

Modeling seasonal and spatial contamination of surface waters and upper sediments with trace metal elements across industrialized urban areas of the Seybouse watershed in North Africa

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Abstract Industrialization and urbanization are the main sources of pollutions worldwide and particularly in developing countries. This study aims the determination of anthropogenic inputs with trace metals in aquatic ecosystems at the Plain of Annaba (NE Algeria), which is known as one of the largest industrial areas in Africa.

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Samples of surface waters and upper sediments were conducted in six stations: four in Meboudja wadi and two in Seybouse wadi. Contents of iron, copper, chromium, nickel, zinc, and manganese were measured by atomic absorption spectrophotometry, whereas Cd and Pb were determined using electrothermal atomic absorption spectrometry. Measurements of Hg were carried out using atomic fluorescence. Spatiotemporal variations of metal concentrations were tested using generalized linear models (GLM), whereas the influence of water pollution on sediment contamination was tested with generalized additive models (GAMs). Metal contents measured in surface water and sediments varied differently from upstream to downstream of the study wadis and between seasons. The results showed that the surface water was polluted with high levels of iron, nickel, chromium, lead, and cadmium. Values of the contamination index revealed that the surface sediments were contaminated by iron, chromium, lead, and cadmium. The GAMs indicated that water-phase metal concentrations had no significant effects on trace metal concentrations in the sediment. This suggests that seasonal metal concentrations in water phase, which are measured during the study period (2012) and are time-dependent, contribute increasingly and gradually over time—not immediately—to the accumulation of metals into the sediments. Therefore, the long-term accumulation of metals in the sediments resulted from the continuous discharges of metals in the water phase. The anthropogenic impacts are marked by high contaminations of Meboudja wadi particularly in downstream areas of the steel factory and the nearby industrial areas. The direct industrial discharges into the

water and atmosphere (iron, lead, cadmium) as well as urban disposals and agricultural activities are at the origin of these contaminations.

Keywords Heavy metals · Industrialized and urban areas · Water pollution · Sediment pollution · North Africa

Introduction

Heavy metals are distributed in all abiotic compartments (water, sediment) and biotic (flora and fauna) and are found in soluble, colloidal, and particulate components; mainly in the form of metal cations (Du Laing et al. 2009). Sediments accumulate high concentrations in estuarine ecosystems and wetlands due to their ecological function of pollutant sink; thus, the sediment occupies a key place in studies of the hydrosphere (Sprovieri et al. 2007). Industrialization, urban development, and intensification of agricultural activities are the main causes behind the increase in pressure threatening these environments (Gao and Chen 2012; Varol and Şen 2012). Industries, especially metallurgical mass producing and large metal consuming, salt out, deliberately, in the environment of large amounts of toxic metals such as Pb, Cd, Cu, Zn, Ni, Fe, and Cr. The entry of trace metal elements into aquatic habitats can also be the result of either direct discharges into marine and freshwater ecosystems due to some point source discharges such as factories or other human activities or indirect path such as the case wet or dry landfills (Praveena et al. 2010).

The presence of metals in waters and sediments can induce toxic effects impacting various organs in aquatic organisms resulting in (i) the appearance of abnormal forms such as necrosis, ulceration, and atrophy.; (ii) alteration of cell membranes with signs of oxidative stress; and (iii) perturbations of metabolism, photosynthesis, and DNA repair (Förstner and Wittmann 1981). During the accumulation of trace metals (TM) in human, several metabolic, endocrine, and urinary dysfunctions are manifested. Among these disorders, lead poisoning is one of the most common (Jaishankar et al. 2014). Heavy metals differently affect living beings. Thus, in a polluted habitat, plants show reduced growth, altered metabolism (inhibition of photosynthesis), lower biomass production, and metal accumulation (Nagajyoti et al. 2010). In aquatic invertebrates, the toxic effects of TM are manifested by delayed growth and reproductive disturbance resulting from tissue damage and metabolic alterations (Mance

1987; Rainbow 2002). Fish are affected by behavioral changes and disturbances in spermatogenesis with carcinogenic or mutagenic effects (Mance 1987).

The areas of El-Hadjar and Annaba are among the largest industrial zones in Africa (CNERU 1980). Discharges of wastewaters contaminate the wadis and the littoral environment, and the pollutants can lead to the eutrophication of water resources (Argillier et al. 2013). At very low levels, heavy metals are essential to the development of the life, but at high concentrations, they are toxic (Varol and Şen 2012; Diop et al. 2015) because they cannot be eliminated through biological processes and accumulate in various components of the ecosystem (water, sediment, flora, and fauna). Because of the accumulative effects of TM in plants and in the food chain, they generate serious ecological risks even for human health and well-being (Romić and Romić 2003; Grisey et al. 2010, 2012; Ahmed et al. 2012; Lenoble et al. 2013; Diop 2014).

Anthropogenic activities generating TM emissions are various and mainly related to urbanization, agricultural intensification, and industrial activities, which lead to increased levels of organic pollutants and heavy metals in the soil, air, and water resources (Gueddah 2003; Romić and Romić 2003; Ahmed et al. 2012; Grisey et al. 2012). Moreover, urban wastewaters drain out huge quantities of TM and pollutant materials (Rodier et al. 1996). The hydrological network and the sediments reflect the various physicochemical processes taking place at the scale of the watershed as well as in aquatic environments. Therefore, the sediments represent excellent indicators of water quality due to their capacity to accumulate heavy metals (Calmano et al. 1994).

In addition, industrial activities cause degradations of increasing importance to the quality of ecosystems. This degradation is mainly caused by massive and uncontrolled pollutions, related to natural organic matter and/or industrial synthetic products (Djabri et al. 2009; Ahmed et al. 2012). When industrial pollution is associated with contaminations from agricultural and urban activities, all combined, they affect all compartments of hydrosystems (water, sediments, flora, and fauna) (Débièche 2002; Gueddah 2003).

The purpose of this investigation is to evaluate the levels of contamination by iron, copper, zinc, manganese, chromium, nickel, lead, cadmium, and mercury in the surface waters and surface sediments of Meboudja and Seybouse wadis, which drain off waters into the Mediterranean Sea through the industrial and urban areas of

El-Hadjar–Annaba (Algeria). Since we are interested here in assessing trace metal pollution at stations located along the water stream of wadis, TM concentrations are expected higher near potentially polluting sources (plants or towns experiencing intensive industrial and/or urbanization activities). Regarding the seasonal trends of water/sediment pollutions, TM concentrations are expected to decrease in autumn and winter, but to increase in spring and summer, because of the dilution of TM with the upsurge of water flow following heavy rainfall occurring in winter and autumn. In addition, TM concentrations are expected to increase in spring and summer for the reason that TM are released in the water after the degradation of organic matters of the colloidal and dissolved phases when water temperatures, salinity, and pH increase (Du Laing et al. 2009; Lesven et al. 2009; Diop 2014). In addition, the effect of short-term water pollution on the contamination of the sediment is tested in this survey. Accordingly, this study assesses the state and quality of the watershed of the plain of Annaba (Seybouse watershed), in which natural habitats are experiencing different forms of degradation and pollution resulted from the expansion and intensification of urbanization, industrialization, agriculture, and tourism (Louhi et al. 1998; Belabed et al. 2013a, b).

Material and methods

Study area

The industrial area of El-Hadjar is located at 10 km south of the city center of Annaba (North-east Algeria). It is bypassed in the East by Seybouse wadi, in the North-West by Meboudja wadi, and in the South by Rassoul wadi. This industrial zone is located in the low plain of Seybouse which is limited by the Mediterranean Sea in the North; in the West, the massifs of Belelieta (287 m), Bouhamra (152 m), and Edough (1008 m); in the South, the oriental Numidia massif (1411 m); and in the East, the aquifer system of Annaba-Bouteldja. The climate is Mediterranean humid with more than 600 mm of precipitation per year and an average temperature of 17.3 °C (Table S1). With more than 1.5 M inhabitants, agricultural and industrial activities mostly characterized by the area of Annaba. The study area is located in the final parts of Meboudja and Seybouse wadis between the city of El-Hadjar and the Mediterranean Sea (Fig. 1).

Meboudja wadi, with 14-km length, represents a discharge system of the Lake Fetzara. It crosses the industrial areas of Sidi Amar, El-Hadjar, and El-Bouni and also receives two small wadis: Taiba and Rassoul. With 240-km length, the watershed of Seybouse wadi stretches over 6471 km². The industrial area of El-Hadjar–Annaba comprises five groups of industrial activities of which three are located in the area drained by Meboudja wadi and two in the area of Seybouse wadi. The watershed of Meboudja wadi includes El-Hadjar complex, a megafactory of iron and steel, which produces nearly 2-M tons of steel per year. It also includes the industrial area of Chaïba comprising various factories (mechanics, cement, glass, paper, wood, recycling of ferrous products) and the industrial area of Pont Bouchet integrating various factories (pharmaceutical, plastic, mechanical repairs, recycling of car batteries). Moreover, Meboudja wadi receives domestic wastewaters and disposals from the towns of El-Hadjar, Sidi Amar, and Chaïba. In the drainage area of Seybouse wadi, there are two industrial areas. The first one in the South consists of two tomato paste plants and the second one in the North includes two plants of milk products and metallic equipment. In this part of Seybouse wadi, flow also domestic wastewaters and disposals from El Bouni town (Fig. 1).

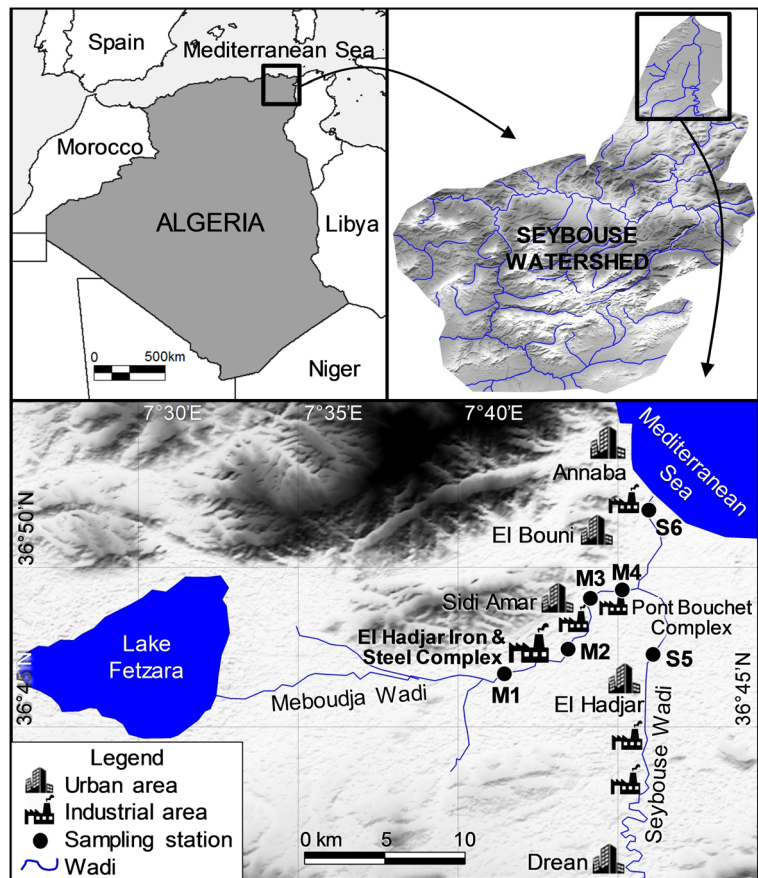
Sampling stations

Six stations were sampled through the study area (Fig. 1). Four stations are selected along Meboudja wadi according to their location towards industrial and urban areas: (i) station M1 (07° 39' 20.5" E; 36° 46' 9.84" N) is located upstream of the iron and steel El-Hadjar complex; (ii) station M2 (07° 44' 0.03" E; 36° 48' 51.5" N) downstream the later complex; (iii) station M3 (07° 53' 6.02" E; 36° 52' 7.27" N) at the exit of the industrial area of Chaïba; and (iv) station M4 (07° 45' 0.71" E; 36° 54' 41.4" N) is situated near the industrial area of Pont Bouchet, whereas two stations belong to Seybouse wadi: (v) station S5 (07° 47' 0.01" E; 36° 54' 17.7" N) is located upstream the adjunction point with Meboudja wadi and (vi) station S6 (07° 46' 0.66" E; 36° 51' 6.47" N) downstream at approximately 1 km from its embouchure in the Mediterranean Sea.

Sampling and analysis of surface waters

From autumn 2011 to summer 2012 and for each season, surface waters and upper sediments of each station

Fig. 1 Geographic distribution of the sampling stations within the industrialized urban area located downstream of Seybouse watershed in northeast Algeria



were seasonally sampled using standard sampling procedures. Samples were collected at the mid of October, February, April, and July for the seasons autumn (2011), winter spring, and summer (2012), respectively. Water samples were conducted at a depth of 50 cm in deep water current or at semi-depth in shallow waters (Rodier et al. 1996). Samples were collected in decontaminated polyethylene bottles. When measurements were not carried out immediately, samples were preserved at 4 °C.

Water samples were acidified using HNO_3 ($D = 1.4 \text{ g/cm}^3$) to reach a pH lower than 2. Using a vacuum pump, 0.5% (v/v) was filtered with a SARTORIUS membrane of 0.45 μm porosity and then preserved at 4 °C prior to TM analysis. Contaminations by Fe, Cu, Cr, Ni, Zn, and Mn were measured using atomic absorption spectrophotometry, whereas Cd and Pb with electrothermal atomic absorption spectrometry (PerkinElmer A Analyst 100). Measurements of Hg were carried out following “International Atomic Energy Agency (IAEA) and United Nations Environment Program (UNEP)” (IAEA–UNEP) method (IAEA

1997, 2001) using cold vapor atomic fluorescence spectrometry in presence of stannous chloride. Results were compared to the reference values of the European Community (EC) (Débièche 2002).

Collection and analysis of upper sediments

Samples (~ 500 g) of fine-grained materials were scraped from the surface sediments with a plastic shovel. Sediment samples were collected concurrently with water samples at a frequency of one sample per season and per station. The topmost centimeters of sediment that we sampled represent the most recent deposit that provides accurate assessment on the spatial and temporal changes in TM contamination. Samples were collected in polyethylene containers and transported in a cooler box to the lab where they were stocked at 4 °C until analysis. After drying, crushing, and sieving, sediment samples were mineralized through a wet process by acid attack in order to eliminate organic materials (AFNOR 1986).

A sample of 0.5 g of sediment, with fractions less than 63 μm , was added to a mixture of pure acids $\text{HNO}_3/\text{HF}/\text{HCl}$ (1 v/1 v/2 v). The mixture was heated at 150 °C for 2 h and then evaporated to almost dryness. Mineralized residues were submitted to successive rinsing in bi-distilled water, filtered without ash using a Whatman filter (0.45 mm), and then supplemented to a final volume of 100 mL. Contents of Pb, Cd, Cr, and Cu were measured using atomic absorption spectrophotometry with graphite furnace, whereas contents of Zn, Ni, and Fe were determined with flame atomic absorption spectrophotometry. Validity of the analytical methods was checked using a reference sediment sample from a Canadian lake (Lake Sediment No. LKSD-1) by (i) CANMET that certified TM contents that were given after extraction and (ii) external control using several inter calibrations (IAEA 1997, 2001). The minimum detection limits for heavy metals in the sediment were 0.06, 0.02, 0.01, 0.04, 0.03, 0.05, 0.04, 0.02, and 0.06 mg/kg for Pb, Cd, Hg, Fe, Cu, Zn, Mn, Cr, and Ni, respectively.

Evaluation of index of contamination (IC)

Reference (or guide) values used in this study for surface sediments are those of the “Agence du Bassin Rhône Méditerranée Corse” (ABRMC 1991). The index of contamination (IC) represents the ratio between the reference value of a given heavy metal and its content in the studied sediment. If IC is lower than 3, the sediment is considered of class 1 (not contaminated). When the IC range is between 3 and 10, the sediment is of class 2 (polluted). If IC is higher than 10, the sediment is of class 3 (high contamination risks). Reference values of the IC are indicated (ABRMC 1991).

Effects of weather conditions on water and sediment contaminations

In order to understand the effect of weather parameters on seasonal variations of TM in both waters and the sediment, we obtained data from the [TuTiempo.net](http://en.tutiempo.net) database (<http://en.tutiempo.net/climate/ws-603600.html>). Three climatic parameters, namely average temperature, precipitation, and wind speed (measured at 10 m above ground level), were considered out of the rest of climate variables because these ones are the main factors that significantly influence changes of water flow/evaporation and thus determine metal mobilization in the water and sediment. Daily meteorological data of

3 months preceding water/sediment sampling were used to compute seasonal values of average temperature (°C), precipitation (mm), and wind speed (km/h). Daily temperatures and wind speeds were averaged, whereas precipitations were cumulated to calculate the seasonal values that were linked to seasonal TM concentrations of the water phase and the sediment.

Statistical analyses

Spatial and seasonal values of trace metals measured both in surface waters and upper sediments were visualized as balloon plots using the package `{ggplot2}` in R (Chang 2013). The variation of these values among study stations and seasons was tested using generalized linear models (GLM) with an identity link function and assuming a Gaussian error distribution (Zuur et al. 2009). Being located upstream of pollution sources (whether of industrial and/or urban origin), compared to other stations, the station “M1” as well as the season of study start “autumn” was included in the intercept of each GLM. These two terms were precisely selected as the initial conditions in order to estimate the variation of metal concentrations along the rest of stations and seasons. Finally, the effects of the factors “stations” and “seasons” on the variation of TM in water and IC values were investigated using *type III F* tests. The Tukey post hoc test was carried out to classify categories of each factor with a significant effect ($P < 0.05$). The effect of water contamination of each metal on its contamination in the sediment was tested using a non-parametric model. In generalized additive models (GAMs), metal contents of the sediment were fitted as a smooth function of water contents (Crawley 2013) using a Gaussian distribution with “identity” as link function. GAMs were carried out using the package `{mgcv}`. The effects of seasonal climate parameters (temperature, precipitation, and wind speed) of seasonal TM concentrations were tested using Pearson correlations. All statistical tests were performed using the software R (R Core Team 2016).

Results

Heavy metals in surface waters

The analysis of surface waters from Meboudja and Seybouse wadis showed that TM concentrations fluctuated following seasons and study stations (Fig. 2).

Iron

In Meboudja wadi, the maximum and minimal values of iron were recorded respectively in summer and spring. Values of iron in autumn, winter, and springs do not exceed 2 ppm. During summer, iron values increased to factor 2 in stations M1 and M3 and to factor 5 in M4. In stations of Seybouse wadi, contents of iron were not

different. However, in summer, an increase of more than 50% occurred in S6 compared to S5 (Fig. 2). The contents of iron in surface waters of Seybouse were, however, lower than those observed in Meboudja, except for the spring period where iron contents were close to the European Community (EC) reference value (0.2 ppm). It is obvious that the surface waters of the two wadis were highly contaminated during all the year. The GLM

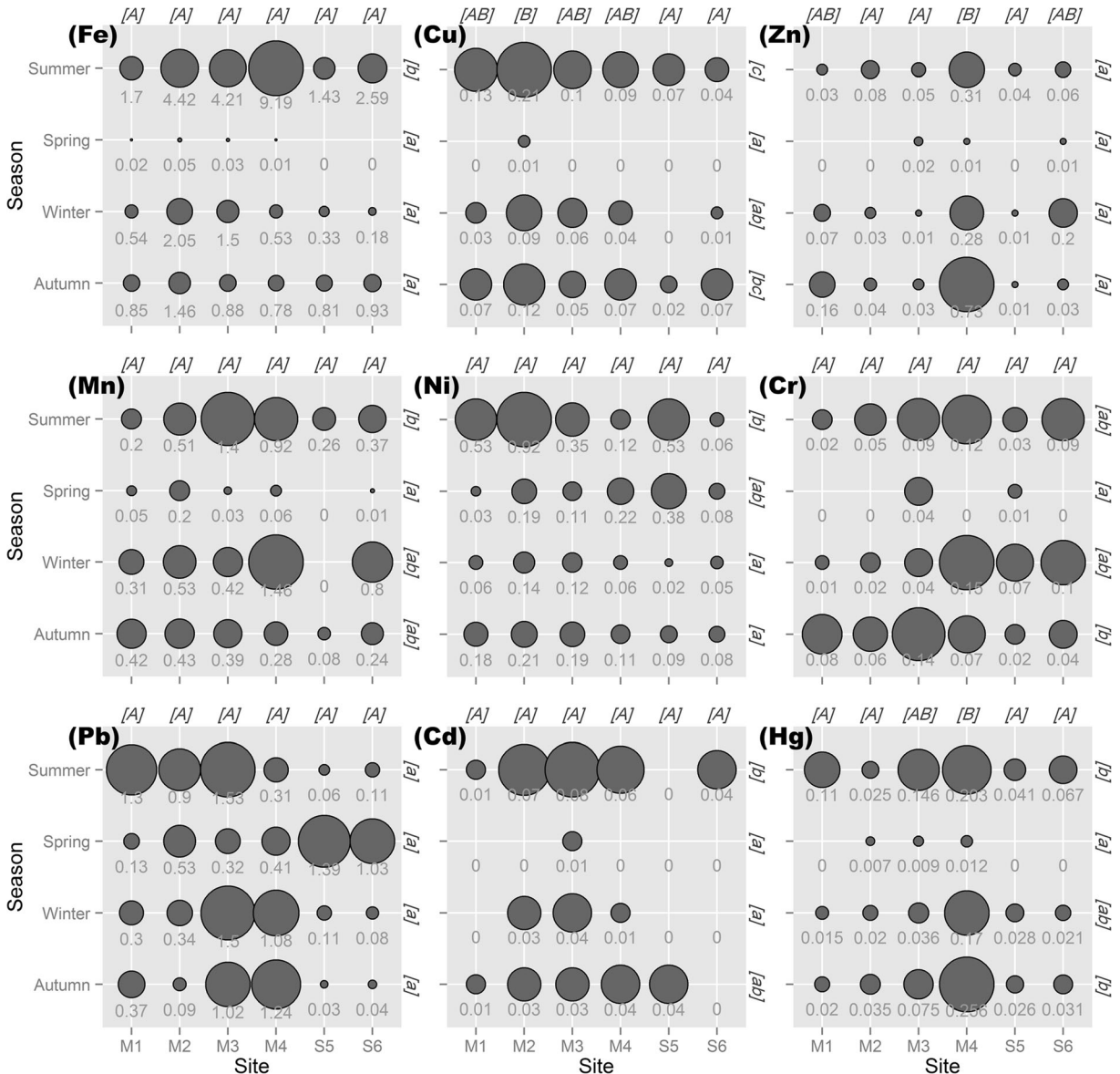


Fig. 2 Spatial and seasonal variations of trace metal concentrations (in ppm) in surface waters of Meboudja and Seybouse wadis at the mouth of the Seybouse Watershed in NE Algeria. *Italic letters between square brackets indicate results of the Tukey HSD tests. The same letters are not significantly different at P > 0.05.*

Uppercase and small letters indicate differences between study sites and seasons, respectively. TM reference values (in ppm) were determined following ABRMC (1991): Fe = 0.2, Cu = 1, Zn = 5, Mn = Ni = Cr = Pb = 0.05, Cd = 0.05, and Hg = 0.001

revealed a significant increase of iron contents during summer ($t = 3.54$, $P = 0.003$) with significant seasonal variations (Table 1), whereas differences between stations were not significant (F test: $F = 1.18$, $P = 0.366$).

Copper

In all study stations, contents of copper in surface waters reached maximum values in summer period (GLM: $t = 2.63$, $P = 0.019$). However, values of copper were significantly higher in M1 and M2 compared to the rest of stations (F test: $F = 5.14$, $P = 0.006$). The Tukey test indicated that these values were low in M1, increased in M2 (from factor 4 to 10 according to seasons), and then dropped gradually in M3 and M4. In Seybouse wadi, copper values in S6 were slightly higher than in S5 particularly in autumn (Fig. 2). However, contents of copper of the two wadis do not exceed 0.2 ppm indicating lower values than the EC reference value (1 ppm). The GLM revealed a significant decrease of copper contents during spring compared to autumn (Table 1). Copper values significantly varied between seasons ($F = 17.07$, $P < 0.001$).

Zinc

Zinc contents in surface waters of both wadis have not exceeded 1 ppm and were lower than the EC reference value (5 ppm). Values recorded during spring were significantly the lowest (GLM: $t = -2.24$, $P = 0.041$), but no significant difference was observed between seasons (F test: $F = 1.69$, $P = 0.212$). Regarding stations, zinc concentrations were the highest in M4 ($t = 3.06$, $P = 0.008$), where they increased during autumn and summer. The Tukey test indicated that values in M2, M3, and S5 were the lowest with a significant variation between stations (F test: $F = 3.76$, $P = 0.021$) (Fig. 2, Table 1).

Manganese

Manganese contents in surface waters of the two wadis were higher than the EC reference value (0.05 ppm), except during spring in Seybouse wadi. Mn values increased along stations of Meboudja wadi and then decreased when waters of the later merged with Seybouse wadi at S5. However, the GLM revealed no significant variation between stations (F test: $F = 1.78$, $P = 0.177$), whereas the season factor had a significant effect (F test: $F = 3.97$, $P = 0.029$). The Tukey test

showed that the lowest values of manganese were recorded during spring, while summer enclosed the highest values (Fig. 2, Table 1).

Nickel

Nickel contents in surface waters of Meboudja and Seybouse wadis clearly exceed the EC reference value (0.05 ppm). GLM revealed that nickel concentrations decreased downstream in both wadis; however, the variation of nickel between study stations was not significant (F test: $F = 1.63$, $P = 0.212$). Regarding seasonal changes in nickel values, minimal and maximum contents of nickel were detected during winter and summer, respectively (Fig. 2). The GLM indicated that nickel values increased significantly in summer ($t = 2.95$, $P = 0.01$), whereas the increase observed in spring was not significant (Table 1). According to the Tukey test, nickel values of these two seasons were significantly higher than autumn and winter. Indeed, F test showed that nickel contents differed significantly from one season to another ($F = 5.18$, $P = 0.012$).

Chromium

In Meboudja surface waters, the highest values of chromium were recorded in winter and summer in M4 and during autumn in M3 (Fig. 2). The GLM indicated a significant increase in M4 ($P = 0.038$) and with a significant decrease in spring ($P = 0.011$) (Table 1). Indeed, chromium contents during spring were lower than the EC reference value (0.05 ppm). However, during autumn, chromium concentrations exceed the EC standard in all sampling stations. In winter and summer, chromium contents rise in S6 exceeding the EC standard, particularly during the cold season in S5 and S6. F test, revealed no significant variation between stations ($P = 0.143$), whereas the effect of season was significant ($F = 4.01$, $P = 0.028$). For the latter factor, the Tukey test indicated that chromium values of the spring were the lowest (group a), while autumnal values were the highest (group b).

Lead

Lead concentrations in surface waters of Meboudja vary between 0.09 ppm (M2 in autumn) and 1.5 ppm (M3 in winter). In M3 and M4, values were higher than those recorded in M1 and M2 (Fig. 2, Table 1). Overall, lead contents in all study stations were higher than the EC reference value (0.05 ppm). Peaks were recorded during

autumn, winter in M3 and M4, and during summer in M1 and M3. In S5 and S6, lead concentrations were close to the European standard except in spring where values are 20 to 30 times higher than those recorded during the rest of study seasons. The GLM showed that there is no significant difference in lead contents between study sites (F test: $F = 1.08, P = 0.412$) and seasons ($F = 0.20, P = 0.896$).

Cadmium

Cadmium values in surface waters of Meboudja wadi exceeded EC standard (0.005 ppm) except during spring where Cd contents were lower than this reference value.

The lowest contents are recorded in M1, but progressive increase of cadmium occurs in winter and summer in M2 and M3 (Fig. 2). The GLM, revealed that Cd increased significantly downstream in M2 ($P = 0.034$) and M3 ($P = 0.010$) compared to M1 (Table 1), with a significant change between stations (F test: $F = 2.98, P = 0.046$). In Seybouse wadi, cadmium contents were detected only in S5 during autumn and in S6 during summer, where both values (0.005 ppm) exceeded the EC standard. GLM revealed that seasonal fluctuations of cadmium were significant (F test: $F = 6.82, P = 0.004$), where Cd concentration decreased significantly during the spring season ($t = -2.43, P = 0.028$).

Table 1 Generalized linear models (GLM) testing the spatial and seasonal variations of trace metal concentrations in surface waters of Meboudja and Seybouse wadis in extreme northeast Algeria

Coefficients	Est.	SE	<i>t</i>	<i>P</i>	Est.	SE	<i>t</i>	<i>P</i>	Est.	SE	<i>t</i>	<i>P</i>
	Iron (Fe)				Copper (Cu)				Zinc (Zn)			
Intercept	0.29	0.89	0.33	0.747	0.07	0.02	4.39	0.001	0.14	0.08	1.84	0.085
Station M2	1.22	1.03	1.19	0.255	0.05	0.02	2.69	0.017	-0.03	0.09	-0.32	0.757
Station M3	0.88	1.03	0.85	0.407	-0.01	0.02	-0.27	0.792	-0.04	0.09	-0.43	0.674
Station M4	1.85	1.03	1.80	0.092	-0.01	0.02	-0.40	0.693	0.27	0.09	3.06	0.008
Station S5	-0.14	1.03	-0.13	0.897	-0.04	0.02	-1.88	0.080	-0.05	0.09	-0.57	0.576
Station S6	0.15	1.03	0.14	0.888	-0.03	0.02	-1.48	0.160	0.01	0.09	0.11	0.910
Winter	-0.10	0.84	-0.12	0.910	-0.03	0.02	-1.86	0.082	-0.07	0.07	-0.93	0.365
Spring	-0.93	0.84	-1.11	0.284	-0.07	0.02	-4.28	0.001	-0.16	0.07	-2.24	0.041
Summer	2.97	0.84	3.54	0.003	0.04	0.02	2.63	0.019	-0.07	0.07	-1.00	0.331
	Manganese (Mn)				Nickel (Ni)				Chromium (Cr)			
Intercept	0.16	0.20	0.82	0.424	0.14	0.10	1.44	0.171	0.04	0.02	2.00	0.064
Station M2	0.17	0.23	0.76	0.458	0.17	0.11	1.45	0.169	0.01	0.03	0.20	0.846
Station M3	0.32	0.23	1.39	0.185	-0.01	0.11	-0.07	0.948	0.05	0.03	1.98	0.066
Station M4	0.44	0.23	1.92	0.074	-0.07	0.11	-0.64	0.535	0.06	0.03	2.28	0.038
Station S5	-0.16	0.23	-0.71	0.491	0.06	0.11	0.48	0.637	0.01	0.03	0.20	0.846
Station S6	0.11	0.23	0.49	0.634	-0.13	0.11	-1.16	0.264	0.03	0.03	1.19	0.253
Winter	0.28	0.19	1.51	0.151	-0.07	0.09	-0.73	0.475	0.00	0.02	-0.16	0.874
Spring	-0.25	0.19	-1.34	0.200	0.03	0.09	0.27	0.792	-0.06	0.02	-2.91	0.011
Summer	0.30	0.19	1.64	0.122	0.28	0.09	2.95	0.010	0.00	0.02	-0.08	0.937
	Lead (Pb)				Cadmium (Cd)				Mercury (Hg)			
Intercept	0.40	0.34	1.17	0.260	0.01	0.01	0.90	0.383	0.05	0.03	2.11	0.052
Station M2	-0.06	0.39	-0.15	0.880	0.03	0.01	2.33	0.034	-0.01	0.03	-0.49	0.628
Station M3	0.57	0.39	1.45	0.169	0.04	0.01	2.97	0.010	0.03	0.03	1.03	0.319
Station M4	0.24	0.39	0.60	0.558	0.02	0.01	1.91	0.076	0.12	0.03	4.23	0.001
Station S5	-0.13	0.39	-0.33	0.750	0.01	0.01	0.42	0.677	-0.01	0.03	-0.43	0.676
Station S6	-0.21	0.39	-0.54	0.600	0.01	0.01	0.42	0.677	-0.01	0.03	-0.22	0.828
Winter	0.10	0.32	0.32	0.751	-0.01	0.01	-1.21	0.244	-0.03	0.02	-1.07	0.304
Spring	0.17	0.32	0.53	0.603	-0.02	0.01	-2.43	0.028	-0.07	0.02	-2.89	0.011
Summer	0.24	0.32	0.74	0.471	0.02	0.01	1.91	0.076	0.02	0.02	1.04	0.316

Est. estimate, SE standard error, *t t* - value, *P* probability value

Mercury

In all stations of Meboudja wadi, mercury contents increased downstream to peak in waters of M4 (GLM: $t = 4.23, P = 0.001$). In the later, peaks occur during the four seasons with a maximum value of 0.26 ppm in autumn (Fig. 2, Table 1). The Tukey test indicated that mercury concentrations in the latter station were significantly the highest, followed by concentrations of M3 (group b), whereas means of Hg in the rest of study stations was statistically different (F test: $F = 6.63,$

$P = 0.002$). In spring, Hg contents decreased significantly (GLM: $t = -2.89, P = 0.011$) and were lower than the EC reference value. In Seybouse wadi, mercury contents in S5 and S6 were quite similar except in summer where they increased with more than 50% in S6. Except for spring, mercury contents in surface waters of Seybouse wadi exceeded the EC reference value. Variations of Hg concentrations were significant between seasons ($F = 5.61, P = 0.009$), where hot seasons (summer and autumn) were significantly the highest (group b according to the Tukey test).

Table 2 Generalized linear models (GLM) testing the spatial and seasonal variations of contamination index (IC) of upper sediments of Meboudja and Seybouse wadis in northeast Algeria

Coefficients	Est.	SE	<i>t</i>	<i>P</i>	Est.	SE	<i>t</i>	<i>P</i>	Est.	SE	<i>t</i>	<i>P</i>
	Iron (Fe)				Copper (Cu)				Zinc (Zn)			
Intercept	16.97	0.62	27.38	0.000	0.57	0.15	3.84	0.002	1.06	0.14	7.50	0.000
Station M2	10.01	0.72	13.99	0.000	0.58	0.17	3.36	0.004	1.28	0.16	7.83	0.000
Station M3	6.88	0.72	9.61	0.000	1.87	0.17	10.93	0.000	1.66	0.16	10.15	0.000
Station M4	1.32	0.72	1.85	0.085	0.52	0.17	3.03	0.008	0.95	0.16	5.81	0.000
Station S5	-3.99	0.72	-5.57	0.000	-0.12	0.17	-0.70	0.495	0.19	0.16	1.15	0.270
Station S6	-1.56	0.72	-2.18	0.046	0.02	0.17	0.09	0.931	0.80	0.16	4.89	0.000
Winter	0.44	0.58	0.75	0.468	0.37	0.14	2.64	0.018	0.07	0.13	0.50	0.625
Spring	-2.14	0.58	-3.66	0.002	0.24	0.14	1.68	0.114	-0.84	0.13	-6.30	0.000
Summer	0.03	0.58	0.05	0.960	0.28	0.14	1.98	0.067	-0.62	0.13	-4.67	0.000
	Manganese (Mn)				Nickel (Ni)				Chromium (Cr)			
Intercept	0.54	0.10	5.38	0.000	1.14	0.09	12.54	0.000	1.89	0.19	9.92	0.000
Station M2	0.74	0.12	6.42	0.000	0.43	0.10	4.13	0.001	0.82	0.22	3.70	0.002
Station M3	0.27	0.12	2.37	0.032	0.56	0.10	5.35	0.000	1.97	0.22	8.92	0.000
Station M4	0.16	0.12	1.37	0.192	0.15	0.10	1.39	0.186	0.15	0.22	0.67	0.513
Station S5	-0.11	0.12	-0.91	0.377	-0.04	0.10	-0.41	0.690	-0.07	0.22	-0.31	0.763
Station S6	0.07	0.12	0.56	0.581	0.15	0.10	1.39	0.186	0.05	0.22	0.20	0.841
Winter	-0.09	0.09	-0.94	0.363	0.22	0.09	2.59	0.020	0.26	0.18	1.47	0.164
Spring	0.04	0.09	0.44	0.664	-0.05	0.09	-0.55	0.593	-0.59	0.18	-3.25	0.005
Summer	-0.01	0.09	-0.11	0.917	0.24	0.09	2.79	0.014	0.11	0.18	0.60	0.556
	Lead (Pb)				Cadmium (Cd)				Mercury (Hg)			
Intercept	1.93	1.47	1.31	0.209	0.11	0.50	0.22	0.829	1.33	0.14	9.36	0.000
Station M2	8.85	1.70	5.20	0.000	2.24	0.58	3.89	0.001	0.44	0.16	2.67	0.017
Station M3	33.15	1.70	19.48	0.000	5.32	0.58	9.24	0.000	0.88	0.16	5.35	0.000
Station M4	5.98	1.70	3.51	0.003	3.66	0.58	6.35	0.000	1.25	0.16	7.64	0.000
Station S5	0.43	1.70	0.25	0.806	0.43	0.58	0.75	0.464	-0.02	0.16	-0.09	0.928
Station S6	4.59	1.70	2.70	0.017	1.77	0.58	3.07	0.008	0.34	0.16	2.06	0.057
Winter	0.00	1.39	0.00	0.999	0.12	0.47	0.25	0.805	0.05	0.13	0.36	0.723
Spring	0.27	1.39	0.20	0.848	0.84	0.47	1.78	0.096	0.16	0.13	1.19	0.255
Summer	-0.83	1.39	-0.59	0.562	0.32	0.47	0.68	0.509	0.38	0.13	2.87	0.012

Est. estimate, SE standard error, *t* *t* value, *P* probability value

Contamination by trace metals in the upper sediment

Iron

In upper sediment of Meboudja wadi, iron concentrations varied from 29,080 to 54,760 mg/kg dry weight (dw) with the highest values recorded in M2 and M3. In Seybouse wadi, values recorded in the sediment S6 are two times higher than those in S5 station during summer and spring, but in autumn and winter, they are close to each other. Iron IC of the surface sediments (Table 2) varied from 14.54 to 27.60 in Meboudja wadi and from 9.93 to 16.46 in Seybouse wadi. Since all IC values were higher than 10, it is obvious that Meboudja and Seybouse wadis involve high risks. The GLM revealed high significant differences between study stations ($F = 110.07$, $P < 0.001$) and seasons ($F = 7.92$, $P = 0.002$), where IC values significantly increased in Meboudja stations (M2 and M3) and decreased in S5 and S6 ($P < 0.001$).

Copper

In Meboudja wadi, copper contents in the sediment have similar seasonal trend from one station to another. The GLM revealed no difference between seasons (F test: $F = 2.53$, $P = 0.096$). Levels of copper were weak in M1, increase gradually in M2, reach a peak in M3, and then decrease in M4. According to the GLM, all variations of Cu concentrations downstream along stations were significant (Table 2), with a significant change of the factor station (F test: $F = 37.53$, $P < 0.001$). The highest concentrations were recorded in winter and summer, with a significant increase during winter ($t = 2.64$, $P = 0.018$). In Seybouse wadi, copper contents were lower than Meboudja stations. Copper IC of surface sediments of Meboudja and Seybouse wadis was relatively low (Fig. 3). Therefore, sediments were not contaminated by copper, except for M3 station during winter where copper IC reached 3.22.

Zinc

In the surface sediments of study wadis, zinc IC varied between 0.45 and 2.89. IC levels displayed particular spatial and seasonal fluctuations. A progressive increase in zinc level was observed in M2 and M3 followed by a slight diminution in M4. According to GLM, all increases that occurred in these stations were significant (Fig. 3, Table 2). The highest values were recorded in autumn and

winter, with maximum values in M3. The Tukey test showed that these seasons were significantly higher than spring and summer. In Seybouse wadi, S6 station presents double zinc values of those found in S5 during autumn and winter. Zinc contents measured in spring and summer decreased significantly ($P < 0.001$); they were less than 100 mg/kg dw. The GLM revealed very high significant differences in Zn between study stations (F test: $F = 30$, $P < 0.001$) and seasons (F test: $F = 22.9$, $P < 0.001$).

Manganese

In each season, manganese concentrations showed similar trends for study stations. Manganese values were low in M1, then significantly increased in M2, with a slight reduction fall in M3 and M4 (Fig. 3). The GLM revealed that increases of Mn in M2, M3, and M4 compared to initial conditions of M1 were significant (Table 2). Mn variations were significant between stations (F test: $F = 13.53$, $P < 0.001$), but no differences were found between seasons ($F = 0.67$, $P < 0.586$). In surface sediments of Seybouse wadi, manganese content in S6 is close to that in M4 but represents less of the one third of the content in M2 in spring. Manganese IC of the surface sediments of the two wadis varies from 0.31 to 1.72. As all IC values < 3 , the upper sediments of the two wadis were considered as not contaminated with manganese (class 1).

Nickel

In Meboudja wadi, nickel levels in the surface sediment vary from 40 to 96 mg/kg dw. They increased significantly in M2 (GLM: $t = 4.13$, $P = 0.001$), reach a peak in M3 (GLM: $t = 5.35$, $P < 0.001$), and then slightly fall in M4. In Seybouse wadi, levels of nickel in the surface sediment were lower than the guide value. Values of nickel IC varied significantly between study stations (F test: $F = 10.53$, $P < 0.001$). The Tukey test indicated that M1 and S5 held the lowest Ni IC values, whereas M3 had the highest IC values (Fig. 3). During winter and summer, nickel significantly increases in sediments (Table 2), with a significant effect of seasons ($F = 8.49$, $P = 0.002$). Following the Tukey test, IC values of both seasons were significantly higher than spring. Values recorded in the latter do not exceed the standard guide value. Moreover, as nickel IC of the surface sediments of both wadis varied between 0.85 and 2.01, they were not contaminated by this metal (Class 1).

Chromium

In the sediments of Meboudja wadi, chromium contents present similar seasonal trend between the stations (Fig. 3). Chromium concentrations increased significantly in M2 (GLM: $t = 3.70, P = 0.002$), reach a peak in M3 (GLM: $t = 8.92, P < 0.001$), and then decreased in M4 but with values slightly greater than those of M1

(Table 2). Chromium IC varied significantly between study stations (F test: $F = 25.96, P < 0.001$), where IC values of M1, M4, S5, and S6 were significantly the lowest following the Tukey test. The GLM revealed that Cr values in the sediments decreased significantly during spring ($t = -3.25, P = 0.005$) and increased in winter and summer. Accordingly, the effect of season on the variations of Cr IC values was significant (F test: $F = 8.49,$

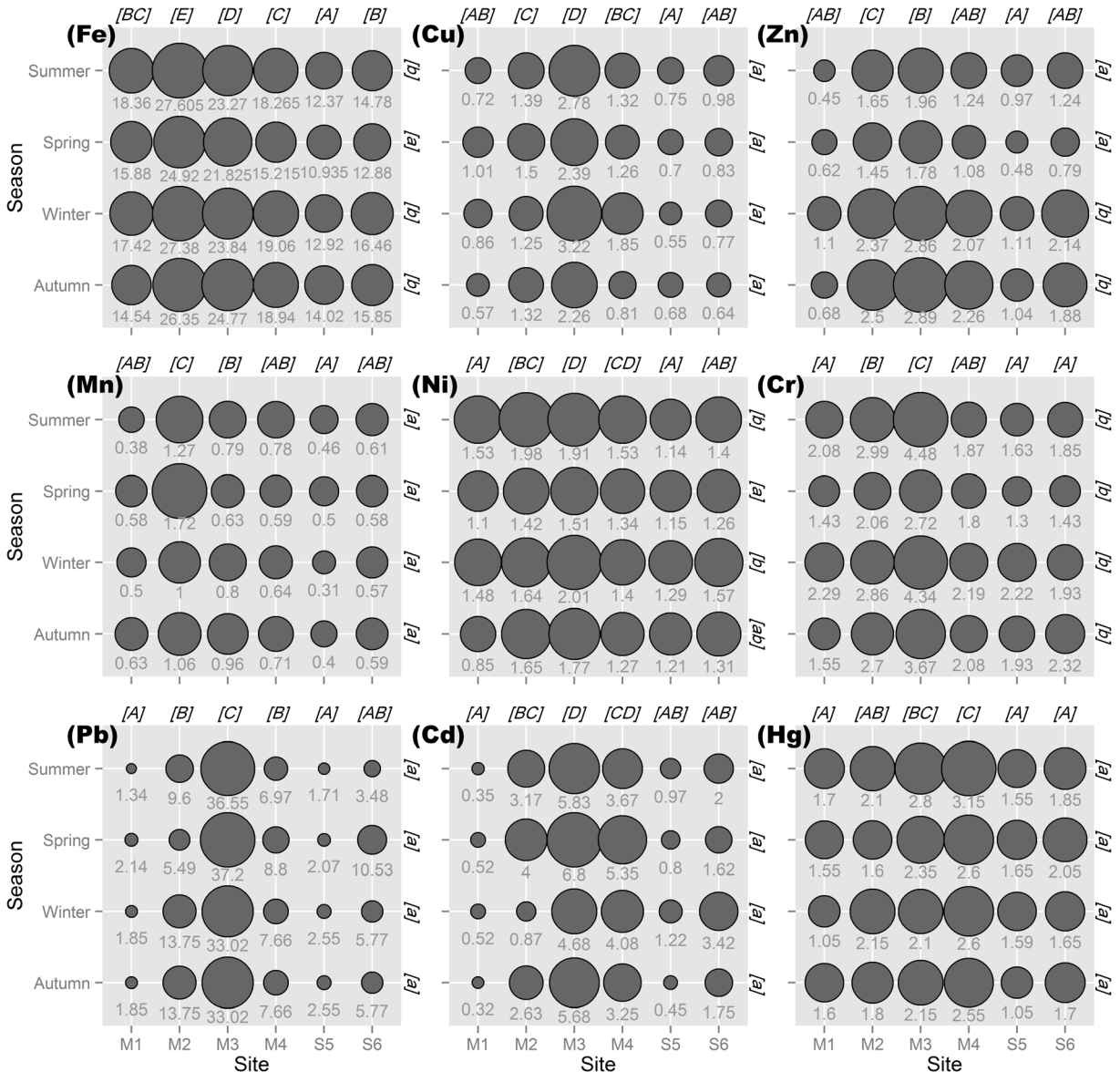


Fig. 3 Spatial and seasonal variations of contamination index for trace metals measured in upper sediments of Meboudja and Seybouse wadis at the mouth of the Seybouse Watershed in NE Algeria. *Italic letters between square brackets* indicate results of the Tukey HSD tests. Values with the *same letter* are not

significantly different at $P > 0.05$. *Uppercase letters* indicate differences between study sites, whereas *small letters* between seasons. TM reference values (in mg/kg dw) were determined following Boust (1981): Fe = 2000, Cu = 26, Zn = 88, Mn = 400, Ni = 45, Cr = 45, Pb = 22, Cd = 0.6, and Hg = 0.2

$P = 0.002$). Like the rest of trace metals, chromium contents in Seybouse wadi were low compared to Meboudja wadi. Chromium IC of the surface sediments of both wadis varied from 1.30 to 4.48. IC was higher than 3 in M3 during all seasons except spring, characterizing the station as contaminated by chromium.

Lead

Lead concentrations displayed similar seasonal fluctuations from study stations. In M1, they were low, then increased to a peak in M3, and then decrease in M4 (Fig. 3). All increases observed in Meboudja stations were significant (GLM: $P < 0.05$) (Table 2). In stations S5, lead contents increased compared to M1, but in S6, the increase was significant ($t = 2.70$, $P = 0.017$). Lead concentrations varied significantly between stations (F test: $F = 105$, $P < 0.001$). According to the Tukey test, lead contents in M3 and M4 were the highest, where they exceeded the EC reference value. Lead IC of the surface sediments in Meboudja and Seybouse wadis showed various classes: class 1 for M1 and S5; class 2 for M4 and S6; and class 3 for M2 and M3 (zones at risk). Changes in lead IC were not significant between seasons (F test: $F = 0.23$, $P = 0.871$).

Cadmium

The lowest cadmium values were recorded in M1 and S5. A progressive increase is recorded in M2 and M3 followed by a slight fall in M4 (Fig. 3). The GLM showed a positive link of Cd contents in M2, M3, M4, and S6 (Table 2), with a significant variation between stations (F test: $F = 24.12$, $P = 0.001$). The maximum values were recorded in station M3 followed by M4. It is noteworthy that cadmium contents in M2 exceeded the standard reference value (0.6 mg/kg dw), whereas they are below the reference value in Seybouse wadi except in S6 during winter. Overall, cadmium IC varied from 0.32 to 6.80. Stations M1, S5, and S6 thus are not contaminated by cadmium. M2 is class 2 in spring and summer whereas M3 and M4 are of class 2 during the whole year and thus are contaminated by cadmium. Variations of cadmium between seasons were not found significant ($F = 1.23$, $P = 0.333$).

Mercury

Mercury concentrations in the surface sediments showed a range difference of 0.34 mg/kg dw

between min and max values. According to the GLM, Hg increased significantly downstream along all stations of Meboudja wadi and peaked in M4 (Fig. 3), whereas Hg contents were not linked to Seybouse stations (Table 2). Mercury contents varied significantly between stations (F test: $F = 18.60$, $P < 0.001$), but this variation followed the same trend between seasons ($F = 3.26$, $P = 0.051$) though a significant increase was detected during summer ($t = 2.87$, $P = 0.012$). The Tukey test indicated that sediments of M4 then M3 possessed higher lead contents than M1, S5, and S6 that were the lowest. Overall, the surface sediments of study stations (excluding M4 in summer, IC >3) were not contaminated by mercury.

Effects of water pollution on sediment contamination

Overall, seasonal variations of trace metal concentrations revealed that the contamination of surface waters in the study wadis had no significant effect on the contamination of upper sediments. All GAMs showed no significant effect ($P > 0.05$) (Fig. 4). This may be explained by the influence of sediment sampling procedures of this study in which samples were scraped and collected from the sediment surface that is expected to be often disturbed or re-suspended, causing the metal concentrations in these samples potentially less relevant to the long-term pollution and accumulation. Also, the complexation and different forms of metals as well as the presences of salts in the water could also be influential. All that said to indicate that the metal concentrations in the water led to the metal pollutions in the sediments, although GAMs suggested that contamination of the sediment is caused by a long-term and cumulative process of water pollution. Despite these non-significant effects, it is noteworthy that lead concentrations in waters influenced sediment pollution more rapidly than other trace metals considering that the GAM revealed 40.6% of deviance explained.

Effects of seasonal climatic conditions on TM concentrations

The relationships between climatic parameters and TM concentrations differed between surface water and upper sediment. For surface waters, the average temperature was negatively correlated with TM concentrations with

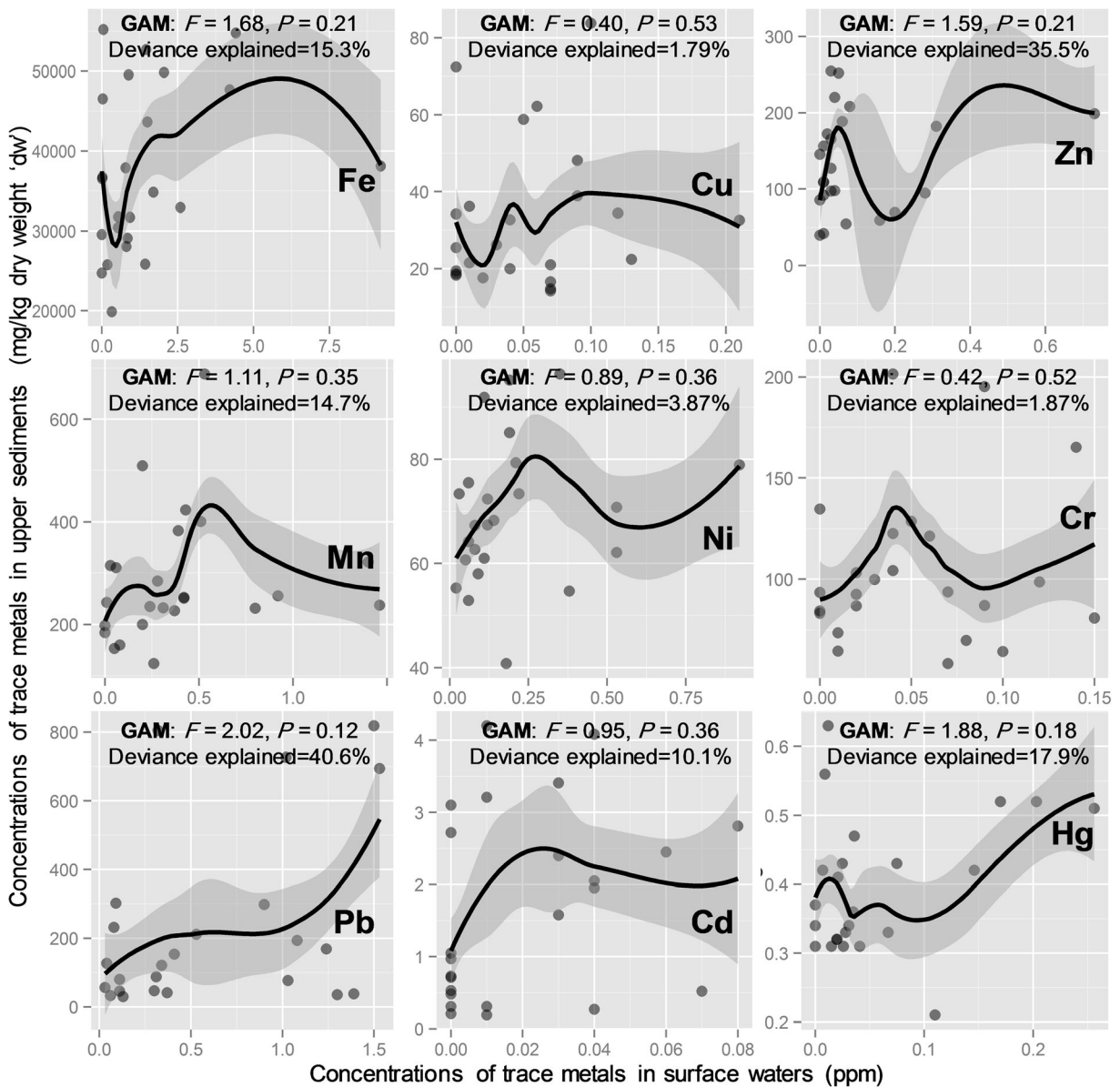


Fig. 4 Relationships between concentrations of trace metals in surface waters and upper sediments in wadis of the Seybouse watershed in North Africa. The *solid lines* represent loess (locally

weighted polynomial) curves smoothed with a GAM fit (generalized additive model) and 95% confidence region in *light gray*. *F*-statistics (*F*) and *P* value (*P*) are results of GAMs

significant correlations ($P < 0.005$) found with Fe, Cu, Mn, Cr, Cd, and Hg. The precipitation and wind speed positively influenced TM concentration, with significant correlations between rainfall and Cd, Hg, Fe, Cu, Ni, and Cr and between wind speed and Fe, Cu, Ni, and Cd. Regarding upper sediments, TM concentrations were not deemed influenced by climatic parameters, except for zinc in relation to rainfall ($r = 0.446$, $P = 0.029$) (Table 3).

Discussion

The current study shows that surface waters of Meboudja and Seybouse wadis are highly contaminated by iron during the whole year because the recorded values exceeded the European reference value (0.2 ppm). These high concentrations originated from iron dust emission from El-Hadjar complex. Similarly, Louhi et al. (1998) confirm the presence of high iron

Table 3 Correlations between seasonal climatic parameters and trace metal concentrations in surface waters and upper sediments of Meboudja and Seybouse wadis in extreme northeastern Algeria

Climatic variables		Surface waters								
		Fe	Cu	Zn	Mn	Ni	Cr	Pb	Cd	Hg
Temperature	<i>r</i>	-0.649	-0.645	-0.163	-0.552	-0.368	-0.456	-0.056	-0.543	-0.439
	<i>P</i>	0.001	0.001	0.445	0.005	0.077	0.025	0.794	0.006	0.032
Precipitation	<i>r</i>	0.654	0.745	0.241	0.400	0.436	0.460	0.018	0.632	0.505
	<i>P</i>	0.001	<0.001	0.257	0.052	0.033	0.024	0.932	0.001	0.012
Wind speed	<i>r</i>	0.640	0.466	-0.079	0.205	0.620	0.038	0.143	0.437	0.253
	<i>P</i>	0.001	0.022	0.713	0.337	0.001	0.859	0.506	0.033	0.234
		Upper sediments								
		Fe	Cu	Zn	Mn	Ni	Cr	Pb	Cd	Hg
Temperature	<i>r</i>	0.019	-0.069	-0.216	0.070	0.053	0.012	0.015	0.080	0.229
	<i>P</i>	0.928	0.750	0.310	0.746	0.805	0.957	0.946	0.711	0.281
Precipitation	<i>r</i>	0.072	0.006	0.446	-0.097	-0.013	0.132	-0.020	-0.155	-0.255
	<i>P</i>	0.737	0.980	0.029	0.651	0.951	0.538	0.926	0.470	0.229
Wind speed	<i>r</i>	0.122	0.142	0.288	-0.144	0.338	0.264	-0.056	-0.063	-0.083
	<i>P</i>	0.569	0.509	0.173	0.502	0.106	0.212	0.796	0.771	0.699

r Pearson correlation coefficient, *P* *P* value

levels in waters of Meboudja near the iron and steel complex. Along Meboudja wadi, the lowest iron concentrations in surface sediments are located in M1 upstream of the industrialized zones, whereas the highest concentrations occurred in M2, M3, and M4 just downstream of El-Hadjar complex. Furthermore, discharges of industrial effluents and wastewaters without any treatment by this metallurgical industry, major producers of heavy metals, represent the main source of iron in water and sediments (Djabri et al. 2009). The high levels of iron may be also explained by the presence of iron dust in the air. Heavy rains, flows of water, and turbulent currents create high levels of oxygenation that increase the precipitation of Fe²⁺ into iron oxides facilitating the formation and aggregation of mineral particles, thus its sedimentation (Salvarredy-Arangren 2008; Djabri et al. 2009; Belabed et al. 2011, 2013a; Diop 2014). Taking all the previously mentioned together, the iron and steel complex of El-Hadjar is clearly pinpointed as the point source of iron pollutions in the area. In Seybouse wadi, the most significant iron variations are in spring and in summer, but contents are lower than those in Meboudja wadi. In S6 station, nearby the embouchure with the Mediterranean Sea, iron concentration in the sediments is the highest due to the dynamic supplies through the hydrologic network. The IC by iron of the surface sediments of the two wadis shows that these sediments are of class 3, thus polluted by iron with higher values compared to other heavy metals. High

concentrations of iron can be related to hydrodynamic and water physicochemical conditions, especially to the precipitation of iron oxides (Asfers et al. 2016).

Zinc and copper concentrations in surface waters and upper sediments of surveyed wadis are homogeneous and vary slightly. They do not exceed the reference values, but the highest values are recorded in Meboudja wadi during summer. The presence of these two metals in stations located downstream industrial areas confirms their anthropogenic origin. Similarly, Louhi et al. (1998) report very high levels of copper contents above the European reference value in various sampling stations with a maximum record nearby El-Hadjar iron and steel complex. Water contamination is likely related to the technological processes of this complex which originate heavy pollution by copper and zinc. This pollution has a heavy impact on groundwater quality of the region (Bougherira et al. 2016).

There are various data on zinc content from North African and European hydrosystems (Appendix Table 4): in Tunisia, Azzaoui (1993) indicates 100 mg/kg dw in lake Ghar El Melh and Ben M'Barek (1995) 180 mg/kg dw in Lake Ichkeul. In Morocco, Benboui et al. (2005) record 210 mg/kg dw in Lake Fouarat whereas in Egypt, Saad and Fahmy (1985) indicate 106 mg/kg dw in Lake Nozha and 94 mg/kg dw in Lake Mariout. No data for Libya were reviewed. In the area of Constantine (NE Algeria), Afri-Mehennaoui et al. (2006) report that industrial and urban effluents substantially influence waters of Rhumel and

Boumerzoug wadis, where copper concentrations ranged between 44 and 778 $\mu\text{g/L}$.

For copper, the annual average contents in Meboudja (21.61 mg/kg dw) and Seybouse (25.38 mg/kg dw) are very close to those of lake Bouseham in Morocco (26 mg/kg dw) (Benbouih et al. 2005). For Meboudja and Seybouse wadis, the IC by copper and zinc show that the values do not exceed 3, characterizing the sediments of the two wadis as class 1, thus not contaminated by these two heavy metals. Angelidis and Catsiki (2002) indicate that copper and zinc distribution depends on the nature of the sediment whose proportions of clay and organic matter play a determining role. They also report high values of copper and zinc in sandy-clay sediments located near disposals. Also, copper and zinc are associated to sandy facieses directly exposed to waste discharges (Lesven et al. 2009; Diop 2014). Several studies (Salvarredy-Arangren 2008; Djabri et al. 2009; Belabed et al. 2011, 2013a; Diop 2014) indicate that deterioration of sulfates (especially chalcopyrite and galenite) can increase sulfates and acidity justifying the presence of copper, zinc, and lead, which increase is mainly related to the mining activity inducing trace metal mobilization.

In waters of study wadis, the lowest manganese values are recorded in M1 and S5 with a maximum content in M2. Except for the spring period, concentrations are higher than European standard (0.05 ppm). Louhi et al. (1998) indicate that in stations of Meboudja wadi near El-Hadjar iron and steel complex, waters are of black color and manganese contents are far higher than the previous standard. In waters of Rhumel and Boumerzoug wadis, manganese values ranged between 10 and 471 $\mu\text{g/L}$ (Afri-Mehennaoui et al. 2006). In the surface sediment of Meboudja and Seybouse wadis, manganese contents present variations according to both sampling station and season. The lowest values are in Seybouse wadi whose highest values correspond to the values in M1 upstream the industrial areas. In M2, manganese doubles or triples in values according to seasons with the maximum concentrations occurring in autumn and spring. Values of contamination index by manganese do not exceed 3 characterizing the sediments of the two wadis as non-contaminated. Djabri et al. (2009) confirm that iron and steel activity is the principal anthropogenic source of pollution by manganese as it is the case in Val de Milluni in Bolivia (Salvarredy-Arangren 2008).

Because of the contiguity to El-Hadjar complex, nickel and chromium in surface waters in M2 and M3

show higher values than the respective European reference value. Indeed, nickel concentrations increase in M2 and M3 at levels close to 100 mg/kg dw during summer and winter. Concentrations higher than the standards are also reported by Louhi et al. (1998) in surface waters of Meboudja wadi nearby El-Hadjar complex (Appendix Table 4). However, sediment contamination indexes by nickel do not exceed 3 characterizing the sediments of Meboudja and Seybouse as not contaminated. On the other hand, chromium shows high-level contents in stations located nearby the industrial area. The indexes of contamination of the sediments of the two wadis show pollution by chromium in M3 in autumn, winter, and summer.

Callender (2003) indicated that even if natural provision of nickel is related to soil erosion, its contents can also come via wastewaters from steel, foundry, and paint factories. Thus, the presence of nickel in study wadis can only be explained by the impact of industrial wastes. Furthermore, high levels of chromium can also come from the sedimentation of dead organisms as well as from the geological origin of rocks (Callender 2003; Belabed et al. 2011, 2013a). This investigation incriminates the local industrial activities as being the source of this pollution source.

Lead contents exceed the European reference value (0.05 ppm) in surface waters of all Meboudja sampling stations and in Seybouse wadi except for the spring period. This is quite similar to findings of Louhi et al. (1998) in waters of Meboudja where lead concentrations were lower than the accepted standards of industrial wastes. In surface waters of Rhumel and Boumerzoug wadis (Afri-Mehennaoui et al. 2006), lead concentrations vary from 0.6 to 1.1 $\mu\text{g/L}$ (Appendix Table 4).

In the surface sediments of Seybouse wadi, lead contents represent about a third of those recorded in Meboudja where in M3 during all seasons. The seasonal variations of lead contents in the sediments are similar in the two wadis. The IC by lead characterizes the surface sediments of Meboudja and Seybouse wadis as being sediments of class 1 (M1 and S5), of class 2 (M4 and S6), and of class 3 (M2 and M3 being zones at risks). The results of this study are slightly higher than those recorded in previous studies (Appendix Table 4) such as the port of Skikda (NE Algeria) where lead contents vary from 118 to 145 mg/kg (Gueddah 2003).

Data of the World Health Organization (WHO 2001) indicate varying lead contents from 0.175 to 0.520 $\mu\text{g/g}$

dw in sediments of the Moroccan coasts; from 23 to 3300 $\mu\text{g/g}$ dw in Spain, from 18 to 1250 $\mu\text{g/g}$ dw in Marseille (France), from 18 to 470 $\mu\text{g/g}$ dw in Gulf of Trieste (Italy), and from 25 to 130 $\mu\text{g/g}$ dw in Gulf of Thermaikos (Greece). Roussiez et al. (2005) pointed out that lead contents in the sediment of Lion Golf (France) reach 39.2 mg/kg dw. Our findings revealed high levels of lead in the sediments of the two wadis, which indicate the presence of emission sources of lead. The pollution with this heavy metal originates essentially from various industrial activities. Moreover, the use of lead as anti-explosive in fuels for cars leads to lead concentration increases in the air, which represents the atmospheric route of water and sediment contamination (Li et al. 2003; Belabed et al. 2011, 2013b; Varol and Şen 2012).

Cadmium contents in surface waters of Meboudja wadi exceed the European reference value (i.e., 5 ppm, Débièche 2002), but in spring, values are lower than this standard (Appendix Table 4). In surface waters of Rhumel and Boumerzoug wadis, cadmium concentrations are lower than 0.5 $\mu\text{g/L}$ (Afri-Mehennaoui et al. 2006). Results of this investigation are close to those indicated in Tunisia by Azzaoui (1993) in lake Ghar El Melh (Cd = 1.5 mg/kg dw) and by Ben M'Barek (1995) in Lake Ichkeul (1 mg/kg dw). In Morocco in lake Fouarat, Benbouih et al. (2005) indicate cadmium concentration of 0.4 mg/kg dw. In Egypt, in Lake Mariout and lake Nozha, cadmium contents are, respectively, 0.2 and 0.15 mg/kg dw (Saad and Fahmy 1985). The presence of cadmium in the sediments can be linked to the leaching of agriculture lands enriched with phosphate fertilizers. Moreover, the iron and steel industry is also the main source of emission of cadmium, which becomes easily water-soluble by acid drainages (Callender 2003; Salvarredy-Arangren 2008; Djabri et al. 2009; Wahsha et al. 2012). It is significant to stress that cadmium is highly nephrotoxic even at low doses (Gunawardana et al. 2006). The principal sources of mercury in the environment are natural degassing of earth's crust and the industrial and agricultural activities (Cossa and Ficht 1999).

The major anthropogenic sources of contamination by trace metals in continental waters are the mining activity, metallurgy, and the iron and steel industry, which are also the principal sources of heavy metals inducing atmospheric pollution (Callender 2003). Thus, as it has been confirmed in many previous studies in North Africa (e.g., Djabri et al. 2009; Belabed et al. 2011, 2013b) or in Europe (Velasco et al. 2005), this investigation confirms that the iron and steel complex of

El-Hadjar is at the origin of the presence of Fe, Zn, Cu, Cd, Mn, and Ni in the surface waters and upper sediments of the regional hydrological network.

Conclusion

The results of this investigation show the impact of the industrial and urban complexes on the levels of contamination by TM of surface waters and sediments of Meboudja and Seybouse wadis (Seybouse watershed, Algeria). The use of multiple sampling stations along the stream of wadis is a relevant technique for assessing pollutions and therefore detects the location of industrial effluents and/or urban wastewater discharges responsible for the contamination of the waters and/or the sediments. Accordingly, because TM concentrations increase downstream the study wadis, the industrial discharges of some factories are pinpointed as the polluting sources in the plain of Annaba. Iron, manganese, nickel, chromium, lead, cadmium, and mercury contents are higher than the reference values, indicating polluted waters with specific metallic pollutants. The most polluted stations were those located downstream of Meboudja wadi (M2, M3, M4) nearby El-Hadjar complex and close to the industrial park of Chaiba and Pont Bouchet. The sediment is classified at high contamination risk with regard to iron and lead, but at medium risk for chromium and cadmium. These findings characterize of the regional hydrological network as being polluted by the discharge effluents from the urban and industrial areas, particularly from El-Hadjar iron and steel complex. Seasonal monitoring of TM contaminations in waters and sediments of lotic hydrosystems deepens our understanding about the processes, such as mobilization, complexation, re-suspension, and accumulation, that control metal concentrations and therefore may be exploited for the remediation of heavy metal pollutions.

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Authors' contributions BEB and BS designed the study. BEB collected water and sediment samples and conducted laboratory analyses. HC analyzed data. BEB, HC, and AM drafted the manuscript. HC and BEB revised and prepared the final version. All authors read and approved the manuscript.

Appendix

Table 4 Documented values of metal concentrations in upper sediments and water phase from various African and Mediterranean hydrosystems

Site and location	Fe	Cu	Zn	Mn	Cr	Ni	Pb	Cd	Hg	Reference
Concentrations in the water phase										
Lake Mariout (Egypt)	42.5	10.6	18.3	-	-	-	0.22	-	-	Saad et al. (1985)
Lake Nozha (Egypt)	40.1	20.5	17.1	-	-	-	0.2	-	-	Saad et al. (1985)
Nile Estuary (Egypt)	2.5	13	8.18	0.46	-	-	-	0.4	-	Saad and Fahmy (1985)
Lake Victoria (Kenya)	-	5-57.6	25-125	50-327	-	-	7-93.6	2-8	-	Onyani and Wandiga (1989)
Annaba (Algeria)	23.33	6.27	-	3.4	2.13	1.081	0.51	-	-	Louhi et al. (1998)
Rhumel river (Algeria)	-	4.4-22.2	12.1-22.6	10.6-29.8	<0.5	<5	0.6-1.1	<0.05	-	Afri-Mehennioui et al. (2006)
Oubera lagoon (Algeria)	4.73-15.61	1.3-2.7	0.7-2.13	-	0.05-1.7	0.11-0.78	0.35-0.55	0.001-0.015	-	Belabed et al. (2011)
Lake Tonga (Algeria)	2-5.6	0.09-0.9	0.3-1.8	0.05-1.65	0.03-0.2	0.01-0.9	0.4-1.15	0.008-0.02	Traces	Belabed et al. (2013a)
Dakar coast (Senegal)	-	1.93	21.29	-	0.45	1.28	0.48	0.23	-	Diop (2014)
Reference values (Europe)	0.2	1	5	0.05	0.05	0.05	0.05	0.005	0.001	Débièche (2002)
Seybouse watershed (Algeria)	0.01-9.19	0.01-0.21	0.01-0.73	0.01-1.46	0.01-0.15	0.02-0.92	0.03-1.53	0.01-0.08	0.015-0.256	Present study
Concentrations in the sediments										
Lake Mariout (Egypt)	25,600	38	94	958	-	-	7.3	0.2	-	Saad et al. (1985)
Lake Nozha (Egypt)	57,800	79.6	106	125	-	-	10.6	0.15	-	Saad et al. (1985)
Nile Estuary (Egypt)	46,000	85.6	139	387	-	-	-	1.06	-	Saad and Fahmy (1985)
Lake Victoria (Kenya)	1180-52,900	0.96-78.6	2.54-265	53.1-616	-	-	6.02-69.4	0.55-1.02	-	Onyani and Wandiga (1989)
Lake Ghar El Melh (Tunisia)	-	15	100	200	-	-	-	1.5	-	Azzaoui (1993)
Lake Iohkeul (Tunisia)	-	20	180	300	-	-	60	1	-	Ben M'barek (1995)
Annaba (Algeria)	-	208	427.6	279.38	295	-	-	-	-	Ghansallah (2005)
Skikda (Algeria)	16,846	18	62.25	260.5	44.25	40	36.5	0	2.01	Gueddadh (2003)
Lake Fouaret (Morocco)	15,200	45.5	219	219	-	-	64.6	0.4	-	Benbouih et al. (2005)
Rhumel river (Algeria)	-	3-19	98-199	100-320	20-45	21-89	23-100	0.26-3.50	-	Afri-Mehennioui et al. (2006)
Port of Bilbao (Spain)	-	23-204	122-778	-	3.5-23	16-32	41-286	0.04-2	0.18-1.43	Casado-Martinez et al. (2006)
Lagoon of Venice (Italy)	-	10-92	97-524	-	14-66	8-59	50-131	0.4-4	0.5-4.8	Zonta et al. (2007)
Gironde estuary (France)	-	0.9-48	4-323	-	1.3-140	0.9-48	5-84	0.011-2.1	0.001-0.37	Larrose et al. (2010)
Oubera lagoon (Algeria)	8700-16,900	15.95-32	70-114	-	71-157	82-128	13-27	0.02-0.05	-	Belabed et al. (2011)
Lake Tonga (Algeria)	7950-17,800	18-56	86-128	70-600	33-86	39.75-98	17-171	0.19-3.2	0.01-0.08	Belabed et al. (2013a)
Golf of Annaba (Algeria)	2265	41.38	164.1	230.25	253.75	38.81	117.25	1.25	0.025	Belabed et al. (2013b)
Eastern Black Sea (Turkey)	-	24.9-3107	102-4259	200-447	13.4-82.3	9.8-26	15.5-208	-	-	Alkan and Ömek (2013)
Reference values (Europe)	2000	26	88	400	45	45	22	0.6	0.2	Boust (1981)
Seybouse watershed (Algeria)	2474-55,210	14.2-83.8	42-254.6	160-509	58.3-201.5	40.8-95.2	32.6-818.3	0.19-4.08	0.21-0.63	Present study

Values (in ppm for water and mg/kg dw for sediment) are given as averages or ranges (min-max)

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