

Metal Pollution Assessment of Sediment and Water in Al-Ghadir River: Role of Continuously Released Organic Matter and Carbonate and Their Purification Capacity

Amale Mcheik^{1,2*}, Mohamad Fakh², Hussein Trabulsi³, Joumana Toufaily², Taysir Hamieh², Evelyne Garnier-Zarli¹, Nouredine Bousserhine¹

¹Laboratory of Biogeochemistry and Ecology of continental regions (IBIOS – BIOEMCO), Department of Biology and Environmental Sciences, Paris-Est University, Creteil, France

²Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), Department of Chemistry, Lebanese University, Hadath, Beirut, Lebanon

³Faculty of Economic Sciences and Business Administration, Lebanese University, Beirut, Lebanon

Email addresses:

Amale.am@hotmail.com (A. Mcheik), fakh.mohamad@gmail.com (M. Fakh), husseintrabulsi@yahoo.fr (H. Trabulsi), joumana.toufaily@ul.edu.lb (J. Toufaily), tayssir.hamieh@ul.edu.lb (H. Taysir), garnier@u-pec.fr (E. Garnier-Zarli), bousserhine@u-pec.fr (N. Bousserhine)

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Abstract: During the discharge of metals in the aquatic environment, metals are partitioned between the sediment and the water column phases. Further partitioning of metals occurs within the sediment chemical fractions. The present study focuses on one of the middle east rivers, Al-Ghadir which is the smallest and the most polluted and found in the most populated region in Lebanon. The aim of this study was to integrate hydrochemical and sediment data- in order to evaluate the distribution pattern of the pollution of Al-Ghadir River. Bed sediments and water were collected from five locations in one dry season (October 2010) and analyzed for more than 40 parameters, including (i) those of the chemical and the physico-chemical nature and (ii) those reporting the pollution caused by the heavy metals partitioned between the sediment and the water column phases by applying a sequential chemical fractionation scheme to the <75 µm sieved sediment fraction. The quality of waters for different uses has been tested and the state of sediments pollution was evaluated by comparison with general quality standards. Data showed that the highest percentages of total metal content in sediment are for: Fe and Mn in the residual and in the Fe/Mn oxides fractions, Cu in the oxidizable fraction, Cd and Zn in the carbonate and in the Fe/Mn oxides fractions, Pb and Cr in the Fe/Mn oxides fraction. Based on the geoaccumulation indices (I_{geo}), the river sediments are considered to be moderately polluted with the measured metals.

Keywords: Mobilization, Heavy Metals, Bed Sediments, Metal Pollution

1. Introduction

Rivers in Lebanon have always been the most important freshwater resources and most developmental activities are still dependent on river water. However, rivers have also been used for cleaning and disposal purposes. Huge loads of waste from industries, domestic sewage and agricultural activities find their way into rivers resulting in the deposition of contaminants, large scale deterioration of water quality and

elevation of sediment concentrations that have the potential to cause toxicity to aquatic biota ([1], [2], [3]).

The optimal management of Lebanon's rivers is limited by a scarcity of both hydrological and water quality data. Both monitoring and research more or less ceased during the long civil war. [4] have discussed in detail the planning problems posed by the present lack of hydrometric data in relation to operational forecasting of water shortages and flood events. Both solid and liquid wastes are everywhere disposed to watercourses without treatment especially in inland villages

and communities. It is essential therefore to conduct studies relating to: (a) surface and subsurface mapping to identify sources and types of contaminants, (b) assessing water quality for multipurpose utilization and (c) continuous monitoring to determine factors relating to self-purification.

This study was done during the dry season of 2010 on one of the smallest rivers in Lebanon, Al-Ghadir River, which has a total length of 15 km. This river originates from Alley (Mount Lebanon) and flows through Shweyfét, then passes through the Tyro in the industrial zone of Shweyfét till reaching the Mediterranean Sea at Ouzeieh, south of Beirut. The climate of the region is dry during the summer and cold wet during winter. The average annual rainfall is about 1000 mm annually, most part of which occurs between November and April while June, July and August are totally dry [4] and the average annual discharge of Al-Ghadir river in the year 2010 was 13.52 m³/s and the average flow rate was 0.47 m³/s according to the Litani River Authority.

Sixty years ago, this river was a source for irrigation, agriculture and industrial issues but overpopulation, agricultural activities, industrial and urban development situated on its banks has caused major reductions in river water quality. The main sources of pollution in the river include municipal and agricultural wastes, industrial effluents of pulp, paper, dyes, tans, batteries, ceramics, distilleries, car oils, stones and marbles and serum products and wastes from the farms of sheep and poultry released along the river and despite these inputs, the pollution state of this river has never been monitored, evaluated or documented.

During dry seasons, the flow of the river became slow and dry from its origin but the industrial effluents and the municipal wastewater generate the flow of the water in the river. Under these low flow river conditions, the system might approximate to that of a closed system, as justified by a correlation of the metal content between sediment and water column and the aqueous chemistry of the river became

closer to an ideal condition. Therefore, pollutants enter the river under these conditions and partition between and within the various solid and aqueous phases at a state nearly similar to a closed system [5]. In this context, the main objective of this study has been to obtain information about both general chemical and physico-chemical parameters and pollution caused by the heavy metals partitioned between the sediment and the water column phases.

2. Materials and Methods

2.1. Sampling Methodology

Five sampling sites were chosen (Figure 1) along a 15 km stretch of the river Al-Ghadir upstream of its confluence with the Mediterranean Sea. The selection of these sites was based upon the practicability of collecting bed load sediments, the observed potential contamination from domestic waste or industrial discharge. Bed load sediments and water were collected simultaneously during the dry season (October 2010). The collection of bed load sediments was in accordance with the methods used for shallow rivers ([6], [7]). The method involves wading in water and scooping sediments from a depth of 10 to 20 cm using an aluminium trowel. At each collecting site, two sub-samples were taken and bulked in polyethylene bag. Water samples were collected using two one-liter polyethylene bottles. All the sample bottles and other containers were soaked overnight in 10% (v/v) nitric acid and rinsed with ultrapure water several times prior to use. The bottles were rinsed twice with the river water and then filled with water running in the direction of river flow. The bottles were labeled with the corresponding sampling site, time and date of collection. The method of analyzing water and wastewater followed those reported by [8].

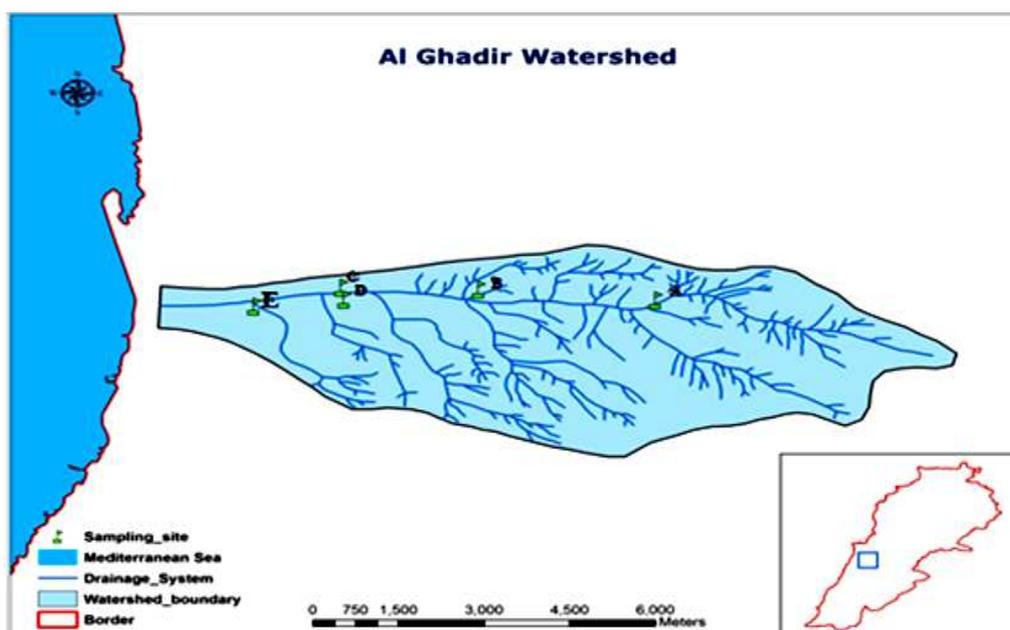


Figure 1. A map of the study area showing the sampling site.

2.2. Sediment Treatment and Analysis

Sediment samples were characterized for both general parameters (pH, organic matter granulometric and mineralogical analyses) and metal contents (Pb, Cu, Zn, Cd, Cr, Fe and Mn). Analyses were performed using standard methods [9].

Analysis of pH in the sediment samples was performed by adding 10 g of the air dried sample into 50 ml distilled water and agitating for 5 min. The solution was left undisturbed for 1h with occasional shaking before measuring the pH. The granulometric analysis was performed from the whole untreated air-dried sample and was realized according to the normes AFNOR NF X31-107. The mineralogical analysis was applied by X-ray diffraction (Bruker, D8 Focus). The porosity of the sediment samples was measured according to the method adapted by [10]. The organic matter in the sediment was determined by wet oxidation-redox titration method using an acid dichromate solution. The reported data are the sum of soluble and insoluble carbon. For metal analysis, sediments were dried at room temperature and sieved while the fraction <75 μm sediment size was retained (clay/silt fraction). Analysis of this fraction is normally carried out in sediment studies because clay and silt particles generally contain the highest concentrations of pollutants and are most readily transported in suspension in natural waters [11]. Samples were digested in closed vessel microwave-assisted digested system for total metal analysis. In addition, one gram of each sediment sample was subjected to a sequential extraction procedure [12] to yield the following "operationally defined" chemical pools. The final volume of the prepared solutions was maintained 100 ml in each case.

Exchangeable fraction (F_1): 1.0 g sediment sample was extracted at room temperature for 1 h with 10 ml of 1.0 M MgCl_2 (pH 7.0) with continuous agitation.

Bound to carbonates (F_2): The residue obtained from step 1 was leached at room temperature with 10 ml of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was agitated for 5 h.

Bound to Fe-Mn oxides (F_3): The residue obtained from step 2 was refluxed at 100°C with 20 ml of 0.04 M $\text{NH}_2\text{OH.HCl}$ in 25% (v/v) acetic acid for 6 h.

Bound to organic matter (F_4): To the residue obtained from step 3, 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 were added and pH adjusted to 2.0 with HNO_3 . The mixture was refluxed at 100°C for 2 h. A second 3 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was again refluxed for 3 h. After cooling, 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 was added. The sample was diluted to 100 ml and agitated continuously for 30 min. The addition of ammonium acetate is designed to prevent adsorption of extracted metals onto the oxidized sediment.

Residual (F_5): The residue obtained from step 4 was digested with a HF-HClO_4 mixture as per procedure followed for the analysis of trace elements.

All recovered supernatants were kept at 4°C before analysis. Metals in solution were subsequently determined by flame atomic absorption spectrometry (Ray Leigh Model WFX-210 AAS) using air-acetylene flame. 7 major elements were analyzed: Cu, Cd, Zn, Pb, Fe, Cr and Mn. Quantification of metals was based upon calibration curves of standard solutions of respective metals. Standard solutions were prepared from Merck. All wares used for metal analysis were cleaned with detergent, thoroughly rinsed with tap water, soaked in 10% HNO_3 solution overnight and finally rinsed with ultrapure water several times prior to use.

2.3. Water Treatment and Analysis

At each collection site, bottles were rinsed three times with the river water before filled. Each sample was analyzed for 20 parameters. The determination of pH, water temperature, electrical conductivity (EC_w), total dissolved solids was performed in situ using a Hach Model 44600 Conductivity/TDS meter. After arriving at the laboratory, water samples were filtered through Whatman 0.45 μm pore diameter membrane filters and divided between two one-litre polyethylene bottles. Analytical parameters were determined with reference to official methods ([13], [14]). One bottle was immediately stored at 4°C, for the analysis of chloride, nitrate, nitrite, sulphate and phosphate and were determined using a spectrophotometer from Shimadzu (CTO-20A prominence column oven). Potassium and sodium were measured using the flame photometer model Sherwood, CL-420. The other polyethylene bottle was acidified with 2% HNO_3 and stored at 4°C for trace metal analysis (Fe, Zn, Cd, Cr, Pb, Cu, Mn). Trace metals were determined by flame atomic absorption spectrometry (Ray Leigh Model WFX-210 AAS) using air-acetylene flame. All chemicals used in the study were obtained from Merck, and were of analytical grade. Working standards were prepared by dilution of stock solution (1mg metal/ml in 2% HNO_3) with ultrapure water and ultrapure water blanks were subjected to the same operations (storage, filtration, analysis) as real samples to control pollution along the sample manipulation stage. All the determinations were in triplicate and average values and their standard deviations were reported.

3. Results and Discussion

3.1. General Characteristics of River Water

All the conductivity values (Table 1) are over the limit for potable water production (1.000 $\mu\text{s/cm}$) [15]. This indicated that we are dealing with waters with a high mineralization. The high conductivity at the different sites could be justified by the calcareous characteristics of this area and the calcareous wastes released. The pH of the river water is highly alkaline (7.2-8.9) (Table 1). These maximum values are related to the gypsum material released from the different types of industries and sewage and due to the agricultural run-off that is usually alkaline in nature due to the presence

of ammoniacal compounds. The high concentration in TDS at the different sites (Table 1) is due to the release and the mobility of the particulate matter. For sodium, the water samples at the site D and E (945 and 1085mg/l, respectively) were above the level for human consumption [16]. The percentage of sodium ions is often taken as an important parameter in deciding the suitability of water for irrigation. The concentrations are over 100mg/l in 90% of the samples (Table 1) and it would be a potential sodium hazard for the crops if this water was used for irrigation. The major anions are sulphate and bicarbonate with the vast majority of samples has sulphate concentrations above 100mg/l (Table 1). The concentrations of bicarbonate expressed the alkalinity of the water which serves as a pH reservoir for inorganic carbon and is taken as an index of productivity potential of the water [17] and high value of alkalinity indicates a great ability of the river to support algal growth and other aquatic life. Chloride concentrations over 100mg/l were found in more than 80% of samples (Table 1). An excess of chloride in river water is usually taken as an index of pollution. Sewage water and industrial effluents are rich in chloride and hence the discharge of these waters results in high chloride levels in fresh water [18]. The nitrate in river water promotes high primary productivity and an excess of this ion in surface

waters can be taken as a warning for algal blooms. The highest values are found at the site A (13.58 mg/l) and seems to be due to local run-off from the adjacent crop fields in this area where the farmers used nitrogen fertilizer.

In contrast, there is no indication of nitrate pollution at the different sites (2.34-13.58 mg/l) (Table 1). The nitrite ions are indicators of organic pollution on very spot and/or recent sources. The nitrite concentrations were over the level of tolerance of 0.5mg/l in all the samples.

Phosphate is present in natural waters as soluble phosphate and organic phosphate species. The concentration of the available phosphate is high at the different sites with the maximum value found at the site B (165mg/l) (Table 1) probably due to waste water containing detergents and agricultural activities. These concentrations are high enough to cause eutrophication, thus the organic pollution is very serious in the river. The reason for this level of pollution is the waste water input released all along the river. Table 1 lists the average values of heavy metals and physico-chemical parameters for the five sampling sites. A one-way analysis of variance ANOVA (Table 1) revealed no statistically significant differences in the order of each parameter and each metal among the study sites.

Table 1. Characteristics of Al-Ghadir River water at the different sites.

| Parameter | A | B | C | D | E | Sig |
|--|--------|---------|--------|--------|---------|-----|
| pH | 7.20 | 6.40 | 7.10 | 7.80 | 8.90 | ** |
| TDS (mg/l) | 620 | 2000 | 1095 | 2000 | 2000 | ** |
| Conductivity ($\mu\text{S}/\text{cm}$) | 1227 | 3999 | 2158 | 3999 | 3999 | ** |
| T ($^{\circ}\text{C}$) | 18.50 | 24.80 | 24.30 | 25.30 | 25.0 | ** |
| Chloride (mg/l) | 63.37 | 3508.50 | 160.50 | 817.75 | 1193.5 | ** |
| Phosphate (mg/l) | 10.63 | 165 | 24.20 | 5.84 | 5.80 | ** |
| Nitrite (mg/l) | 2.14 | 2.14 | 0.28 | 1.17 | 1.21 | ** |
| Nitrate (mg/l) | 13.58 | 3.47 | 2.34 | 3.45 | 3.74 | ** |
| Sulphate (mg/l) | 103.14 | 3317.10 | 75.09 | 146.60 | 216.75 | ** |
| Potassium (mg/l) | 7.30 | 10.0 | 18.50 | 35 | 35.0 | ** |
| Sodium (mg/l) | 53.30 | 100 | 115.30 | 945 | 1085 | ** |
| Bicarbonate (mg/l) | 427.47 | 752.30 | 620.82 | 945.13 | 1025.72 | ** |
| Cd ($\mu\text{g}\cdot\text{l}^{-1}$) | 3.04 | 3.65 | 2.83 | 3.48 | 4.11 | ** |
| Cr ($\mu\text{g}\cdot\text{l}^{-1}$) | 62.80 | 41.80 | 25.30 | 53.30 | 53.70 | ** |
| Cu ($\mu\text{g}\cdot\text{l}^{-1}$) | 23.74 | 73.85 | 29.18 | 63.35 | 74.12 | ** |
| Fe ($\mu\text{g}\cdot\text{l}^{-1}$) | 506.30 | 613.20 | 609.70 | 516.60 | 559.70 | Ns |
| Mn ($\mu\text{g}\cdot\text{l}^{-1}$) | 197.70 | 167.20 | 109.60 | 423.50 | 458.40 | ** |
| Pb ($\mu\text{g}\cdot\text{l}^{-1}$) | 15.12 | 19.50 | 13.90 | 42.57 | 51.10 | ** |
| Zn ($\mu\text{g}\cdot\text{l}^{-1}$) | 63.30 | 136.20 | 195.70 | 266 | 279.70 | ** |

** $P < 0.01$; ns: not significant

3.1.1. Characteristics of the River Sediments

The river sediments are made up of fine sand, silt and clay. The triangle of texture [19] whose three sides correspond to percentages of sand, silt and clay in a given soil is used to classify the studied sediments in the 5 sites under the classification of sediments with a clay texture for the sites A and D, clay-loamy texture for the sites B and E and sandy-clay-loamy texture for the site C. The fine silt and clay ($< 50\mu\text{m}$ fraction) content in sediment samples ranges from 15.12-23.12 and 30.15-51.25%, respectively (Table 2).

The content of limestone is, as expected, very high as in all alkaline soils. Active limestone represents the fractions of

calcium carbonate present in the silts and clays [20]. The content of active limestone is high due to the high contents of silts and clays.

The pH of the river sediments varies from 7.52 to 8.25 indicating slightly alkaline nature of the sediments. The pH of the sediments and the soil being alkaline, heavy metals will tend to insolubilise hence reducing their toxicity toward microorganisms and delaying their toxicity to underground water. The pH measured in the sediments was shown higher than that in the water and this may be partly contributing to the increased concentration of heavy metal ion in the sediments due to precipitation of dissolved metals. The

organic content of the sediment vary from 10.54 to 14.72% (Table 2). The maximum value of organic content is observed at site E (14.72%, respectively) which may be due to direct discharge of large amount of sewage and municipal solid wastes and the microflora susceptible to develop in these

sediments is characteristic of organic sediments. This tendency is confirmed by the enumeration of the total microflora on nutrient agar. The results obtained (Table 2) are characteristics of the sediments rich in microflora.

Table 2. Characteristics of Al-Ghadir River sediments at different sites.

| Parameter | A | B | C | D | E | Sig |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----|
| pH | 7.52 | 7.85 | 7.81 | 8.2 | 8.25 | * |
| Sand (%) | 25.6 | 41.12 | 50.62 | 40.12 | 44.87 | ** |
| Silt (%) | 23.1 | 20.62 | 19.20 | 15.12 | 16.37 | ** |
| Clay (%) | 51.25 | 38.25 | 30.15 | 44.75 | 38.75 | ** |
| Total limestone (g/kg) | 157 | 92 | 45 | 74 | 122 | ** |
| Active limestone (g/kg) | 16 | 10 | 7 | 13 | 15 | ** |
| Bulk density (g/cc) | 1.19 | 1.20 | 0.99 | 1.01 | 1.05 | Ns |
| Particle density (g/cc) | 2.48 | 2.24 | 1.94 | 1.90 | 1.87 | * |
| Porosity (%) | 52.04 | 46.26 | 49.00 | 46.85 | 43.78 | Ns |
| Organic matter (%) | 14.10 | 10.98 | 10.54 | 12.81 | 14.72 | ** |
| CEC (meq/kg) | 70 | 52 | 41 | 57 | 50 | ** |
| Cd ($\mu\text{g.g}^{-1}$ dry sediments) | 7.42 | 10.37 | 9.78 | 13.10 | 25.40 | ** |
| Cr ($\mu\text{g.g}^{-1}$ dry sediments) | 73.52 | 63.76 | 59.07 | 59.17 | 61.45 | Ns |
| Cu ($\mu\text{g.g}^{-1}$ dry sediments) | 57.42 | 107.40 | 44.02 | 131.05 | 157.90 | ** |
| Fe ($\mu\text{g.g}^{-1}$ dry sediments) | 2215.57 | 3227.07 | 3202.04 | 5266.12 | 5207.3 | ** |
| Mn ($\mu\text{g.g}^{-1}$ dry sediments) | 277.30 | 356.13 | 187.20 | 640 | 747.22 | ** |
| Pb ($\mu\text{g.g}^{-1}$ dry sediments) | 27.18 | 48.17 | 45.42 | 73.22 | 78.10 | ** |
| Zn ($\mu\text{g.g}^{-1}$ dry sediments) | 93.50 | 234.50 | 244.74 | 2.85 | 353.71 | ** |
| Bacterial count (CFU.g ⁻¹ dry sediments) | 10 ⁷ | 10 ⁷ | 10 ⁶ | 10 ⁷ | 10 ⁷ | ** |

** P<0.01; * 0.05< P<0.01; ns p>0.05 (not significant)

Cation exchange capacity (CEC) allows to evaluate the amount of cations retained by the soil and this amount is related to the presence of negatively charged clay and organic soils colloids [21]. The values found at the different sites are relatively high due to the high organic matter and clay contents (Table 2). This high CEC greatly increases the probability of adsorption of metallic cations on the clay-humus complex. It also corresponds to the values found in the soil with clay texture.

The mineralogical analysis of the sediments collected from the 5 sites showed the presence of large amounts of quartz and calcite in addition to the presence of different minerals and many contaminants. Most of the heavy metals showed maximum concentration at site E due to influx of large volume of domestic sewage and industrial discharges. Heavy metal adsorption was also found high at locations with high organic matter content. However, the distribution of heavy metals in the sediment is not uniform in the entire course of the river.

The variation in the total concentration of heavy metals may be due to differences in the sources of the heavy metals and prevailing physico-chemical conditions and complex reactions such as adsorption, precipitation and redox conditions that may be taking place in the sediments. In general, the concentration of organic bound fractions of heavy metals in the sediments has been high where there has been high organic matter.

Therefore, the organic fraction released in the oxidisable step is not considered very mobile or available because it

may be associated with stable, high molecular weight humic substances that release small amount of heavy metals slowly [22]. Table 2 lists the average values of physico-chemical parameters and heavy metals for the 5 sampling sites in river sediments. A one-way analysis of variance ANOVA (Table 2) revealed no statistically significant differences in the order of each parameter and each metal among the study sites.

3.1.2. Heavy Metals in the River Sediments

Figure 2 represents the variation of the total metal content in sediment and water along the sampling sites. The sediments existing at the bottom of the water column play a major role in the pollution scheme of the river systems [23]. They reflect the current quality of the water system and can be used to detect the presence of contaminants that do not remain soluble after discharge into surface waters. Moreover, sediments act as carriers and possible sources of pollution because pollutants are not permanently fixed by them and can be released back to the water column due to changes in environmental conditions [23]. Therefore, the analysis of pollutants in sediments permits to detect pollution that could escape to water system and also provides information about the critical sites of the water system under consideration [24]. For the spatial distribution of the heavy metals, results obtained in figure 2 showed that the trend of the heavy metals at the different sites of the river occurred to be the same as that of the metal concentrations in the associated water column where the maximum concentrations of these metals occurred downstream site of the river due to water

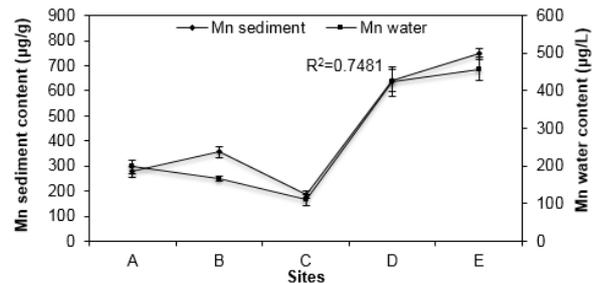
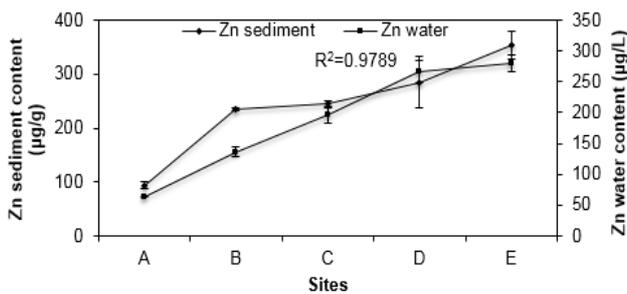
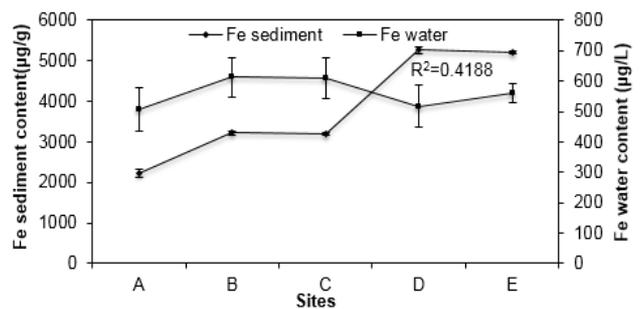
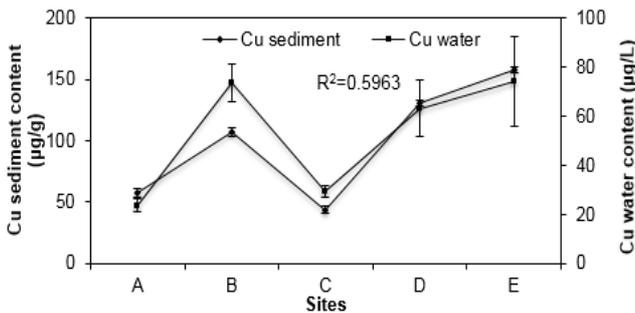
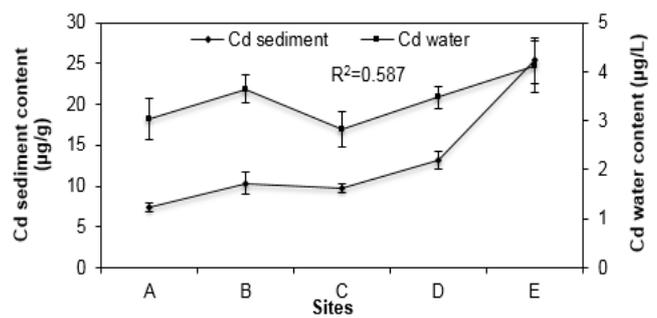
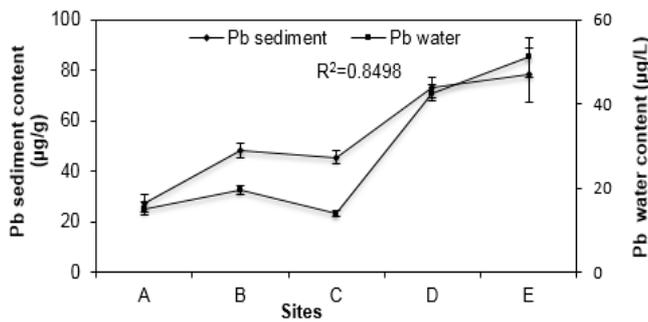
impoundment for longer periods. These results let us to focus our next studies on downstream sites where the results obtained at these sites can be representative of the pollution present at the different sites of the river. These same results showed that the concentration of heavy metals in sediments are higher than those obtained in river water but a high positive correlation coefficient (r^2) was exhibited between the total metal concentrations in sediments and water among the different sampling sites for Pb, Zn, Cd and Mn and to a lesser extent for Fe, Cr and Cu suggesting that some kind of water-sediment interaction is taking place especially in the dry season when the river discharge is very low and where an interaction or reaction occurs between bed load sediments and water, thus an equilibrium between the bed load and water may be achieved ([6], [25], [26]). In addition, due to the very low discharge of the river water, it would be plausible to assume that the metal pollutants enter the river where the conditions approximately are that of the closed

system, and then interact with sediment and with the existing water complexes and differentiate into different chemical species ([5], [27]). This positive correlation of metals in sediments and water suggests that their content in sediment is due to human activities (Pb, Zn, Mn). The occurrence of heavy metals in river water and sediments is due to discharge of industrial effluents from various sources including untreated sewage, municipal waste and agrochemical runoff from nearby industries directly into the river. Zinc was found to have its highest sediment content at site E in the industrial zone with content higher than the standard shale value (Table 3).

The other sites showed a lower content for Zn. Lead and Cd content in sediments were, at all sites, higher than the standard shale value, the highest appearing at sites D and E in the industrial zones. The higher values of Fe in this river may be attributed to geological source coupled with anthropogenic inputs from the catchment area.

Table 3. Comparison between metal contents of average shale (after Martin and Meybeck 1979) and results obtained.

| Metal | Standard shale | Sites values |
|-----------|----------------|---|
| Zn (µg/g) | 95 | 234 (site B), 244 (site C) and 353 (site E) |
| Pb (µg/g) | 20 | 27(site A), 48 (site B), 45(site C),73(site D) and 78 (site E) |
| Cd (µg/g) | 0.3 | 7.42 (site A), 10.37 (site B), 9.78(site C), 13.10 (site D)and 25.4(site E) |



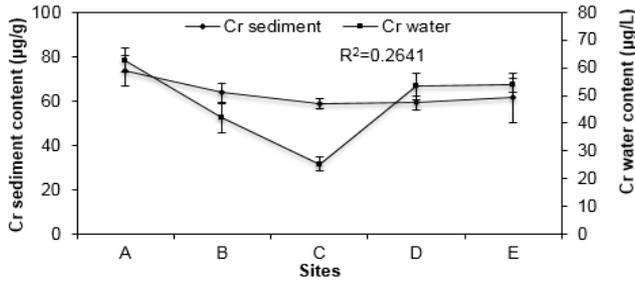


Figure 2. Variation of total metal content in sediment and water along sampling sites (R^2 is correlation coefficient). Data columns and error bars represent mean ($n=3$) and S.D., respectively.

3.2. Metal Fractionation

In this study, the sequential extraction procedure proposed by [12] has been used to obtain the five fractions. By studying the distribution of the metals between the different phases, their bioavailability and toxicity can be ascertained. The fractions introduced by man’s activity include the adsorptive and exchangeable and bound to carbonates which are considered to be weakly bound and may equilibrate with aqueous phase thus becoming more rapidly bioavailable [28]. The Fe-Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals. The fractionation pattern of different metals in the bed sediments of the river at the different sites are shown in figure 3.

Iron was found the most abundant metal in all sediments because it is one of the most common elements in the earth’s crust. Fractionation profile of iron in bed sediments of the river indicated that a high portion (>50%) is associated with the residual fraction (Figure 3). This is consistent with a natural source for Fe in the river sediments. The chemistry of Fe can explain the speciation of Fe in the reducible and organic matter sediment fractions and its small concentration in the carbonate fraction. Iron occurs in the oxide and hydroxide forms under alkaline oxidizing conditions, while the formation of Fe carbonates needs reducing conditions [29]. The samples represented the oxidized surface sediments. The assumption of an oxic sediment surface is based on the natural setting of the river basin during the dry season and the depth at which sediments were collected [30].

Manganese, which is also abundant in nature, behaves in a way similar to that of iron. The fractionation profile of manganese indicates that it is mostly bound to residual followed by reducible fractions, the rest being associated with organic matter, carbonate and exchangeable fractions. The high percentage of Mn total content in the residual sediment fraction (Figure 3) are ascribed to the natural source of Mn in the sediment (similar to speciation of Fe pattern). Fractionation profile of copper indicated that a high portion is bound to the organic matter fraction. As reported in earlier studies on polluted sediments ([30], [31], [32], [33]) extractable copper is mainly associated with oxidizable phase, where it is likely to occur as organically complexed metal species. This behavior can be explained by the well-known high affinity of copper to humic substances, which are a

fraction of natural organic matter and chemically very active in complexing such metals [34]. Under an oxic water column, a significant fraction of the copper reaching the sediment surface may be returned to the overlying water column by mineralization of the host organic material at the surface and in the oxic upper layers of the sediment. A high portion of copper was found associated with the exchangeable fraction indicating the dominance of anthropogenic sources through atmospheric deposition and municipal discharges.

The concentration of total cadmium was found to vary from 7.42 to 25.4 $\mu\text{g}\cdot\text{g}^{-1}$ at the different stations. The fractionation profile of cadmium indicated that a high portion of cadmium is associated with carbonate fraction and a lower association with the reducible fraction (Figure 3). This shows an important role for sediment carbonates in the deposition of Cd irrespective of a higher content in other sediment fractions. The strong association of Cd with the carbonate fraction is most probably owing to the similarity of the ionic radii of Cd (0.97 Å) and Ca (0.99 Å), since Cd will coprecipitate with carbonates and enter the calcite crystal as a camouflaged element ([35], [36], [37]).

The concentration of lead was found to vary from 27.18 to 78.10 $\mu\text{g}\cdot\text{g}^{-1}$ in the sediments of the river. The high association of Pb in the reducible fraction is due to the higher stability constant of Pb-oxides than Cd-oxides [38]. Furthermore, the variation in speciation of Cd and Pb in the carbonate and in the reducible fractions parallel that reported by [39] and [40] in alkaline media. Cadmium associates mainly with the carbonate fraction whereas Pb associates with the carbonate fraction for lower Fe oxides. [41] reported that the percentage of the total Pb in the carbonate fraction ranged (30–40%) when the iron oxide was less abundant in sediment. Others ([42], [43]) have reported that the reducible fraction is dominant for Pb speciation when the carbonates constituted a minor portion in sediment.

This important role for the carbonates would not have been observed if the sediments had been unpolluted. Studies of unpolluted sediments [44] in carbonate basins have reported low metal speciation (Pb and Cd) in the carbonate sediment fraction, the speciation of Pb and Cd was mainly residual and this speciation was a reflection of catchment geology. Al-Ghadir river sediments were found highly contaminated with Pb and Cd metals and the percentages of both metals in the residual sediment fraction are lowest.

The speciation pattern of Zn in the sediments in some respects paralleled Cd speciation pattern. The highest (~30–40% total Zn sediment content) was in the carbonate fraction, followed by the reducible (~20–30%) fraction. At the sites A and D, the total Zn sediment contents were lower than the average standard shale value, whereas total Zn sediment contents at sites B, C and E were higher than the average standard shale value (near the industrial zone) (Table 3). These sites have a low concentration of Zn total content in the residual fraction and high concentration in the carbonate fraction.

This observation supports a role for carbonates in scavenging Zn introduced into the river through pollution.

The nearly equal percentages of the total Zn content in the carbonate and the reducible fractions (Figure 3) are a consequence of the limestone-dominated river basin ([5], [45], [46]). Therefore, a water chemistry dominated by carbonate species implies that carbonates precipitated on to sediment particles have a major role in adsorbing Zn. In this aspect, Zn showed the parallel speciation pattern in sediments with those of Pb and Cd speciation pattern. The carbonate sediment fraction of the river which is produced mostly from the industrial effluents is affected less by environmental changes, such as microbial sediment activity. Whereas, metals bound to reducible (Fe oxides and hydroxides) and oxidized (organic) sediment fractions have a potential for remobilization due to microbial activity [43].

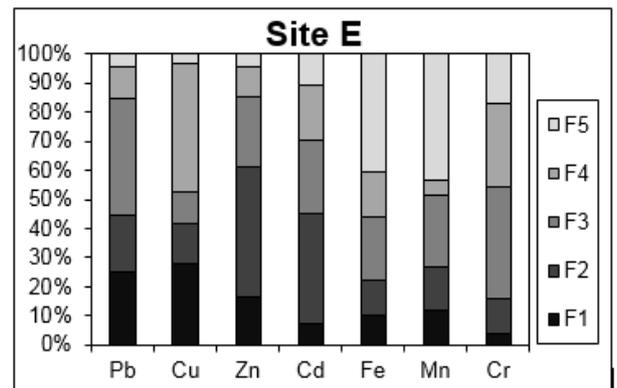
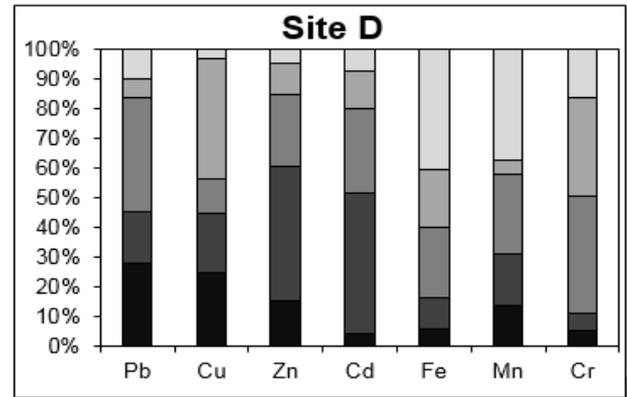
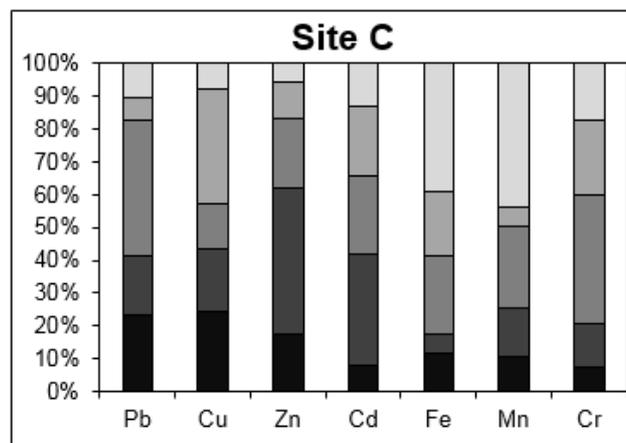
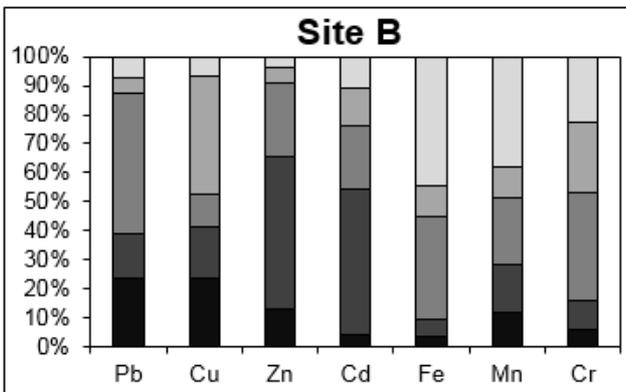
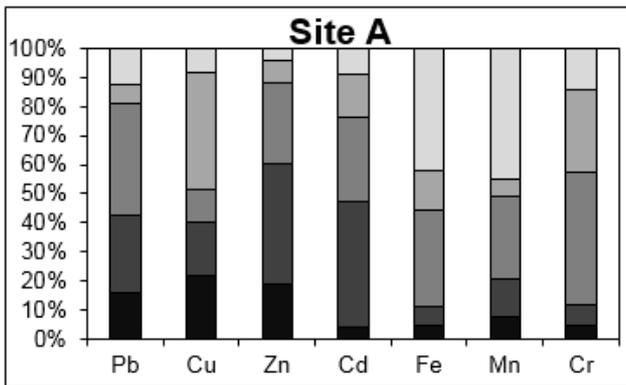


Figure 3. Heavy metal fractionation in bed sediments of Al-Ghadir river (F_1 -Exchangeable; F_2 -Bound to carbonates; F_3 - Bound to Fe-Mn oxides; F_4 - Bound to organic matter; F_5 -Residual).

In the sediment samples of the river, the concentration of total chromium was found to vary from 59.07 to 73.52 $\mu\text{g}\cdot\text{g}^{-1}$. The fractionation profile of chromium indicated that more than 50 % of chromium is associated with the reducible and the organic matter fractions at most of the stations.

3.2.1. Environmental Impact

Normally, reducing microorganisms in sediment are able to reduce insoluble Fe (III) oxides to soluble Fe (II) oxides and thereby release metals associated with oxide phase. Whereas, oxidizing microorganisms in sediments might oxidize the organic sediment constituent and expel the metals associated with the organic fraction [5].

Results of fractionation of heavy metals showed that 5 to 10 % of some metals (Pb, Cd and Cr) have been mobilized from the reducible phase.

In our case, wastewaters which contain large amounts of organic matter are continuously released at the different sites and may result in a continuous re-adsorption of heavy metals. What happens is that when wastewaters are released, for example between the source (point A) and point B, we remark that the sequence of reduction in the sediments is similar to that reported by [47]. At point B, when a new quantity of organic matter is released, this release may affect the sequence of reduction [47] and can poison the soil Eh for several days where autochthonous bacteria consume the newly released organic matter as a source of carbon [48] and

release another type of organic matters (organic acids). The increase in the specific area of the degraded organic matter may explain the raise of absorption or adsorption of the heavy metals to the newly released organic matter.

Between the points B and C, a new typical reduction sequence will take place. At the point C, when wastewater is newly released this release can poise the soil Eh for several days during which reduction will be stopped and the released metals will be adsorbed to the newly released organic matters and the cycle continuous at each site. This alternation is of great importance for the immobilization of heavy metals in and can be planned and used to reduce the toxic effect of mobilized metals at sites of high contamination.

3.2.2. Geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) developed by [49] is used to determine the quantitative extent of metal pollution in aquatic sediment using the following expression

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

Where C_n is the concentration of the examined metals in the sediment; B_n is the geochemical background value of a given metal in shale (average shale) [50] and 1.5 is the background matrix correction factor. The factor 1.5 is used for possible variation in the background data due to lithogenic effects. The

I_{geo} consists of seven grades (0 to 6), indicating various degrees of enrichment above the background values ranging from unpolluted to very highly polluted sediment quality. Table 4 presents the geoaccumulation index for the quantification of heavy metal accumulation in the river sediments.

The following description classification is given for the index of geoaccumulation by [51] as follows:

- <0 Practically unpolluted
- 0-1 Unpolluted to moderately polluted
- 1-2 Moderately polluted
- 2-3 Moderately to strongly polluted
- 3-4 Strongly polluted
- 4-5 Strong to very strongly polluted
- > 5 Very strongly polluted

The I_{geo} for the river sediments in this river varies from metal to metal and place to place. Chromium, manganese and iron remain in class 0 (Table 4). The I_{geo} for lead and zinc is found to be 0 at the sites A, B and C and 1 at the sites D and E. The I_{geo} for copper is found to be 0 at the first 4 sites and increases to 1 at the last site.

Table 4. Geoaccumulation index of Al-Ghadir sediments.

| Sites | A | B | C | D | E |
|-------|---|---|---|---|---|
| Cd | 4 | 4 | 4 | 4 | 5 |
| Cr | 0 | 0 | 0 | 0 | 0 |
| Cu | 0 | 0 | 0 | 0 | 1 |
| Fe | 0 | 0 | 0 | 0 | 0 |
| Mn | 0 | 0 | 0 | 0 | 0 |
| Pb | 0 | 0 | 0 | 1 | 1 |
| Zn | 0 | 0 | 0 | 1 | 1 |

Throughout the mainstream, Cd remains in class 4 except at the site E where it falls in class 5. Based on the geoaccumulation indices (Table 4), the river sediments from the site A to E are considered to be unpolluted with respect to chromium, copper, iron, manganese, lead and zinc. In case of cadmium, it varies from moderately to highly polluted which may be attributed to the atmospheric deposition of vehicular and industrial pollutants.

4. Conclusion

This study showed that during the dry season, Al-Ghadir River whose drainage basin is characterized by a high aqueous pH and alkalinity, possess a self purification capacity for metal pollution primarily through an association of the metal with the carbonate species and to a certain extent with the organic matter species. This was demonstrated by the speciation of the metals in the sediments where Fe and Mn exhibited a high percentage association with the residual fraction followed by the Fe/Mn oxide fraction, Cu showed its high percentage association with the oxidizable fraction, Cd and Zn exhibited a high percentage occurrences as carbonate species which assumedly reduces the toxic effect of the free hydrated ion, and finally Pb and Cr showed their high percentage association with the oxidizable fraction. The association of Pb and Cr and the other metals but to a lesser extent with the Fe/Mn oxide fraction may play an important role in limiting the toxic metal content. Furthermore, work is needed to investigate the important role of the continuously released organic materials in forming adsorbed organic metal species, which might reduce the toxic effects of pollutant metals and their mobilisation toward underground water.

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