degree of trace metal pollution in suspended particulate matter (SPM) (Guendouzi *et al.*, 2021; Turner and Millward, 2000), which is depicted below:

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

Where C_n is the concentration of trace metals and B_n is the geochemical background value. In this paper, we use a local background value (Inal *et al.*, 2018). To account for any variations in the background values, a factor of 1.5 is applied.

Muller (1969) proposed seven Igeo classes, corresponding to practically unpolluted (Igeo < 0), moderately polluted (1–2), strongly polluted (3–4) and extremely polluted (> 5). The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index.

The enrichment factor (EF) is frequently used to identify metals from both anthropogenic and natural sources. The EF can be expressed as follows (Simex and Helz, 1981):

$$EF = \frac{(C_n/C_{Fe})_{sediment}}{(C_n/C_{Fe})_{reference}}$$

Where (C_n/C_{Fe}) is the ratio of the measured concentrations of trace metals in sediment or for reference concentrations. In this study, iron (Fe) was used as the conservative tracer (Schiff and Weisberg, 1999).

Seven enrichment classes based on EF values (Kouidri *et al.*, 2016) were considered; i.e. no enrichment (EF<1), minor enrichment (1 < EF < 3), moderate enrichment (3< EF < 5), moderately severe enrichment (5 < EF < 10), severe enrichment (10 < EF < 25), very severe enrichment (25 < EF < 50) and extremely severe enrichment (EF> 50). Where EF > 1.5, that indicates an important proportion of trace metals is delivered from non-crustal materials, *e.g.* pollution drainage (Zhang and Liu, 2002).

The pollutant load index (PLI) provides a simple and comparative way to assess the toxicity of suspended particulate metal (SPM) for each site, as introduced by Tomlinson *et al.* (1980).

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$$

$$\text{With } CF = C_n/B_n$$

where CF is the contamination factor, C_n is the concentration of trace metals and B_n is the geochemical background value. Thus a PLI value > 1 suggests that the site is contaminated, whereas a $PLI \leq 1$ indicates a lack of pollution (Arienzo *et al.*, 2020; Guendouzi *et al.*, 2021)

2.8 Ecological risk assessment of particulate metals

The potential ecological risk index (RI) developed by Håkanson (1980) is an approach to estimate the level of risk that trace metals pose to organisms. The RI is calculated using the equation as follows:

$$RI = \sum Er_i = \sum C_f^i \times T_r^i$$

Where, Er_i is the risk factor. C_f^i is the contamination factor of the selected particulate metal i , and T_r^i is the toxic response factors for metal i . The C_f^i value is equal to 1 for Mn and Zn; 2 for Cr and V; 5 for Pb, Co, Ni and Cu; 10 for As; and 30 for Cd (Xu *et al.*, 2008).

According to Håkanson (1980), there is a range of four cases for RI values: low (< 150), moderate (150–300), severe (300–600) and serious risk (> 600). To evaluate the degree of particulate metal contamination in the river water, which can adversely affect the aquatic organisms, the sediment quality guidelines (SQGs) can be used for this assessment. The particulate metal concentrations were thus compared with TEL/PEL guidelines (MacDonald *et al.*, 2000) and those for ERL/ERM (Long *et al.*, 1995).

The potential acute toxicity ($\sum TU_i$) of particulate metal contaminants is defined as the sum of the individual toxic units which, in turn, are defined as the ratio of the concentration of the particulate metal analyzed (C_i) to its PEL value (PEL_i) (Pedersen *et al.*, 1998).

$$\sum (TU_i) = \sum \left(\frac{C_i}{PEL_i} \right)$$

According to the results from bioassay tests Pedersen *et al.*, (1998), a sum $\sum TU_i$ value below 4 indicates no significant toxic effects (mortality) by the metals.

3 RESULTS AND DISCUSSION

3.1 Environmental parameters

Environmental parameters such as water temperature, pH, conductivity and suspended particulate matter were recorded semi-monthly in the El Harrach and Mazafran rivers (Fig. 2; Suppl. Table 1). The values of semi-monthly variation of environmental parameters were significantly higher ($p < 0.001$) in the El Harrach and Mazafran rivers.

During the study period (August, 2017 to July, 2018), water temperature (Fig. 2a) shows the same semi-monthly variation in the two rivers ($p > 0.05$), with a clear seasonal cycle of water temperature, *i.e.* water temperature followed the fluctuation of atmospheric temperature, which showed a maximum in summer and a minimum in winter. A maximum difference in temperature between the two rivers (2.9 °C) was observed in January with the higher temperature in El Harrach river. According to the temporal pH values (Fig. 2b), the waters from the two rivers are alkaline, with averages of 7.80 ± 0.25 (range 7.43-8.47) and 7.90 ± 0.20 (range 7.52-8.30) measured in El Harrach and Mazafran rivers, respectively ($p > 0.05$). Two peaks of pH were recorded in both rivers during the same period (March and April 2018) ($p > 0.05$). The average conductivity values in both river waters was 1474 ± 590 $\mu\text{s}/\text{cm}$ (range 676-3130) and 1245 ± 300 $\mu\text{s}/\text{cm}$ (range 531-1649,) in the El Harrach and Mazafran river ($p < 0.001$), respectively (Fig. 2c). The greater difference in conductivity between the two rivers was recorded in June ($p > 0.05$), which can be explained by the entrance of the mouth of El Harrach river in the sea and the resultant intrusion of sea water, *i.e.* the environment becomes more and more estuarine (Conductivity is increased) at that time. The suspended particulate matter (SPM) concentrations (Fig. 2d) ranged between 35-1888 mg/l in El Harrach river and 47-2197 mg/L Mazafran river ($p > 0.05$). We observed a seasonal trend with higher values of SPM at the end of October 2017 in Mazafran river, and from February to April in both rivers ($p > 0.05$). Typically, SPM ranged from 30 to 165 mg/L ($p > 0.05$), except for the high peaks (> 300 mg/L) measured during winter and spring in both rivers. According to Bouras *et al.* (2021), the suspended solids flow rate is 42 t/km²/year in Mazafran river. In comparison to the other Algerian rivers, this flow rate is quite low which is probably linked to the crystalline rocks (eruptive and metamorphic) found in the upstream portions of the rivers. Thus the observed high levels of SPM are likely caused by leaching from adjacent farmland soils.

3.2 Trace metal levels

The certified concentrations (*Cert. Val.*) and measured concentrations (*Meas. Val.*) of the trace metals in three standard reference materials are listed in Table 1. The dissolved and particulate metal concentrations in El Harrach and Mazafran rivers during the monitoring program, from August 2017 to July 2018, are summarized in Fig. 3 and Suppl. Tables 2-5.

3.2.1 Dissolved trace metals

Typically, the range of concentrations is a better parameter to represent metal quantification than the arithmetic mean, since the peak concentration of metal (*e.g.*, Ni and Pb) influenced their mean concentration. The dissolved metal concentrations in El Harrach river varied by four orders of magnitude (Fig. 3a; Suppl. Table 2) in which Fe, Mn and Zn were the highest [0, 350] µg/L except in September (438.67 ± 6.58 µg Zn/L), followed by Cr, Cu and Ni [0, 16] µg/L except in October (797.70 ± 24.73 µg Ni/L); followed by Co, As, V and Pb [0, 4] µg/L except in August and June with 12.23 ± 0.10 and 11.71 ± 0.26 µg Pb /L, respectively. Cd was the lowest with 0-250 ng/L except in October (422.00 ± 31.23 ng/L). During the monitoring program in El Harrach water, the toxic metal Cd (422.00 ± 31.23 ng/L) has a maximum concentration in October, whereas concentrations of Pb (12.23 ± 0.10 µg/L) and As (3.88 ± 0.17 µg/L) were a maximum in August and November, respectively.

In the Mazafran river, the dissolved metal concentration varied by six orders of magnitude (Fig. 3b; Suppl. table. 3) in which Fe and Zn were the highest [0, 400] µg/L, followed by Mn [15, 250] µg/L, Ni [0, 14] µg/L except in August (118.97 ± 3.57 µg Ni/L) and in October (87.61 ± 1.93 µg Ni/L), Pb, Cu, Cr, As and V [0, 7] µg/L and Co [0, 2] µg/L, Cd was the lowest at 0-60 ng/L except in August (173.00 ± 17.65 ng/L), October (111.00 ± 13.54 and 258.00 ± 24.51 ng/L), November (134.00 ± 20.77 ng/L) and May (98.80 ± 19.56 ng/L). The levels of dissolved toxic metals in the Mazafran river are highest for: Pb (4.98 ± 0.02 µg/L) and Cd (258.00 ± 24.51 ng/L) in October; and for As (5.92 ± 0.36 µg/L) in September.

The highest concentrations of dissolved metals (*e.g.* Pb, Cd, Ni and Zn) in both rivers were observed between June and October. Since the rainfall is very low in this region, the leaching phenomena is negligible and the river flows are not significantly altered during this period. In conclusion, the peak concentrations of these dissolved metals are caused by anthropogenic activities rather than the geochemical composition of the local geology.

The dissolved Pb, Cd, Cu, Zn, Cr and Ni concentrations are more available in El Harrach river than in Mazafran river, however, the dissolved concentrations of Co, Mn, As, V and Fe are

more available in the Mazafran river ($p < 0.001$). Overall, the dissolved metal concentrations in both rivers followed a similar descending order, *i.e.* $Fe > Mn > Zn > As > Cu > Cr > V > Pb > Co > Cd > Ni$ ($p > 0.05$).

3.2.2 Particulate trace metals

Particulate metal in El Harrach river varied by six orders of magnitude (Fig. 3c; Suppl. table. 4) in which Zn is the highest [100-950] $\mu\text{g/g}$; followed by Mn [100, 450] $\mu\text{g/g}$, Pb, Cr, Cu and V [0, 250] $\mu\text{g/g}$, Fe, Ni and As [0, 50] $\mu\text{g/g}$. Co is less than 16 $\mu\text{g/g}$ and the Cd was the lowest at < 2 $\mu\text{g/g}$. In this river, peak concentrations of particulate toxic metals such as Pb (205.50 ± 8.40 $\mu\text{g/g}$) and Cd (1.46 ± 0.06 $\mu\text{g/g}$) were measured in November, and the As (29.21 ± 0.76 $\mu\text{g/g}$) is measured in December.

A four orders of magnitude difference is observed for the levels of particulate metals in Mazafran river (Fig. 3d; Suppl. table. 5), in which the Mn and Zn concentrations were the highest [100, 600] $\mu\text{g/g}$, followed by Pb, Cr, V and Cu [10, 200] $\mu\text{g/g}$, with the exception of April and May, when the highest levels recorded were for Cu with 328.46 ± 3.94 and 306.17 ± 3.67 $\mu\text{g Cu/g}$, respectively, and 5-70 $\mu\text{g/g}$ for Fe and Ni. In contrast, Co, As and Cd concentrations were the lowest at 0-30 $\mu\text{g/g}$ for that time. In the Mazafran river, the particulate toxic metal concentrations such as Pb (127.36 ± 1.53 $\mu\text{g/g}$), As (26.87 ± 1.10 $\mu\text{g/g}$) and Cd (13.28 ± 0.25 $\mu\text{g/g}$) are higher in April, November, and December, respectively.

In general, the particulate Pb, Zn, Cr and Mn are more available in El Harrach river ($p < 0.001$), and those for Cd, Cu, Ni, Co, Fe, As and V are more available in Mazafran river ($p < 0.001$). According to the mean concentrations of particulate metal in both rivers, their concentrations decreased in the following order $Fe > Zn > Mn > Cr > Cu > V > Pb > Ni > As > Co > Cd$ ($p > 0.05$).

The abundance of Fe, Zn and Mn, reflects the geologic composition of the watershed. Furthermore, the particulate metals do not contribute significantly to the contamination of sea water. Yoshida *et al.* (2005) observed the 'Natural Buffer' effect in El Harrach river. In fact, a portion of the metal associated with suspended particles was cation-exchanged by clay minerals such as the smectite-mica mixed layer and was deposited on the estuary bottom sediment. Furthermore, biomineralization by cyanobacteria contributes to metal immobilization (*ibid*). In fact part of the particulate metals are fixed and cemented in the

sediments due to chemical changes associated with early diagenesis in sediments (Helali *et al.*, 2016).

3.2.3 Correlation analyses

In order to identify the relationships between the environmental parameters and dissolved and particulate metal concentrations in the two rivers, the correlation coefficients were calculated (Suppl. Table 6).

A significant negative correlation is shown between temperature and particulate metals, *e.g.* T & Pb (-0.32); T & Cr (-0.35); T & As (-0.44) T & Fe (-0.45); T & Ni (-0.47); T & Co (-0.49); T & Mn (-0.56); and T & V (-0.56). Therefore, a decrease in river water temperature is accompanied by an increase in the metal content of the SPM.

A highly significant positive correlation was found between particulate Co and Ni (0.90), and these two particulate metals (Co and Ni) have a significant positive correlation with certain dissolved metals such as Mn (0.32), As (0.29) and V (0.44); thus particulate Co and Ni have a similar behavior as dissolved Mn, As and V.

A significant positive correlation is also evident between dissolved Co and dissolved and particulate Mn (0.68 and 0.39), Ni (0.36 and 0.51), As (0.54 and 0.53) and V (0.65 and 0.31), respectively. Dissolved Co also has a positive correlation with dissolved Cu (0.50), Zn (0.45) and Cd (0.40), as well as with particulate Fe (0.46) and Pb (0.29). Dissolved Co displays the most correlations with the other dissolved and particulate metal in this study.

A highly significant positive correlation was found between dissolved Fe and Mn (0.71). Both of these dissolved metals have a highly significant positive correlation with Co (0.93 and 0.73), Ni (0.89 and 0.65), As (0.83 and 0.82) and V (0.76 and 0.57). Thus it appears that dissolved Fe, Mn, Co, Ni, As and V have similar behaviors in the El Harrach and Mazafran rivers. With respect to particulate Ni, a highly significant positive correlation is noted with the particulate metals Co (0.90), Fe (89), As (0.78), and V (0.76), respectively.

In this study, except for particulate Pb and Cu, the dissolved and particulate Cd showed that there was a very low significant correlation between those phases and the other metals ($-0.15 < R < 0.08$). To a lesser extent, no significant correlation ($R = 0$) was found between dissolved Cd and Cu, and particulate Cd and Cr as well.

3.2.4 K_d

The distribution of metals in the rivers between different phases, *i.e.* dissolved and particulate forms, affects their transport to the ocean and provides important information on their interactions with biota, their biogeochemical cycling and elemental budgeting (Fang *et al.*, 2022; Prabakaran *et al.*, 2020). Log K_d could be considered an important index to better understand circulation of contaminants among different environmental compartments (Pavoni *et al.*, 2020).

For all metals analyzed (Fe, Mn, Pb, Cr, Co, Ni, Cu, Zn, As, Cd, and V), the calculated Log K_d values were between 2 and 6 (Suppl. Tables 7 and 8), this range of values are typical for freshwaters (Tomczak *et al.*, 2019). In both river's water, Fe, Pb, and Cu had the highest Log K_d values, followed by Cr, indicating that these elements are highly reactive to the SPM. The same observation reported in Isonzo/Soča river (Gulf of Trieste, northern Adriatic Sea) by Pavoni *et al.* (2020). According to Tomczak *et al.* (2019), the metals characterized by high Log K_d values form stable complexes with the particulate phase, which implies that the particulate metals are predominant at the both river.

The Mn has the lower Log K_d values, confirming its affinity to the dissolved phase in both rivers. Manganese is a redox sensitive element, and the fact that particulate Mn increases when total dissolved Mn decreases and vice versa is likely due to the relative prevalence of oxidation and reduction or dissolution processes (Pavoni *et al.*, 2020).

Among the 11 metals, there were less than 10 % (5 of 48) of all samples exceeding the 7 Log K_d value, *i.e.* the Log K_d calculated for Fe on March 27th and April 16th in both rivers, and the Log K_d of Cu for July 26th in Mazafran river. Two values of Log K_d (below 2) were recorded for Ni during the October 23rd and August 8th sampling in El Harrach and Mazafran rivers, respectively.

The Log K_d values are known to be affected by certain environmental factors, such as pH, dissolved and particulate organic carbon, salinity and temperature (Alkhatib *et al.*, 2016) as well as masse/volume ratio (Barreto *et al.*, 2011) and particle sizes (Fan *et al.*, 2017).

3.2.5 Overall comparison

The average concentrations of the dissolved metals Cu, Zn, Co, V and Fe in both rivers are of the same order of magnitude; however, a difference between the average concentrations of particulate Cd, Cu, Zn and Cr is observed in these rivers.

Unlike the dissolved Cu, the average dissolved concentration of the other metals analyzed in El Harrach and Mazafran rivers are higher than those reported in a compilation of global averages of dissolved metals for rivers (Gaillardet *et al.*, 2003). On the other hand, compared to a similar global compilation of particulate trace metals in fresh waters (Viers *et al.*, 2009), the average concentrations of particulate Pb, Ni, Co, Mn, As, V and Fe in both rivers were lower than those considered as worldwide average values.

3.3 Environment risk assessment of particulate metals

The geoaccumulation index (I_{geo}) values for the El Harrach river (Suppl. Table 9) decreased in the following order: Zn > Cu > Pb > Cr ~ Cd > Mn ~ As > Co ~ Ni > Fe > V. In the Mazafran river (Suppl. Table 10), the I_{geo} values decreased as follows: Cu > Zn > Pb > Cd > Mn ~ As > Ni > Co > Cr > Fe > V. According to Muller (1969), the computed I_{geo} values for these Algerian rivers would indicate that both are slightly polluted by particulate Zn and Cu ($0 < I_{geo} < 1$), and there is no indication of pollution by the other particulate metals ($I_{geo} \leq 0$).

According to the enrichment categories established by Birch (2003), in El Harrach river (Suppl. Table 11) there is a severe enrichment of particulate Zn ($10 < EF < 25$), a moderately severe enrichment of particulate Cu ($5 < EF < 10$), a moderate enrichment for particulate Pb, Cr and Cd ($3 < EF < 5$) and only a minor enrichment ($EF < 1$) of particulate As, Co, Ni, Fe and V. In the Mazafran river (Suppl. Table 12) data indicate a moderately severe enrichment for particulate Cu, Zn and Cd, a moderate enrichment of particulate Pb, and a minor enrichment for particulate Mn, As, Co, Ni, Cr and V. Furthermore, very severe enrichments of particulate Cd, 41.52 and 62.80 were observed in the Mazafran river on 10 April and 10 May, respectively, along with severe enrichments of particulate Cu, 22.84 and 21.29, and a moderately severe enrichment of particulate Zn (9.56 and 5.94) and Pb (8.86 and 6.32), respectively, on the same days (Suppl. Table. 12). Thus these findings give a clear indication of anthropogenic pollution for certain trace metals in both rivers.

In addition, except for particulate Co and V concentrations, according to EF criteria of Zhang and Liu (2002) and Arienzo *et al.* (2020), a significant portion of all the particulate metals analyzed in our study are coming from anthropogenic sources ($EF > 1.5$), *i.e.* they originate from non-crustal inputs. In fact, the environment of El Harrach river is greatly disturbed and highly varied. The river water is heavily contaminated and emits foul-smelling fumes. This degree of pollution can be attributed to inflowing wastewaters from the industrial zones of El Harrach, Baba Ali, and Oued Smar directly into the river without appropriate treatment.

Moreover, the Mazafran river receives many discharges of wastewater and discharges from industrial units using metal-based dyes (Cd, Cr, etc.). Kolea's water treatment plant, which is located upstream of the river, could be a source of POC (Bouras *et al.*, 2021). Furthermore, the adjacent agricultural lands are fertilized using plant protection products such as organochlorines, nitrate-based fertilizers, phosphates and potassium and copper-based products.

However, in contrast, the mean values of the pollution load index (PLI) were similar with 0.88 ± 0.35 in El Harrach river and 0.85 ± 0.36 in the Mazafran river. Both mean values are below 1, which would suggest a lack of pollution caused by the particulate metals analyzed (Suppl. Table. 13 and 14). Interestingly, such indexes and criteria for usage that have been developed do not always lead to the same conclusion.

3.4 Ecological risk assessment of particulate metals

The mean values of Eri calculated for El Harrach river decreased in the following order: Cd (35.14) > Cu (10.84) > Pb (7.86) > As (6.99) > Zn (3.64) > Ni (3.06) > Co (2.93) > Cr (2.17) > V (0.91) > Mn (0.37); while in the Mazafran river the Eri mean values decreased as follows: Cd (73.58) > Cu (14.51) > As (7.93) > Pb (7.55) > Ni (3.34) > Co (3.21) > Zn (2.32) > Cr (1.21) > V (0.98) > Mn (0.73). A high risk of Cd (87.59) was observed in November and a moderate risk of the same metal was recorded from December to April in El Harrach river. In the Mazafran river, during the sampling periods of 10 April and 10 May 2018, a potentially disastrous risk of pollution by Cd, 526.83 and 796.97, respectively, and a moderate risk by Cu, 48.30 and 45.02, were noted (Suppl. Table. 15 and 16).

According to the mean values of the potential ecological risk index (RI), the SPM from both rivers has a low risk ($RI < 150$), *i.e.* with $RI = 74.27 \pm 33.34$, range 36.18-139.78, and $RI = 114.60 \pm 198.04$, range 34.28-871.09 in the El Harrach and Mazafran rivers, respectively.

Two peaks of RI were recorded in the Mazafran river during 10 April and 10 May 2018 with RI values of 614.41 and 871.09, respectively. Consequently, the SPM during this observational period presented a very high ecological risk ($RI > 600$). These two peaks are influenced by the maximum Eri values of Cd (526.83 and 796.97), Cu (48.30 and 45.02) and Pb (18.73 and 13.37), respectively. It is noteworthy that during these two sampling periods, the concentrations of particulate Cd were 700 and 1080 times higher than the overall mean concentration of that particulate metal (Suppl. Table. 15 and 16).

In El Harrach and Mazafran rivers, the mean concentrations of particulate Ni, As and Cd are below the effects range low (ERL) values for these metals. The particulate Pb and Cu are between the ERL and the effects range median (ERM) values proposed by Long *et al.* (1995). The particulate Zn concentration is considerably above the ERM value in El Harrach river (Fig. 4). In the probable-effects ranges defined by ERL and ERM values (*ibid*), the incidence of adverse effects of particulate Ni, As and Cd are considered to be very low “minimal effects” with values of 1.9%, 5.0% and 6.6%, respectively. Finally, there is a 33% likelihood of the incidence of biological effects from the toxicity of Pb and Zn in both rivers.

In the Mazafran river, the mean concentration of particulate metals such as Pb, Cr, Ni, Cu, Zn, As and Cd is between the threshold effects level (TEL) and probable effects level (PEL) values published by Macdonald *et al.* (1996). In El Harrach river, the mean concentration of particulate Cd was near the TEL value, whereas the mean concentrations of particulate Pb, Ni, Cu and As are between the TEL and PEL values (Fig. 4). In contrast, the mean concentrations of particulate Cr and Zn in the Harrach river are above the PEL values, with 52.9% and 64.8% effects in the probable effects range, respectively.

Regarding the Potential acute toxicity (ΣTU_i) values (Suppl. Table. 17 and 18) in El Harrache river (4.95) and Mazafran river (4.32), significant toxic effects by a mixture of metals (*e.g.* Pb, Cr, Ni, Cu, Zn, As and Cd) are possible ($\Sigma TU_i > 4$) based on results from the amphipod *Corophium volitator* bioassay test realized by Pedersen *et al.* (1998).

The contribution of monomial particulate trace metal (TU_i) to the sum of the toxic units (ΣTU_i) shows the major toxicity contributions are from particulate Cr (30.40%) followed by particulate Zn (21.51%) in El Harrach river. Nevertheless, regarding the important contribution of Cr in the sum of the toxic units ΣTU , and given its carcinogenic character, this metal's inputs into the marine environment via this river should be better monitored, and its real toxicity should be investigated. The toxicity contributions by the other particulate metals are below 20% in both rivers (Fig. 4). The contributions of particulate Pb, Ni, Cu, As and Cd to the ΣTU_i are lesser in El Harrach river than in the Mazafran river. In contrast, the particulate Cr and Zn make a greater contribution in the Mazafran river compared to the El Harrach river. The particulate metal contribution (%) of the toxic units (ΣTU_i) follows the order Cd < 5% < Cu < 10% < Pb < Ni < As < 15% < Zn < 25% < Cr < 35% in El Harrach river, compared to the order in the Mazafran river, *i.e.* Cd < 10% < Pb < Cu < As < 15% < Cr < Ni < Zn < 25%.

4 CONCLUSION

The waters of El Harrach and Mazafran rivers are alkaline, characterized by a seasonal fluctuation of temperature and a content of suspended particulate matter ranging from 30 to 165 mg/l. Iron, Mn and Zn are the metals most available in water and SPM, and the dissolved Co has a similar behavior as all the other dissolved and particulate metals analyzed in both the rivers. With respect to the computed Log K_d values, all the metals analyzed in this study form stable complexes with the SPM.

With regard to the environment risk assessment, a 'no pollution category' ($PLI < 1$) was found for the particulate metals examined, unlike a slightly polluted situation ($0 < I_{geo} < 1$) resulting from particulate Zn and Cu in both rivers. All the particulate metals analyzed, with the exception of Co and V, most likely originate from anthropogenic sources ($EF > 1.5$).

For the ecological risk assessment, a low risk ($RI < 150$) was observed in both rivers with a major contribution of Cd and Cu in the calculation of this index. In El Harrach river, particulate Zn concentration was above the ERM and the PEL values, with 64.8% effects in the probable effects range. Furthermore, the particulate Zn and Pb have a 33% likelihood of toxicity for the incidence of biological effects in both rivers. According to Potential acute toxicity (ΣTU_i) values, significant toxic effects ($\Sigma TU_i > 4$) are noted from a mixture of metals (*e.g.* Pb, Cr, Ni, Cu, Zn, As and Cd), with a major metal contribution (between 14.5 and 30.4 %) of toxic units (ΣTU_i) mainly from particulate Cr, Zn and Cd.

Overall, these results and assessment essentially indicate that the two rivers basically are not substantially polluted by the metals analyzed, with only a slight contamination caused by the Pb, Cr and Zn in the El Harrach river.

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FIGURES CAPTIONS

Figure 1: Study area.

Figure 2. Semimonthly environmental parameters recorded in the El Harrach river and Mazafran river (August 2017-July 2018). **a.** river water temperature, **b.** pH, **c.** conductivity, **d.** suspended particulate matter (SPM).

Figure 3. Semimonthly levels of dissolved and particulate metals in El Harrach and Mazafran rivers.

Figure 4. Ecological risk assessment of particulate metals: **a.** Mean concentration of particulate metals ($\mu\text{g/g}$) in El Harrach and Mazafran rivers, ERL, ERM (Long *et al.*, 1995), TEL and PEL values (MacDonald *et al.*, 2000); **b.** Particulate metal contribution ($\text{TU}_i / \Sigma\text{TU}_i$) (%) to the Potential acute toxicity value (ΣTU_i).

TABLE

Table 1. Analysis of certified reference materials: certified values (Cert. Val.) and measured values (Meas. Val.) (mean \pm s.d. $\mu\text{g/g}$ d.w.)

Metals	STSD-3		MESS-4		Light Sandy Soil n° 7002	
	Cert. Val.	Meas. Val	Cert. Val.	Meas. Val	Cert. Val.	Meas. Val
Pb	40	44.74 \pm 1.07	21.50 \pm 1.20	19.44 \pm 0.49	58.90 \pm 4.90	56.52 \pm 2.31
Cd	1	1.11 \pm 0.12	0.28 \pm 0.04	0.25 \pm 0.02	0.31 \pm 0.04	0.38 \pm 0.02
Cu	39	35.15 \pm 0.11	32.90 \pm 1.80	29.43 \pm 0.42	29.30 \pm 0.60	30.60 \pm 1.25
Zn	204	214.27 \pm 2.36	147.00 \pm 6.00	145.33 \pm 1.26	69.00 \pm 7.70	78.83 \pm 3.22
Cr	80	61.52 \pm 0.12	94.30 \pm 1.80	81.78 \pm 1.23	179.00 \pm 8.00	178.42 \pm 7.66
Ni	30	30.72 \pm 0.68	42.80 \pm 1.60	36.38 \pm 0.29	42.00 \pm 1.70	50.26 \pm 2.05
Co	16	15.22 \pm 0.20	13.00 \pm 0.80	11.09 \pm 0.15	12.60 \pm 0.90	13.04 \pm 0.53
Mn	2.73	2.75 \pm 0.03	0.30 \pm 0.01	0.28 \pm 0.01	0.95 \pm 0.04	0.68 \pm 0.03
As	28	25.13 \pm 0.75	21.70 \pm 2.80	21.47 \pm 0.44	32.40 \pm 1.90	37.75 \pm 1.54
V	134	125.08 \pm 1.25	216.00 \pm 8.00	199.54 \pm 2.93	54.90 \pm 6.80	60.85 \pm 2.49
Fe	44	41.75 \pm 0.21	39.90 \pm 1.60	36.44 \pm 2.40	-	-

STSD-3: Stream Sediment Reference Materials 3, MESS-4: Canadian Certified Reference Materials Project, and Light Sandy Soil n° 7002.